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# Nanostructured materials for Li-ion batteries with enhanced performance

Doctoral dissertation presented by

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# Chapter 1

Introduction

1.1	Li-ion Battery (LIB): an energy storage device	3
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#### Abstract

Lithium-ion batteries (LIBs) are rechargeable batteries, which utilize the reversible movements of Li<sup>+</sup> ions between the negative and positive electrodes for the storage and release of energy. Generally, LIBs consist of anodes, cathodes, electrolytes, separators and current collectors. Thanks to their high energy density, long cycle life and easy accessibility, LIBs have attracted considerable attention and become widespread in various applications. Nanostructured materials can offer large electrochemically active surfaces, high electronic and ionic conductivities, and enhanced mechanical properties, resulting in superior battery performance compared to bulk materials. Nanostructured materials can be classified into zero-dimensional, onedimensional, two-dimensional, three-dimensional materials, and their composites. Utilizing nanostructured materials as electrodes or electrolytes, their enhanced performance can be systematically determined by electrochemical characterization techniques.

KEYWORDS: Li-ion battery, nanostructured material, electrochemical properties, electrochemical characterization techniques

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#### 1.1 Li-ion battery (LIB): an energy storage device

#### 1.1.1 Development of LIBs

A LIB is a type of rechargeable battery which takes advantage of the reversible movements of Li<sup>+</sup> ions between the negative and positive electrodes for the storage and release of energy. Tracing the origins, the oil crisis in the 1970s urged the invention of LIBs. Stanley Whittingham discovered the intercalation electrodes and established the first rechargeable LIB to develop fossil-free energy technologies. Titanium disulfide (TiS<sub>2</sub>) was innovatively utilized as a cathode in that battery, of which the layer structure accommodated the intercalated Li<sup>+</sup> ions (Figure 1.1A) [1]. However, the battery did not get commercialized, since it exhibited low voltage and was not safe enough. Then in 1980, John Goodenough expanded on the work by replacing a metal oxide for a metal sulfide. The improved battery using lithium cobalt oxide (LiCoO<sub>2</sub>, LCO) as a cathode exhibited a voltage as high as 4 V (Figure 1.1B) [1]. Based on the LCO cathode, in 1987, Akira Yoshino assembled the battery with a coke-carbon anode and a LCO cathode in a propylene carbonate (PC) and diethyl carbonate (DEC) electrolyte, which is the first patent called the rechargeable LIBs (Figure 1.1C) [1]. Goodenough, Whittingham, and Yoshino were awarded the 2019 Nobel Prize in Chemistry for the development of LIBs [1]. For the last 36 years, LIBs have rapidly developed for pursuing superior energy density and safety. Nowadays, LIBs replace some traditional rechargeable battery technologies, such as the nickel-cadmium battery, and become a popular battery type in the battery market.



**Figure 1.1** Illustrations of main discoveries by Whittingham (A), Goodenough (B), Yoshino (C) [1].

LIBs have attracted considerable attention thanks to their

superior characteristic features, such as high energy density, long cycle life and easy accessibility. To date, LIBs are widespread in various applications. LIBs have become predominant in portable electrical devices, e.g., cell phones, electric bracelets, tablets, laptops, electric toothbrushes and electric shavers. Besides, LIBs are also widely used in electric vehicles and hybrid electric vehicles, including electric bicycles, electric cars and electric scooters. Additionally, LIBs are significantly utilized for renewable energy storage, ranging from gridscale storage, stationary energy storage, to portable energy storage. These practical applications of LIBs are briefly summarized in the Figure 1.2.



Figure 1.2 Properties and practical applications of LIBs.

However, safety hazards (e.g., fire hazards) of traditional LIBs are serious issues in practical applications of cell phones and electric



vehicles, and have recently gained public concerns (Figure 1.3).

**Figure 1.3** Destruction of UPS plane in Philadelphia in 2006 caused by the ignition of LIBs, resulting in the intense fire and toxic fumes and the death of two crew members (A) [2]. A fire incident caused by a hoverboard during charging in Louisiana in 2015 (B) [3, 4]. Recall of ~2.5 million Galaxy Note 7 phones in 2016, due to a manufacturing design fault of internal short-circuiting in Samsung's batteries (C) [5-7]. A fire incident of the Tesla Model S closely following an alert about a problem with charging, during its test drive in Biarritz in 2016 (D) [8].

Fire incidents of LIBs can be caused by (i) thermal abuses, such as poor cooling or external fires, (ii) electrical abuses, such as overcharges or external short circuits, (iii) mechanical abuses, such as penetration or crash, or (iv) internal short circuits, due to manufacturing flaws or aging [9].

Taking an overcharge as an example, overcharging can cause thermal runaway of LIBs without overcharge protection, further leading to internal degradation, and what is worse oxidization processes can keep cell temperatures above 500 °C, with the possibility of self-igniting secondary combustibles, as well as extreme fire incidents [10]. Taking

an internal short circuit as another example, short-circuiting can be caused by the formation and growth of Li dendrites, which may produce immense heat in a short period of time, leading to a dramatic increase in temperature. Especially in the case of flammable organic solvents used as electrolytes, short circuits may result in self-ignition and fire incidents. The resulting smoke in a LIB is both flammable and toxic (Figure 1.4).



Figure 1.4 Illustration of short-circuiting caused by Li dendrite formation [11].

To avoid these safety issues, the improvement of electrolytes is one of the key directions. Solid-state electrolytes are prospective alternatives to replace traditional liquid electrolytes. The superior properties effectively avoid safety issues, such as thermal and mechanical stability, have no issues of the leakages of toxic organic solvents, low flammability and non-volatility, etc. In the last decade, academia and industry have dedicated considerable effort to develop solid-state Li-ion batteries.

#### 1.1.2 Compositions and working principle of LIBs

Generally speaking, LIBs are comprised of five major components: anodes, cathodes, electrolytes, separators and current collectors. The configuration is illustrated in Figure 1.5.



Figure 1.5 Compositions, structure and working principle of a LIB [12].

An anode is an electrode where the electrons leave the battery *via* a current collector during discharge. During discharging of batteries, oxidation reactions occur at anodes. Generally, the battery terminal marked with a minus is an anode. Nowadays, the most common commercial anode material is graphite, with a theoretical specific capacity of 372 mAh g<sup>-1</sup>. Other carbon-based anode materials, such as graphene, are used as experimental materials in labs, but remain far from commercial accessibility due to their high cost. Moreover, silicon and lithium are also promising anode materials, with theoretical specific capacities more than 10 times that of graphite. However, the principal challenge is the instability of materials during cycling. For example, the volumetric change of Si can be as large as 300 - 400% after lithiation [13], and the uneven deposition of Li on Li anodes can cause the formation of dendrites [11].

A cathode is an electrode opposite to an anode. A cathode is an electrode of a battery where the electrons enter the battery *via* a

current collector. During discharging of batteries, reduction reactions occur at cathodes. Generally, the battery terminal marked with a plus is a cathode. Commonly used cathodes include lithium cobalt oxide (LiCoO<sub>2</sub>, LCO) and lithium manganese oxide (LiMn<sub>2</sub>O<sub>4</sub>, LMO). Cobaltbased cathode materials are commonly used thanks to their high theoretical specific capacities (274 mAh g<sup>-1</sup> of LCO), low self-discharge, high discharge voltages and good circularity, but the disadvantages are high cost, ethical issues and low thermal stability [14]. Manganesebased cathodes are also attractive because of low cost and low toxicity, but the disadvantage is that Mn is apt to dissolve into the electrolyte leading to poor cycling stability [14]. Nowadays, the most promising cathode materials are lithium iron phosphate (LiFePO<sub>4</sub>, LFP) and lithium nickel manganese cobalt oxide (LiNiMnCoO<sub>2</sub>, NMC) due to low cost, excellent safety and high cycle durability. Both of them have become popular options for electric vehicles in Tesla, Nissan Motor, etc.

A liquid electrolyte is a medium containing ions and their polar solvents. An electrolyte conducts ions but not electrons. For traditional liquid electrolytes, ions originate from the dissociation of salts in their polar solvents. For example, lithium hexafluorophosphate (LiPF<sub>6</sub>), lithium tetrafluoroborate (LiBF<sub>4</sub>), lithium perchlorate (LiClO<sub>4</sub>), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) lithium or bis(fluorosulfonyl)imide (LiFSI) is dissolved in some organic solvents, e.g. propylene carbonate (PC), ethylene carbonate (EC), ethyl methyl carbonate (EMC), dimethyl carbonate (DMC) or diethyl carbonate (DEC). Solid-state electrolytes (SSEs) also have gained great attention. For example, polar solvents are substituted by solid polymers that conduct ions, which are so called solid polymer electrolytes (SPEs). Common ion-conducting polymers used in SPEs are poly(ethylene oxide) (PEO) and polyacrylonitrile (PAN).

A separator is usually a polymeric film that is located between a cathode and an anode. When a separator is wetted by the electrolyte, it can accelerate the movement of ions from one electrode to the other. However, separators are not electrically conductive, acting as isolators to avoid electrical short circuiting. The first separator for a battery was made up of wood. Today, the materials for separators are prepared from cellulose, glass fiber, polypropylene and so on [15, 16].

Current collectors are bridging components to collect the current generated from electrodes and convey it to external circuits for further usage. Commercial current collectors are Al and Cu foils for cathodes and anodes, respectively. Their thickness has become thinner to ~10  $\mu$ m during development over the last three decades. Except for the foil shape, the current collector can be designed into various forms, e.g., meshes and foams, and treated by chemical etching and coating to improve the performance.

Then how does a LIB work?

During the discharging of a LIB, electrons are collected by current collectors and travel from anodes to cathodes *via* an external circuit. Meanwhile, Li<sup>+</sup> ions transfer from anodes to cathodes by passing the electrolytes and the separators, and eventually stabilize in the cathodes. During the charging of a LIB, the movement directions of electrons and Li<sup>+</sup> ions are opposite. The charging and discharging processes are also illustrated in Figure 1.5, with the arrows of ions and electrons suggesting the movement directions.

Concretely, taking a LFP-graphite battery as an example, the cathodic and anodic reactions are listed in Equations 1.1-1.3. Directions of reactions from left to right are charging, and directions

from right to left are discharging.

Cathodic:	$LiFePO_4 \rightleftharpoons FePO_4 + Li^+ + e^-$	(1.1)
Anodic:	$Li^+ + e^- + 6C \rightleftharpoons LiC_6$	(1.2)
Overall:	$LiFePO_4 + 6C \rightleftharpoons FePO_4 + LiC_6$	(1.3)

Understanding the working principle of LIBs, the development goal of each component is clear. For instance, the requirements for anode and cathode materials are high specific capacity for Li<sup>+</sup> ions and broad electric potentials of operation in order to target high energy density of LIBs. The primary requirements for electrolytes are high ionic conductivity and stability in order to obtain fast Li-ion migration and safety properties.

## 1.2 Nanostructured material: an enhanced design for LIBs

#### 1.2.1 Overview of nanostructured materials in LIBs

It has been extensively reported that materials with nanostructured features open doors for improved power and cycle life of LIBs. Thanks to the nanoscale dimension, nanostructured materials can offer large electrochemical active surfaces, high electronic and ionic conductivities, as well as better mechanical properties, leading to superior battery performance compared to bulk materials. Neverthless, there are several disadvantages of nanostructured materials for LIBs. For instance, the large surface areas trigger side reactions and relatively low packing density leads to limited energy density.

The nanomaterials with diverse structures can be classified into several categories: 0-dimensional (0D), 1-dimensional (1D), 2dimensional (2D), 3-dimensional (3D) materials and their hybrids. Structural diagrams of diverse nanostructured materials are listed in Table 1.1, with their advantages and downsides for application [17].



 Table 1.1 Overview of 0D, 1D, 2D, and 3D nanostructured materials [17].

Advantages	<ul> <li>Small in all dimensions</li> <li>Surfaces on all sites are accessible to electrolytes</li> <li>No bulk solid-state diffusion</li> <li>Can be integrated into multiple systems</li> <li>Can be used in stable inks for printing</li> </ul>	<ul> <li>Mechanical reliability</li> <li>Possibility to integrate with wearable devices</li> <li>Porous flexible freestanding films</li> </ul>	<ul> <li>Open 2D channels for ion transport; all surface is accessible enabling fast charge storage</li> <li>Compatible with flexible devices</li> <li>Small nanoflakes can be used in inks for printing</li> </ul>	<ul> <li>Can be used to create thick electrodes with large areal and volumetric storage properties</li> </ul>
Limitations	<ul> <li>Agglomeration</li> <li>Do not densify and form only low density non- uniform structures</li> <li>Numerous points of contact lead to high resistance</li> <li>Poor chemical stability</li> </ul>	<ul> <li>Low packing density and cannot exhibit high volumetric performance</li> <li>Low yield and high cost of synthesis</li> <li>Diffusion pathways can be relatively long</li> </ul>	<ul> <li>Re-stacking</li> <li>Low out-of-plane electronic and ionic conductivity</li> <li>High cost of synthesis</li> </ul>	<ul> <li>Design</li> <li>Stability</li> <li>Manufacturing</li> </ul>

Zero-dimensional nanostructured materials, such as carbon onions, nanoparticles and guantum dots, are small in all dimensions. When utilized as electrodes, the all-sided surfaces of the nanomaterials are accessible to electrolytes, which benefits the diffusion of electrons or ions compared to that of bulk materials. Thanks to the high compatibility, OD nanostructured materials can be integrated into multiple systems, allowing for the synthesis of multifunctional composites. Additionally, it has been extensively reported that functional nanoparticles are commonly used for ink recipes in ink-jet printing. Their good dispersibility in both aqueous and organic solvents guarantees the stability of active components in the inks and thus ensures the quality of printed films for further use in LIBs. While the intrinsic downside of OD nanostructured materials is the tendency towards aggregation, an effective way to alleviate this issue is to incorporate nanoparticles into 1D, 2D and even 3D nanostructured materials, and disperse them uniformly within the hosts. When utilized as electrode materials, another challenge of low electrical conductivity occurs, due to the high resistance caused by the numerous contact points. Lastly, it is also important to address the poor chemical stability of 0D nanostructured materials resulting from their high chemical reactivity. Thus, a protective coating layer may be required during synthesis and handling. Based on these factors, the expected properties for OD nanostructured materials include high diffusion of ions and electrons, wide compatibility and effective dispersion within a multi-component system, as well as high stability

to prevent excessive reactivity.

In terms of 1D nanostructured materials, examples include singlewall and multiwall carbon nanotubes, as well as nanowires. Conductive carbonaceous materials, e.g. carbon nanotubes (CNTs), are useful in forming electrically conductive continuous networks, which can be applied in fast electron transport. In addition, 1D nanostructured materials possess superior mechanical characteristics. For example, their high mechanical strength can prevent the deformation of electrode materials. Besides, the flexible feature makes 1D nanostructured materials attractive for usage in wearable electronics [18]. Moreover, the fabrication of 1D nanostructured materials can produce a porous structure. The resultant porous materials can be used as electrodes, allowing for electrolyte penetration. Also, the empty space of porous structures can accommodate the volumetric expansion of electrodes, e.g. Si, Ge, or Sn, leading to increased lifetime and decreased mechanical and resistive losses [17, 19]. Besides, such porous materials can be utilized as porous inert separators in liquid electrolytes or preformed frameworks in composite solid electrolytes [20]. The challenge of 1D nanostructured materials is their low packing density, which makes it difficult to achieve high volumetric performance for the corresponding electrodes [19]. In terms of practical manufacturing, the high costs and low yields of 1D nanostructured materials (e.g. CNTs or Si nanowires) create a barrier to large-scale production. Besides, another limitation of 1D nanostructured materials is that diffusion pathways are oriented along the length, which results in relatively long diffusion distances. As a typical example, this phenomenon has been reported in tunnel manganese oxide nanowires [21, 22]. To sum up, what are the expected characteristics for 1D nanostructured materials include high conductivity, mechanical strength as well as flexibility, and accessible fabrication into porous frameworks for further usage; however, the issues of low packing density and high production costs should be alleviated.

For 2D nanostructured materials, their 2D surface can be accessible for ionic and electronic transfer, allowing for fast charge storage [23, 24]. Like 1D nanostructured materials, 2D materials may enable the formation of flexible devices. Besides, 2D nanostructured materials, e.g. nanoflakes, can be used as ink components for ink-jet printing, serving the same function as their 1D counterparts [17]. In addition, compared with 1D nanostructured materials, 2D materials can achieve higher packing density and further areal/volumetric energy density. On the other hand, the intrinsic feature of re-stacking brings the limitations of 2D nanomaterials. Re-stacking hinders the penetration of electrolytes and ionic transfer [25]. Introducing porosity and enlarging interlayer distance can be effective strategies used to alleviate the issue of re-stacking. Although 2D nanostructured materials can offer high conductivity in-plane, the electronic conductivity and ionic transport are inferior in the out-of-plane direction [25, 26]. Finally, the high costs of synthesis are a practical problem in production. In short, the expected features for 2D

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nanostructured materials include superior conductivity and packing density. However, it is necessary to address how to prevent restacking and manage high costs.

More complex 3D nanostructured materials can be assembled by using the aforementioned low-dimensional nanomaterials. It is possible for 3D nanomaterials to create thick electrodes. The resulting thick electrodes can display large areal and volumetric densities of energy storage, and optimized ionic and electronic transfer [17]. Furthermore, the 3D structure can minimize the occupation of inert components in batteries, reducing the additive volume and weight from the insert parts [17]. For example, 3D Ni materials can be used as a support for the electrodeposition of cathode material, which saves the addition of foreign current collectors and conductive carbon [27]. However, compared to low-dimensional nanostructured materials, 3D materials may require more complicated designs and manufacturing, as well as higher costs. Hence, as for 3D nanostructured materials, the balance between the advantage of large unitary density and the challenge of manufacturing should be taken into consideration.

Such a large diversity of nanostructured materials offers numerous available options for battery design. Indeed, various nanostructured materials have been designed to be used as different compositions of LIBs, such as anodes, cathodes and electrolytes, in order to further improve the performance or address specific needs.



#### 1.2.2 Nanostructured electrode materials

**Figure 1.6** Diverse geometries of nanostructured electrodes and electrolytes, adapted from [28-39].

Nano-engineering of electrode materials has been extensively developed in recent decades, with designed nanostructured materials featuring diversely geometrical configurations ranging from 0D [28, 32], 1D [29, 33], 2D [30, 34] to 3D [31, 35] structures, as shown in Figure 1.6.



#### Zero-dimensional nanostructured electrodes

**Figure 1.7.** Two strategies applied in the development of 0D nanostructured materials. Illustration (A) and TEM image (B) of a Si nanocore coating by a conductive polyphenylene (PPP) shell, with a comparison of its cycling performance (C) against pristine Si at 100 mA g<sup>-1</sup> during the first 10 cycles and at 500 mA g<sup>-1</sup> during the later cycles. Illustration (D) and TEM image (E) of Si embedded in flexible carbon nanofibers (CNFs) and graphene sample (denoted as FSiGCNF), with a comparison of its cycling performance (F) against other references at a current density of 700 mA g<sup>-1</sup>. Figures A-C are adapted from [28] and Figures D-F are adapted from [42].

Zero-dimensional nanostructured electrodes are commonly

presented in the form of nanoparticles or nanodots. It is well known that OD nanomaterials, due to their high surface areas and small sizes, can significantly reduce the diffusion pathways of ions and electrons in all dimensions, compared to bulk materials that are micron-sized or even larger. Additionally, the structural instability of electrode materials can be alleviated by nano-engineering. Taking an Si nanoparticle as an example, Liu et al. have reported that the fracture issue of Si anode materials strongly depends on the size of material; that is, there exists a critical particle diameter of ~150 nm, below which the particles neither cracked nor fractured upon lithiation, and above which the particles initially formed surface cracks and then fractured due to lithiation-induced swelling [40]. Thus, downsizing particles to a nanoscale size can prevent cracking and fracture of Si nanoparticles. However, one limitation of OD nanomaterials is the existence of numerous interparticle junctions that interrupt continuous conductivity. Worse still, the large surface areas of electrodes can contact with electrolytes and then trigger significant side reactions.

To address these drawbacks, introducing a highly conductive component can improve electronic conductivity and create barriers against direct contact with electrolytes. Firstly, coating 0D nanostructured electrodes with an additional carbon layer is an effective strategy [17, 28, 41]. The role of the carbon coating is diminishing side reactions between electrodes and electrolytes and maintaining an electrical connection between nanometer-size electrodes. For instance, Si nanoparticles are coated by polyphenylene (PPP) sheets through a mechanochemical reaction using the sandmilling process (Figure 1.7A and B). This coated electrode material achieves higher capacity retention compared to the bare sample (Figure 1.7C) [28].

Another common strategy is embedding OD nanostructured electrodes in a carbon host, which is based on the good compatibility of OD nanostructured materials in host materials of various morphology [42-45]. Similar to the carbon coating strategy, the OD nanostructured electrodes embedded in a carbon host are equipped with highly efficient pathways for the electrons, and prevent large direct contact with electrolytes. Note that an extra advantage of the carbon host is its excellent mechanical strength to overcome the structural instability of electrodes during charging and discharging. For instance, the 0D Si nanoparticles are embedded in flexible graphene/ carbon nanofibers, which are synthesized using a sequence of methods, including atomic layer deposition, electrospinning, calcination, acid soaking, and drying, followed by another round of calcination (Figure 1.7D and E). Consequently, the synthesized material enhances the specific capacity and long-term cycling stability (Figure 1.7F) [42].

#### One-dimensional nanostructured electrodes

As far as 1D nanostructured electrodes are concerned, nanowires [46, 47], nanofibers [33] and nanotubes [29, 48] are commonly reported shapes. Their extended dimension along one axis allows faster charge/ion transfer without crossing junctions, and their flexible nature makes them useful in wearable devices.



**Figure 1.8.** Three strategies applied in the development of 1D nanostructured materials. Illustration (A) and TEM image (B) of a Si/SiC/CNT 1D nanocomposite, with a comparison of its rate performance (C) against pure Si. Illustration (D), SEM and TEM image (E and inset) of a double-walled Si-SiO<sub>x</sub> nanotube (denoted as DWSiNT), with a comparison of its cycling performance (F) against the solid Si nanowire. Illustration (G), TEM images (H and I) and cycling performance (J) of a Si-C wool-ball consisting of Si/C nanowire building blocks. Figures A-C are adapted from [29], Figures D-F are adapted from [50] and Figures G-J are adapted from [53].

Furthermore, diverse designs have been applied to further develop 1D nanostructured electrodes. Firstly, multifunctional components are introduced in 1D nanostructured materials to improve the electrochemical performance [29, 33, 48]. For example, as anode materials, high-capacity Si nanoparticles have been attached to the surface of conductive CNTs, with intermediate silicon carbide (SiC) on the interface to immobilize Si nanoparticles on nanotubes, which are synthesized by magnesiothermic reduction (Figure 1.8A-B). Compared to the single-component samples, the composite nanotubes achieve improved electrochemical performance, attributed to the synergistic effect of multifunctional compositions (Figure 1.8C) [29]. The second example is a 1D hybrid nanofiber ultilized as a sulfur cathode, using aligned CNT fibers as conductive supports, mesoporous carbon particles as hosts to store sulfur and graphene oxide layers as physical barriers to prevent polysulfides from seeping out. Thanks to the combined merits of multiple compositions, the hybrid nanofibers exhibit decent physical properties and high electrochemical performance [33].

Secondly, introducing pores to 1D nanostructured electrodes allows buffer space for the volumetric change of electrode materials, especially for anodes [49, 50]. As for nanowires, their geometrical configurations become more similar to nanotubes after introducing a hollow space. Take a double-walled Si-SiO<sub>x</sub> nanotube as an example, which is synthesized using an electrospun nanofibre templating method (Figure 1.8D and E). Thanks to the buffer spaces, the resulting porous/hollow electrodes show highly stable capacity, morphology and interface during charging and discharging, compared to the solid ones (Figure 1.8F).

Moreover, 1D nanostructured electrodes can also be used as subunits to build more complicated structures, such as interconnected networks [51] and micro-balls [52-54]. The accordingly fabricated electrodes exhibit reinforced performance and stability, attributed not only to the transport highways for ions and electrons in the networks, but also to the ample buffering voids formed during the assembly of 1D nanostructured materials. These voids allow for the volumetric change of electrode materials. These advantages are demonstrated in the example of a Si-C wool ball consisting of Si-C nanowires (Figure 1.8G-I), which is synthesized using a radio frequency induction thermal plasma system combined with a spray-drying procedure. The thin nanowires and buffering spaces within the wool ball accelerate the diffusion of ions and eletrons and stabilize the high capacity over 1000 cycles (Figure 1.8J) [53]. On the other hand, a downside of 1D nanomaterials is their low packing density, resulting in low volumetric performance.

#### Two-dimensional nanostructured electrodes

Due to the layered structures with nanoscale thickness and large lateral dimensions, 2D nanostructured electrodes are equipped with ideal conductive matrixes, mechanical supports and large surface areas for embedded units. Additionally, most of them possess the flexibility to shape free-standing electrode membranes and buffer spaces for the expansion of electrodes. Hence, using the 2D nanomaterials as electrodes can improve the interfacial stability, decrease the resistance and suppress the structural instability of active materials, leading to enhanced cycling performance. Recently reported 2D nanostructured materials used as anodes and cathodes, include graphene [55-58], MXenes [30], carbon films [59], vermiculites [60] and LFP nanosheets [34], just to name a few.

#### • Three-dimensional nanostructured electrodes

Three-dimensional nanostructured electrodes can have the most complex nanostructure among nanomaterials, which can further boost electrochemical performance. The synthetic processes towards 3D nanostructured electrodes can be categorized into two main classes: (i) utilizing 3D nanostructured materials as templates, and (ii) assembling/reshaping 0D-2D nanomaterials into complex 3D structures.



**Figure 1.9.** Two strategies applied in the synthesis of 3D nanostructured materials. Illustration of the synthetic route (A) and TEM image (B) of the Si@SiO<sub>x</sub>/C 3D material, with a comparison of its cycling performance (C) against the Si nanoparticle. Illustration (D) and SEM images (E and F) of a micrometer-sized Si pomegranate consisting of Si@C nanoparticles, with a comparison of its cycling performance (F) against other references. Illustration (H) of hierarchically porous Si nanosphere and its inwards expansion during lithiation, with its cycling performance (I). Figures A-C are adapted from [61], Figures D-G are adapted from [31], and Figures H and I are adapted from [66].

In the first synthesis strategy, the 3D nanostructured templates determine the shapes of resultant replicas. Double gyroid mesoporous silica (e.g., KIT-6) [61], MnCO<sub>3</sub> nanocubes [34, 38] and zeolitic imidazolate frameworks (ZIFs) [62, 63] have been reported as 3D nanostructured templates for electrode materials. Generally speaking, voids and pores are observed after sacrificing the templates, which can accommodate the volume variations of active materials and provide sufficient contact areas with electrolytes. Besides, the resultant thin walls of electrodes promote the transport of Li<sup>+</sup> ions. These advantages are demonstrated by the example of a 3D Si@SiOx/C nanoarchitecture, which is synthesized using a polymer template to shape the 3D nanostructure, followed by magnesiothermic reduction and carbonization. (Figure 1.9A and B). Note that the cycling performance of Si@SiOx/C is more stable than that of pristine Si nanoparticles, thanks to the synthesized 3D nanostructure (Figure 1.9C) [61].

The second strategy is assembling/reshaping 0D-2D nanostructured materials to complex 3D structures. It is a limitation for nanostructured materials that their large specific surface can trigger side reactions between electrodes and electrolytes, such as the formation of thicker and thicker solid electrolyte interphase (SEI). When low-dimensional nanostructured materials are assembled into a microscale edifice, e.g. secondary microparticles, the exposed surface area to electrolytes can be reduced. Such an assembly can improve the interfacial stability, avoid the structural degradation and
increase the capacity retention. Besides, a microscale edifice of nanostructured materials can increase the tap density compared to the individual nanomaterials, leading to an enhanced volumetric capacity. Reports on secondary microparticles of Si@C nanoparticles (Figure 1.9D-G) [31], LiMn<sub>0.85</sub>Fe<sub>0.15</sub>PO<sub>4</sub> nanoparticles [64] and LiNi<sub>0.75</sub>Co<sub>0.1</sub>Mn<sub>0.15</sub>O<sub>2</sub> nanorods [65] have clearly demonstrated the above advantages of secondary structures. On the other hand, evolving from low-dimensional nanomaterials towards more complex 3D nanomaterials via reshaping is also a widely popular method, e.g., through constructing hierarchical porosity on nanospheres [66-68]. This can be demonstrated in the example of hierarchically porous Si nanospheres, which are synthesized through the hydrolysis and condensation of SiO<sub>2</sub> precursor, followed by magnesiothermic reduction (Figure 1.9H). The resulting hierarchically hollow and porous structure can accommodate volumetric changes and induce the electrode to expand inwards, achieving the highly cycling stability (Figure 1.9I) [66].

To sum up, representative examples of 0-3D nanostructured materials showcasing capacity retention and cycle life are presented in Figure 1.10. Their corresponding synthetic protocols are also mentioned, as various synthesis techniques influence battery performance. For the majority of 0-3D nanostructured materials, both capacity retention and cycle life are significantly higher than those of conventional graphite electrode material (which exhibits a capacity retention of 66% over 500 cycles [69]). Notably, an outstanding illustration involves a 3D Si/C pomegranate microparticle, which demonstrates a capacity retention of over 95% even after 1000 cycles [31]. Consequently, LIBs utilizing these nanostructured materials have great promise for achieving high capacity performance and extended cycle life.



**Figure 1.10.** Capacity retention and cycle life of representative examples of 0-3D nanostructured electrode materials in LIBs [28-31, 42, 50, 60, 61, 66, 69].

## 1.2.3 Nanostructured fillers in solid electrolytes

Inorganic fillers have been widely studied in order to improve the limited ionic conductivity and mechanical properties of SPEs. When inorganic fillers are incorporated into SPEs, organic-inorganic composite solid electrolytes (CSEs) are obtained. According to the Liion conductivity, inorganic fillers can be divided into two main kinds: inert fillers and active fillers. Inert fillers cannot conduct Li<sup>+</sup> ions, but can improve the ionic conductivity of SPEs and enhance their mechanical and thermal properties. Inert fillers include oxide ceramics (e.g. Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and TiO<sub>2</sub>), ferroelectric ceramics (e.g. BaTiO<sub>3</sub>, PbTiO<sub>3</sub> and LiNbO<sub>3</sub>) and clay-based fillers [70]. While active fillers are capable of conducting Li<sup>+</sup> ions, such as garnet type, perovskite type and NASICON type. The CSEs with active fillers combine both advantages of SPEs and inorganic solid electrolytes (ISEs). When the concentration of active fillers in CPEs is low, usually lower than 20 wt%, this kind of CPEs is the ceramic-in-polymer type. When the concentration of active fillers exceeds a threshold, usually more than 50 wt%, this kind of CPEs is referred to the polymer-in-ceramic type, in which an ionically conducting network can be formed by connected active fillers [70].

The mechanism responsible for ionic conductivity enhancement by fillers has been intensively investigated. For inert fillers, firstly, the crystallinity of polymers is reduced by inorganic fillers. The dispersed fillers can suppress the crystallization of polymers, and thus, increase the amorphous phase of polymers to facilitate Li-ion transport [70, 71]. Secondly, based on Lewis acid-base interactions, the surface groups of fillers can interact with polymer segments, solvated cations and/or solvated anions to increase the proportion of free Li<sup>+</sup> ions on the surface of fillers, which can then migrate on the surface [70-72]. For active fillers, the ceramic-in-polymer type may produce in addition to the above mechanisms a higher Li-ion concentration on the interface between fillers and polymers due to the space charge effect, leading to an ionic conductivity enhancement [70, 73]. For the polymer-inceramic type, ionic conductivity can be further improved by a percolated network which is established by the connected active fillers [70].

Nanostructured fillers bring abundant contact surface areas between fillers and electrolytes and enhance the interfacial effect, which may effectively boost the electrochemical performance. The morphology of nanostructured fillers ranges from 0D [36], 1D [37], 2D [38] to 3D [39], as shown in Figure 1.6.

#### Zero-dimensional nanostructured fillers

Zero-dimensional nanostructured fillers possess nanoscale sizes and large surface areas [74-81]. However, the agglomeration of ceramic fillers and weak polymer-ceramic interactions limit the enhancement effect on ionic conductivity by 0D nanostructured fillers. To address this problem, (i) *in-situ* synthesis and (ii) surface modification are effective strategies. As a typical example, the *in-situ* synthesized SiO<sub>2</sub> nanoparticles have higher ionic conductivity than the *ex-situ* synthesized ones (Figure 1.11A and B) [74, 77]. Besides, the surface of fillers modified by functional components can increase the interactions (i) between fillers and polymer matrixes and/or (ii) between fillers and solvated Li salts, further improving the homogeneous dispersion of fillers and the dissociation of Li salts [76, 79, 80]. But the low aspect ratios of 0D nanostructured fillers may lead to short and isolated ion transport pathways.



**Figure 1.11.** Illustration (A) of a CSE consisting of *in-situ* OD nanostructured fillers and PEO polymers, along with a comparison of its ionic conductivity (B) against that of *ex-situ* OD nanostructured fillers. Enhanced effects of OD nanoparticle fillers, random 1D nanowire fillers and oriented nanochannel fillers on ionic conduction (C and D). Figures A and B are adapted from [74] and Figures C and D are adapted from [82].

#### One-dimensional nanostructured fillers

Common 1D nanostructured fillers include nanowires, nanotubes and nanofibers, which possess high aspect ratios. It has been reported that the electrochemical property enhancement by 1D nanostructured fillers is superior, compared to 0D nanostructured fillers, since 1D nanostructured fillers are able to create prolonged ion transport pathways [83]. Additionally, the orientation of 1D nanostructured fillers is an important factor in ionic conductivity. Vertically aligned structures to electrodes show enhanced ionic conductivity, in comparison with randomly aligned structures (Figure 1.11C and D) [82]. The reasons are that the vertically aligned structures to electrodes possess shortened ionic transfer routes and a significant reduction in crossing junctions among fillers [37, 82, 84]. Magnetic fields [85], electrospinning [37] and orderly porous molds [82] have been reported as effective methods to form aligned 1D nanostructured fillers. Moreover, porous networks assembled by 1D nanostructured fillers can also be utilized in CSEs. Such a continuous and interconnected filler network may increase the ionic conductivity, immobilize the anions of Li salts, alleviate the formation of Li dendrites and enhance the mechanical strength [86-88].

### Two-dimensional nanostructured fillers

Like 1D nanostructured fillers, 2D nanostructured fillers are commonly used in CSEs, e.g. garnet nanosheets [89], layer-doublehydroxide nanosheets [90], MXene nanosheets [91] and layered clay [92]. It has been reported that 2D nanosheet fillers effectively improve the electrochemical and mechanical properties, in comparison with their counterparts of nanoparticles [89, 90].

#### Three-dimensional nanostructured fillers

Three-dimensional nanostructured fillers have diverse morphologies and complex structures. There are two main ways to incorporate 3D fillers into polymers. On one hand, a polymer matrix is blended with 3D nanostructured fillers (Figure 1.12 A-C) [93, 94]. On the other hand, a polymer-based solution is introduced into a preformed framework of a 3D nanostructure, e.g. silica aerogels (Figure 1.12 D and E) [39], TiO<sub>2</sub> 3D frameworks [95], NASICON-type 3D frameworks [96] and garnet-type 3D frameworks [97]. Their interconnected frameworks play the role of continuous ion transfer paths and structural scaffolds, which may be more beneficial for improving the ionic conductivity and enhancing the mechanical strength, compared to 0D, 1D and 2D nanostructured fillers.





In short, representative examples of 0-3D nanostructured filler materials demonstrating temperature-dependent ionic conductivity are depicted in Figure 1.13, accompanied by their corresponding synthetic protocols. In comparison to the filler-free PEO electrolyte, 0-3D nanostructured fillers notably enhance ionic conductivity. Note that the 1D LLTO nanowire [83], 2D garnet nanosheet [89], and 3D SiO<sub>2</sub> aerogel [39] improve ionic conductivity by nearly five orders of magnitude at 20 °C, showing the considerable promise of these nanostructured fillers for solid-state electrolytes.



**Figure 1.13.** Temperature-dependent ionic conductivity of representative examples of 0-3D nanostructured filler materials incorporating with composite solid electrolytes[39, 76, 80, 83, 85, 86, 89, 91, 94].

## 1.3 Electrochemical characterization techniques

Electrochemical characterization techniques give a clear insight into basic electrochemical properties of a substance. So, herein, we introduce various electrochemical characterization techniques referring to Li-ion diffusion coefficient, electrochemical impedance, ionic conductivity, Li-ion transference number, electrochemical stability window and overpotential.

# 1.3.1 Li-ion diffusion coefficient

Diffusion is the movement process of substances (e.g. ions, atoms and molecules). Diffusion is oriented generally from a region of higher concentration to a region of lower concentration, which is driven by a gradient in Gibbs free energy or chemical potential.

The diffusion coefficient or diffusivity (D) is usually defined as the proportionality constant between the molar flux and the negative value of the gradient in the concentration of the species. According to Fick's law, the diffusion coefficient (D) is as Equation 1.4:

$$D = -J \times \frac{dx}{d\varphi} \tag{1.4}$$

where J is the diffusion flux, referring to the amount of a substance per unit area per unit time;  $\varphi$  is the concentration and x is the position.

In terms of LIBs, the Li-ion diffusion coefficient can be utilized in describing the diffusion behavior of Li<sup>+</sup> ions in electrodes, denoted as  $D_{Li}$ . And  $D_{Li}$  can be determined by, e.g., galvanostatic intermittent titration technique (GITT), electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) [98, 99].

According to the data collected by GITT,  $D_{Li}$  can be derived from GITT data, as shown in Equation 1.5:

$$D_{Li} = \frac{4}{\pi\tau} \times \left(\frac{n \times V_m}{S}\right)^2 \times \left(\frac{\Delta E_s}{\Delta E_\tau}\right)^2 \tag{1.5}$$

where  $\tau$  refers to the time of the current pulse; n and  $V_m$  are the mole number and the molar volume of the active material in the electrode, respectively; S is the surface area of the electrode;  $\Delta E_s$  is the steady-state voltage change due to the current pulse; and  $\Delta E_{\tau}$  is the voltage variation during a galvanic titration time  $\tau$  [100].

According to the data collected by EIS, Warburg impedance can reflect the Li-ion diffusion in the electrode materials. Therefore,  $D_{Li}$  can be derived with the following Equation 1.6:

$$D_{Li} = \frac{1}{2} \times \left(\frac{V_m}{\text{SFA}_w} \times \frac{\text{dE}}{dx}\right)^2 \tag{1.6}$$

where  $V_m$  is the molar volume of the active material in the electrode; S is the surface area of the electrode; F is the Faraday constant;  $A_w$  is the Warburg coefficient; dE/dx is the slope of galvanostatic charge-discharge curves [98].

According to the CV curves collected at different scan rates,  $D_{Li}$  can be calculated by the relationship of the peak current and the CV scanning rate, shown as Equation 1.7:

$$I_p = 0.4463 \times (nF)^{\frac{3}{2}} CS(RT)^{-\frac{1}{2}} (D_{Li}v)^{\frac{1}{2}}$$
(1.7)

where  $I_p$  is the peak current; n is the charge transfer number; F is the Faraday constant; C is the bulk concentration of Li in the electrode; S is the surface area of the electrode; R is the gas constant; T is the absolute temperature; v is the scanning rate [95].

### 1.3.2 Electrochemical impedance

Impedance is a measure of the ability of a circuit to resist the flow of electrical current. Electrochemical impedance spectroscopy (EIS) is a technique to estimate the electrochemical impedance by applying an alternating current (AC) voltage to a cell and determining the current through it, which is a powerful tool to investigate the properties of materials and electrode reactions. The data of EIS can be presented by Nyquist Plot, Bode plot, etc [101].

EIS data are generally analyzed by fitting to an equivalent

electrical circuit model. Resistors, inductors and capacitors are the three common kinds of electrical elements (Figure 1.14A-C) [102]. As for a resistor, its impedance is independent of frequency and has no imaginary component, suggesting the through current keeps pace with the phase of the applied voltage. As for an inductor, its impedance increases as frequency increases, has only an imaginary component and the through current is phase-shifted -90 degrees with respect to the voltage. As far as a capacitor is concerned, its impedance increases as frequency decreases, has only an imaginary component and the through current is phase-shifted 90 degrees with respect to the voltage [101].



**Figure 1.14** Impedance of (A) a resistor, (B) an inductor, and (C) a capacitor. (D) Typical Nyquist plot of a LIB and the inset of an equivalent circuit model [102].

In a real battery, electrical elements, e.g. resistors, inductors,

capacitors and their hybrids, can be used to fit the impedance of battery components, e.g. solution resistance, double layer capacitance, charge transfer resistance and Warburg impedance (Figure 1.14D) [102].

(1) Solution resistance, or electrolyte resistance, is an important property of electrolyte materials. The solution resistance is influenced by temperature, nature of ionic species, ionic concentrations and the areas applied under currents.

(2) An electrical double layer exists at the interface between an electrode and its surrounding electrolyte. When some ions of the solution are adsorbed onto the electrode surface, the charged electrode is separated from the charged ions by an insulating space on the length of Angstroms, which separates charges and behaves like a capacitor. Thus, a double layer capacitance is used to explain the impedance of the electrical double layer at the interface between an electrode and an electrolyte.

(3) Charge transfer resistance is formed by electrochemical reactions. When metal electrodes contact with an electrolyte, metals can be oxidized into positively charged metal ions, which further diffuse into the electrolyte. Meanwhile, the generated electrons enter into the metals which corresponds to the so-called charge transfer. The reaction is presented in Equation 1.8.

$$M = M^{n+} + ne^{-} (1.8)$$

The speed of the charge transfer reaction depends on the kind of reaction, the temperature, the concentration of the reaction products, and the potentials.

(4) Diffusion can generate the so-called Warburg impedance  $(Z_W)$ . It depends on the frequency of the applied potential, with the relationship as Equation 1.9:

$$Z_W = \frac{\sigma}{\sqrt{2\pi f}} - j \frac{\sigma}{\sqrt{2\pi f}}$$
(1.9)

where  $\sigma$  is the ionic conductivity, and f is the frequency. On a Nyquist plot,  $Z_W$  is drawn as a line with a slope of 45°.

### 1.3.3 Ionic conductivity and activation energy

lonic conduction is related to the movement of ions. lonic conductivity ( $\sigma$ ) is a measure of a substance tendency towards ionic conduction. For electrolytes, ionic conductivity is an essential property for the migration of Li<sup>+</sup> ions.

Ionic conductivity can be determined from the resistance measured by EIS in a SS/electrolyte/SS cell configuration, where SS is a stainless-steel spacer. The calculation refers to Equation 1.10:

$$\sigma = \frac{l}{RA} \tag{1.10}$$

Where  $\sigma$  (S/cm) is the ionic conductivity of the electrolyte sample, l (cm) is the thickness of the electrolyte sample, R ( $\Omega$ ) is the bulk resistance measured by EIS, and A (cm<sup>2</sup>) is the contact area between the electrolyte and the SS [103].

In a polymer-based electrolyte, Li<sup>+</sup> ions coordinate with the specific polarized groups of the polymer hosts, and conduction of Li<sup>+</sup> ions is obtained by the ion-hopping between coordination sites. The relationship between temperature and ionic conductivity is based on the Arrhenius equation, shown as Equation 1.11.

$$\sigma = A_{Arr} \times e^{-\frac{E_a}{T}} \tag{1.11a}$$

$$\ln \sigma = \ln A_{Arr} - \frac{E_a}{T} \tag{1.11b}$$

where  $A_{Arr}$  is the Arrhenius pre-exponential factor,  $E_a$  is the activation energy and T is the absolute temperature. Thus, the  $E_a$  can be calculated with respect to the slope of the  $\ln \sigma$  vs.  $T^{-1}$  curve [104].

In case of high-temperature operation, especially above the melting temperature T<sub>m</sub>, the segmental movement of polymer chains also helps Li<sup>+</sup> ions transfer among the coordination sites. The Li-ion transfer mechanism is then suitable to be simulated by the Vogel-Fulcher-Tammann (VFT) equation. The relationship between temperature and ionic conductivity is interpreted as Equation 1.12:

$$\sigma = A_{VFT} T^{-\frac{1}{2}} \times e^{-\frac{E_a}{R(T-T_0)}}$$
(1.12a)

$$\ln\left(\sigma T^{\frac{1}{2}}\right) = \ln A_{VFT} - \frac{E_a}{R(T - T_0)}$$
(1.12b)

where  $A_{VFT}$  is the VFT pre-exponential factor, T is the absolute temperature,  $E_a$  is the activation energy, R is the gas constant, and  $T_0$  (K) is the reference temperature, related to the glass transition temperature T<sub>g</sub> of the sample.[105] By plotting the  $\ln \left(\sigma T^{\frac{1}{2}}\right)$  vs.  $(T - T_0)^{-1}$ ,  $E_a$  can be determined with respect to the slope [104].

## 1.3.4 Li-ion transference number

The transference number (t) is an important parameter for

characterizing electrolytes [106]. The Li-ion transference number  $(t_{Li^+})$  is defined as the ratio of the current from Li<sup>+</sup> cations to the total current as shown in Equation 1.13, reflecting the contribution of the positive charge carriers (Li<sup>+</sup>) to the total conductivity.

$$t_{Li^+} = \frac{I_{Li^+}}{I_{tot}}$$
(1.13)

where  $I_{Li^+}$  is the current contributed by Li<sup>+</sup> cations and  $I_{tot}$  is the total current in the system. The value of  $t_{Li^+}$  ranges from 0 to 1. Ideally, when  $t_{Li^+}$  equals to 1, the current is only contributed by Li<sup>+</sup> ions and the anions are immobilized.

In turn,  $t_{Li^+}$  also implies the degree of polarization due to the negative carriers in the electrolyte systems. An electrolyte with a high  $t_{Li^+}$  value is highly pursued since the ionic current is dominated by the Li<sup>+</sup> cations with less polarization due to its anionic counterpart [106, 107].

In a SPE, the common method to measure  $t_{Li^+}$  is the Bruce-Vincent method [108, 109]. This method detects current under a small applied voltage in the cell configuration of Li symmetric electrodes, until the system reaches a steady state, as shown in Figure 1.15A.



**Figure 1.15** Schematic diagram of concentration profiles across the cell along with the time under a small applied voltage (A). The migration and diffusion of Li<sup>+</sup> cations and anionic counterparts at the steady state (B) [110].

In the initial case, the current depends on the applied voltage and the conductance of the cell. Lastly, at the steady state, the concentration gradient does not change. The migration of anions is exactly balanced by their diffusion in the opposite directions. The total current is contributed by Li<sup>+</sup> migration and diffusion (Figure 1.15B). Hence, the  $t_{Li^+}$  can be interpreted by the initial current and the steady current. Additionally, considering the interfacial resistances from surface layers and charge transfer kinetics,  $t_{Li^+}$  can be calculated by the following Equation 1.14:

$$t_{Li^{+}} = \frac{I_{ss}(\Delta V - I_0 R_0)}{I_0(\Delta V - I_{ss} R_{ss})}$$
(1.14)

where  $I_{ss}$  and  $I_0$  are the initial and steady-state current, respectively;  $R_0$  and  $R_{ss}$  are the initial and steady-state interfacial resistances measured by EIS, respectively;  $\Delta V$  is the applied voltage [103].

### 1.3.5 Redox reaction and electrochemical stability window

A redox reaction involves the transfer of electrons between chemicals. The common detection methods for redox reactions of electrode materials include linear sweep voltammetry (LSV), cyclic voltammetry (CV), differential capacity (dQ/dV) plots and so on.

The principle of LSV is to measure the current while the potential is ramped linearly as a function of time. CV is based on the same principle, while the difference is after the set potential is reached in a CV experiment, the applied potential is reversely swept to the initial potential. The cycling can be repeated as required. The relationship and difference between LSV and CV are clearly shown in Figure 1.16A, where the slope of voltage-time refers to the potential sweep rate, the voltage is the difference between the working electrode and the reference electrode. Due to the close relationship between LSV and CV, herein, we briefly introduce how to determine the potentials at which redox reactions occur by the CV method [111]. Taking the half-cell reaction as an example, during the increase of applied voltage from E<sub>1</sub> to E<sub>2</sub> (Figure 1.16B), the anodic peak begins to be observed when electrode material is oxidized at the specific potential. The current is influenced by the rate of diffusion of Li<sup>+</sup> ions to the electrode, as well as the proportion of the electrode converted to the oxidized form. The potential where the current reaches the maximum is called the anodic peak potential. Then, the current starts to decrease and finally stabilizes, as the potentials are swept more positively. For the reversed

scan from  $E_2$  to  $E_1$ , the cathodic peak begins to be observed when electrode material is reduced at the specific potential. The potential where the current reaches the minimum is called the cathodic peak potential. Then, the current starts to increase and finally stabilizes, as the potentials are swept more negatively.



**Figure 1.16** (A) The voltage-time profile for LSV and CV. (B) Typical CV plotting a cathodic and an anodic peak. (C) The CV curve and the dQ/dV plot of LMO vs. Li metal system with CV scan of 0.04 mV/s and constant current of 0.33 mA/cm<sup>2</sup>, respectively [111].

Besides, CV can be used to investigate the kinetics of Li-ion diffusion by changing the scan rate. More information about calculation has been shown in section 1.3.1.

The differential capacity (dQ/dV) plot also provides information about the redox reactions of batteries. The dQ/dV is plotted on the yaxis versus the voltage on the x-axis, where Q is the capacity and V is the voltage. The dQ/dV plot is obtained by calculating the derivative of Q with respect to V, which can originate from the galvanostatic chargedischarge curve with the x-axis of Q and y-axis of V. Note that the difference between the dQ/dV plot and the CV curve lies in the experimental conditions (Figure 1.16C). In a dQ/dV plot, the current is kept the same during galvanostatic charging-discharging. While a CV is collected with a constant potential sweep rate, where the potential increases linearly with time, this approach may cause an extreme increase in current, potentially exceeding the kinetic limit of the cell. As a result, some capacity might not be accessible [112]. Hence, the resulting capacities from these two experimental methods can be different. Additionally, the ohmic drops (IR drops) of the battery are influenced by the current [111]. IR drop of the cell remains unchanged during constant currents can but varies during a CV sweep, which alters the peak shape and position. Note the lower resolution of the CV curve in comparison to the dQ/dV plot, both of which may become similar when the potential sweep rate of the CV is slowed down.

An electrochemical stability window (ESW) of a material is the electric potential range between which the material is neither oxidized nor reduced, namely the potential gap between the oxidation and reduction potentials [113]. The ESW is an essential parameter for electrolyte materials.

To ensure the stability, the electrochemical potential of the electrodes should be located within the ESW of the electrolyte (Figure 1.17A). Otherwise, the electrolyte can be reduced when a reduction potential of an anode is below that of the electrolyte; the electrolyte can be oxidized when an oxidation potential of a cathode is above that of the electrolyte [113-115].



**Figure 1.17** (A) Energy diagram of the electrolyte interface with an anode and a cathode. ESW of the electrolyte is determined by its reduction and oxidation potentials.  $\mu$ A and  $\mu$ C are the electrochemical potentials of the anode and the cathode, respectively [116]. (B) Scheme of a traditional cell for ESW evaluation by LSV measurement [117].

LSV is a commonly used measurement method to evaluate the ESW. The LSV measurement is carried out in a cell configuration of Li/electrolyte/inert electrode. The inert electrode, e.g., SS, can prevent parasitic reactions and interference from background current. The applied potential is ramped linearly. When the potential increases to the specific value, the current starts to increase. Such a specific potential is where the electrode material begins to be oxidized (Figure 1.17B). When the potential decreases to the specific value, the current starts to decrease. Such a specific potential is where the electrode material begins to be reduced.

## 1.3.6 Overpotential

Overpotential potential difference is the between а thermodynamically determined voltage and the actual voltage for a redox reaction. For electrolytes, the profile of overpotential-time has been extensively studied in the galvanostatic cycling of symmetric Li cells. The variations of overpotential depend on the current density, the electrolyte composition, etc [118]. Taking an ideal galvanostatic cycle of an Li/electrolyte/Li cell as an example, the voltage-time plot is presented in Figure 1.18A [119]. In the first half cycle, a constant current is applied to the cell causing Li<sup>+</sup> to strip from one electrode, migrate through the electrolyte and finally plate on the other electrode. The corresponding voltage is plotted as a function of time. In the remaining half cycle, the applied current is reversed, causing the plating or stripping behavior of Li<sup>+</sup> to be reversed on both electrodes, and the corresponding voltage to also be reversed.



**Figure 1.18** The galvanostatic cycle of a symmetric Li cell with an electrolyte (A), adapted from [119]. Peaking behavior of galvanostatic cycles (B). Arcing behavior with a characteristic arc reaching a plateau at the end of each half cycle (C). Figures B and C are adapted from [118].

In fact, different shapes are observed in the voltage-time plots, such as peaks and arcs. The peak shape can be observed at the beginning of the cycles due to the transitions between the different kinetic pathways in the interfaces between electrodes and electrolytes (Figure 1.18B) [120]. The different kinetics may originate from the spatial heterogeneity along the interfaces between electrodes and electrolytes (e.g., spatially inhomogeneous impedance) [118]. The peak shape can gradually transform into an arc-plateau shape along with the cycling time (Figure 1.18C). The reason may be the mass transport limitation coming from tortuous paths of Li<sup>+</sup> ions in the extended cycles. Tortuous paths may originate from a compact interphase layer evolved from accumulated dead Li [118, 120].

Failure modes of a symmetric Li cell in galvanostatic cycling have been intensively studied [121]. When the erratic voltage is observed, the reason can be the formation of fractal dendrites. Furthermore, the growth of fractal dendrites easily causes short-circuiting and dramatically varies the operating voltage of a battery [122]. When the overpotential remarkably rises during cycling, this phenomenon is attributed to the electrolyte depletion, leading to a decreased interface area between electrodes and electrolytes [121].

The measurement of the overpotential during galvanostatic cycling is a way to detect the migration behavior of Li<sup>+</sup> ions across electrolytes, as well as the interfacial stability between electrodes and electrolytes. Especially, the voltage-time profile is a commonly measured parameter in the solid electrolyte field.

The above-mentioned characterization techniques establish a toolbox for detecting the electrochemical properties of electrode and electrolyte materials, and they disclose the charge/discharge mechanism of LIBs.

# 1.4 References

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# Chapter 2

**Objectives of the thesis** 

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# 2.1 Aim of the thesis

LIBs, exhibiting high energy density and long cycle life, are utilized in a wide range of practical applications. With the ever-growing energy requirements of our society, electrode and electrolyte materials with superior performance are highly pursued for enhanced energy density, durability period and safety properties.

Various choices of materials can dramatically change the voltage, energy density, life and safety of a LIB. Considerable effort has been devoted to obtaining novel architectures of nanomaterials fabricated by nano-engineering. The resultant creative nanostructured materials are promising alternatives to be utilized as electrodes or electrolyte materials, just to name a few. The research aim of this thesis is to design and synthesize nanostructured materials for LIBs, in order to boost the electrochemical performances and overcome the shortcomings of bulk structures used today.

# 2.2 Objectives of the thesis

The research objectives of this thesis are listed in Figure 2.1. Through investigating the limitations of electrodes or electrolytes, uniquely nanostructured materials are designed and synthesized. To verify the successful synthesis of targeted materials, the as-made samples are systematically characterized, including morphology, structure, composition and so on. The accordingly synthesized samples are prepared as electrodes or electrolytes, and further incorporated in LIBs. The electrochemical performances of samples are analyzed, such as the impedance, Li<sup>+</sup> diffusion coefficient, cycling test, stability after running, etc. Lastly, the reasons for the enhanced performances by the synthesized samples are further unraveled, which aims to understand the relationship between performance and nanostructure, and provide optimized synthetic strategies for nanostructured materials of LIBs.





To face with the fracture issue of Si anodes, Chapter 3 develops a novel strategy to synthesize a Si anode material characterized by a hollow porous nanostructure, 3D carbon shells and SiC interlayers. The accordingly obtained hierarchical nanostructures are further characterized by TEM, SEM, DLS and N<sub>2</sub> sorption techniques. The compositions of the synthesized materials are determined by XRD, ESR, Raman and FTIR characterization techniques. The weight ratio of the active component is quantified by XPS and TGA, to calculate the specific capacity of LIBs. In terms of electrochemical application, the influence of particle sizes on Li<sup>+</sup> diffusion coefficients is investigated by comparing nanostructured samples and bulk samples. The influence of hierarchical nanostructures on impedance, SEI formation and galvanostatic cycling is further determined by comparing hierarchical samples. Finally, the compositional and structural advantages of the synthesized nanomaterials on electrochemical properties are discussed.

To improve the low ionic conductivity and the limited mechanical properties of SPEs, Chapter 4 proposes original dual-functional fillers, constructed by hollow porous SiO<sub>2</sub> nanospheres three-dimensionally wrapped by poly(2,2,6,6-tetramethylpiperidin-4-yl methacrylate) (PTMPM) layers. The nanostructure and compositions of fillers are investigated by TEM, SEM, TGA and FTIR characterization techniques. CSEs are constructed by blending the synthesized fillers, polymers and Li salts. Morphological, thermodynamic and mechanical properties of CSEs are determined by SEM, EDX, DSC and DMA characterization techniques. Compositions and the interactions among components are analyzed by FTIR and Raman characterization techniques to explore the Li<sup>+</sup> coordination multi-environments. In terms of electrochemical properties, the relationship between the amount of fillers and the ionic conductivity is determined, as well as between the amount of Li salts and the ionic conductivity, in order to optimize the compositions of CSEs. The activation energy between the synthesized CSEs and other control samples are compared and discussed. The influence of fillers on Li-ion transference number, ESW and interfacial stability is investigated by comparing CSE samples and SPE samples. Finally, the electrochemical application of the synthesized CSEs is validated by galvanostatic charging-discharging tests.

To enhance the ionic conductivity of SPEs, Chapter 5 proposes a one-pot synthesis process of long-range aligned nanochannels for Li<sup>+</sup> transfer highways. The thermodynamic and morphological properties of the synthesized aligned samples are characterized by DSC and SEM techniques. The ionic conductivity and activation energy between the synthesized aligned samples and the random samples are compared. The Li<sup>+</sup> coordination multi-environments are explored among a series of samples with different amounts of Li salts or dicyandiamides (DCDs) by FTIR characterization.

At the end of the thesis, the benefits of the nanostructured materials proposed in this thesis are summarized and discussed in the general conclusion Chapter 6.

# Chapter 3

# Hollow porous silicon nanospheres with 3D SiC@C coating as high-performance anodes

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# Abstract

Silicon is regarded as one of the most promising anode candidates for next-generation Li-ion batteries because of its high theoretical capacity. However, the main challenge for the practical application of Si anodes is the huge volume change during (de)alloying with lithium, which leads to the pulverization of the active material and severe loss of electrical contact after cycling. Here, we develop hollow porous silicon nanospheres with three-dimensional carbon coating and SiC transition interlayer (C@SiC@Si@SiC@C) via a simple and straightforward polymer-directed strategy in order to tackle the challenges encountered with Si anodes. The accordingly synthesized C@SiC@Si@SiC@C anode shows high utilization of the active substance, high measured capacity (3200 mAh g<sup>-1</sup>) with almost 100% Coulombic efficiency and stable cycling performance (0.7‰ per cycle decay rate at 0.2 C). Such superior performances are related to the uniquely designed structure. Firstly, the 3D carbon coating provides high electronic conductivity, and the extremely small size of silicon shortens the diffusion distance for Li ions and electrons. Secondly, the stable cyclability originates from the nanoscale silicon particles reinforced by a SiC transition interlayer which effectively prevents fracture and provides robust outer layers, respectively.

KEYWORDS: silicon anode, three-dimensional coating, polymer template, Li-ion battery, hollow porous nanospheres

# 3.1 Introduction

Rechargeable Li-ion batteries (LIBs), which feature high energy density and long cycle life, are utilized in a wide range of practical applications, e.g., portable electrical devices, electric vehicles, aerospace industry and so forth [1-3]. While the ever-growing energy requirements of our society are still not satisfied with the energy density of current LIB technologies, electrodes and electrolyte materials with superior performance are highly pursued. In terms of anode materials, compared with graphite (~372 mAh g<sup>-1</sup>), silicon presents more than ten times higher theoretical storage capacity, and endows with moderate lithium-uptake electrochemical potential (≤0.4 V vs. Li/Li<sup>+</sup>) [4]. Therefore, Si has been regarded as one of the most promising anode candidates for next-generation LIBs [5]. However, the biggest challenge for its practical application is the huge volumetric variation (>300%) during the lithium insertion and extraction processes [6]. The resulting lithiation-delithiation strains incur the pulverization of active silicon materials as well as the repeated destruction of the solid electrolyte interface (SEI) layer, which, as a consequence, leads to severe loss of active material and electrical contact [7]. Inevitably, the overall capacity degrades along with longtime running.

To date, significant advances have been achieved to solve the above-mentioned problems, which can be generally divided into two categories. The first strategy comprises decreasing the dimension of silicon particles. In this respect, Liu et al. reported that the fracture of silicon nanoparticles during lithiation strongly depends on the particle size, with a critical "no-fracture" size of ~150 nm [8]. Therefore, considerable efforts have been devoted to downsizing Si particles by nano-engineering, e.g. by preparing nanowires [9-13], nanoparticles [14-17], nanodots [5], and hollow structures [18-21]. For instance, hierarchically porous Si nanospheres with a thickness of 75 nm effectively prevent fracture and also accommodate volume expansion, achieving excellent cyclability for hundreds of cycles [18]. The second method is to encapsulate silicon with an outer coating layer (e.g. coreshell [22-25], yolk-shell [26-29], and their derivatives [6, 30]) which has been proved as an effective strategy to alleviate the volumetric expansion characteristic not only of silicon-based anode materials but also of other anode materials suffering from the same problem [31, 32]. In particular carbon as the outer layer has attracted wide attention, due to its supplement of electrical conductivity for the inner Si material. A successful example is shown in a pomegranate-inspired design of silicon nanoparticles encapsulated by a carbon layer that protects from pulverization, stabilizes the SEI, and ensures good electrical connection between particles, resulting in high capacity and superior cyclability [30]. In those previously reported studies, carbon coating invariably requires post introduction of foreign carbon by e.g. chemical vapor deposition (CVD) [5, 20] or post impregnation [21]. However, introduction of extrinsic carbon source requires additional organic

precursors and complicated processes which increase the resources and energy consumption. Moreover, a single layer of amorphous carbon is reported to be brittle and tends to break when exerted to mechanical stress during the expansion of silicon [33]. Therefore, the development of novel nanoscale silicon anodes wrapped by robust and conductive coatings obtained *via* cost-effective and straightforward approaches is of great importance and interest.

Herein, we introduce a novel and innovating strategy to synthesize an original Si anode material characterized by a hollow porous nanostructure, 3D carbon shells and SiC interlayer. Thanks to the spontaneous migration of the polymer segments due to the external polarity change of the solvent, the poly(2,2,6,6-tetramethyl-4-piperidyl methacrylate) (PTMPM) polymer template directs the formation of three-dimensional carbon outer layers. In addition, a hard SiC interlayer is further formed by the reaction between Si and C during the reduction of the SiO<sub>2</sub> precursor. Such a uniquely designed structure of nanoscale silicon core/functional shell effectively inhibits the fracturing of Si particles, enhances their electrical conductivity and shortens the pathway of electrons and Li<sup>+</sup> ions in the active materials, further allowing outstanding LIB performance. The originality of our approach is not only related to the unique nanosized design of the Sibased electroactive nanoparticles but also on the disclosed fabrication method based on a stimuli-responsive polymer template. The ability of polymer chains to migrate through the nanopores of the precursor SiO<sub>2</sub> shell upon exposure to a specific solvent offers the possibility to wrap

the particles by a polymer layer. This unique reorganization process of the polymer template is at the origin of the three-dimensional design of the particles investigated in this study. Furthermore, this fabrication process does not require external sources of carbon precursor.

# 3.2 Experimental section

# 3.2.1 Materials

2,2,6,6-Tetramethyl-4-piperidyl methacrylate (TMPM, C<sub>13</sub>H<sub>23</sub>NO<sub>2</sub>), and vinylene carbonate (VC) were supplied by TCI. Ethanol (EtOH, 99.97%), hydrochloric acid (HCl, 37%), ammonia (NH<sub>3</sub>·H<sub>2</sub>O, 32%), sodium hydroxide (NaOH) and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 95%) were supplied by VWR. 2,2'-Azobis(2-methylpropionamidine) dihydrochloride (C<sub>8</sub>H<sub>18</sub>N<sub>6</sub>·2HCl) was supplied by Acros Organics. CTAB (C<sub>19</sub>H<sub>42</sub>BrN) was supplied by Carl Roth. TEOS, magnesium (20 - 230 mesh, 98%), and lithium hexafluorophosphate (LiPF<sub>6</sub>) solution in ethylene carbonate (EC) and diethyl carbonate (DEC) were supplied by Sigma-Aldrich. Lithium metal foils were supplied by Alfa Aesar. N-methylpyrrolidone (NMP) was supplied by Tisher. Super P and polyvinylidene difluoride (PVDF) were supplied by XIAMEN TOB. Glass fiber membrane was supplied by Whatman. All chemicals were used as received without any further treatment. Milli-Q water was used.

## 3.2.2 Sample synthesis

#### • Synthesis of TMPM-Cl

TMPM (5 g) were dissolved in EtOH (25 ml) at room temperature, and further stirred for 30 min. Then a HCl solution (6.5 mL, 4.1 M) was added into the solution, at a syringe speed of 13 mL h<sup>-1</sup>, and stirring was continued for 1 h. The dry TMPM-Cl was obtained by removing the solvent with a rotary evaporator followed by drying in a vacuum oven at 40 °C overnight.

#### • Synthesis of PTMPM

TMPM-Cl (1 g) was dissolved into a mixture of water (3 mL) and EtOH (3 mL). Then  $C_8H_{18}N_6$ ·2HCl (50 mg) was added into the above solution. After thoroughly degassing with argon, the mixed solution was placed in an oil bath of 70 °C for 3 h. Finally, PTMPM was obtained.

#### • Synthesis of C@SiC@Si@SiC@C nanospheres

#### (a) Synthesis of PTMPM-silica composite nanospheres

PTMPM (0.3 mL) and water (9.7 mL) were mixed and stirred for 1 h. Afterwards, a NaOH solution (1 mL, 1.25 M) was dropwise added into the above solution and stirred overnight. The suspension was centrifuged at 5000 rpm for 20 min. The precipitate was collected and washed with water until the pH reached a value of 7 - 8. The washed sample was dissolved into EtOH (8 mL) and dropwise added into a CTAB solution (20 mL, 3.75 mg mL<sup>-1</sup>). Successively, NH<sub>3</sub>·H<sub>2</sub>O (30 µL) and TEOS (200 µL) were thoroughly mixed into the solution. The mixed solution was heated in an oil bath at 38 °C for 24 h. The P@SiO<sub>2</sub> particles were

finally collected by centrifugation at 9000 rpm for 20 min.

#### (b) Swelling of PTMPM and *in-situ* carbonization

The P@SiO<sub>2</sub> sample was swelled in EtOH for 24 h and freeze-dried, to obtain the swollen sample, denoted as P@SiO<sub>2</sub>@P. P@SiO<sub>2</sub>@P (0.2 g) was impregnated by a H<sub>2</sub>SO<sub>4</sub> aqueous solution (0.6 mL, 10 wt%) for 2 h at room temperature, followed by 12 h at 100 °C, and finally 12 h at 160 °C. The pre-carbonized sample was calcined for 2 h at 900 °C in a tubular furnace under argon atmosphere, with a ramp rate of 2 °C min<sup>-1</sup>. The carbonized sample was obtained and denoted as C@SiO<sub>2</sub>@C.

#### (c) Magnesiothermic reduction reaction

C@SiO<sub>2</sub>@C sample, magnesium powder, and NaCl were thoroughly mixed in an agate mortar, where the molar ratio of SiO<sub>2</sub> (in C@SiO<sub>2</sub>@C) and Mg was 1:2.1, and the mass ratio of Mg and NaCl was 1:10. The mixture was then sealed in a boron nitride reactor under argon. In a typical magnesiothermic reduction reaction, the reactor was heated at 650 °C for 2.5 h under argon atmosphere, with a ramp rate of 10 °C min<sup>-1</sup> below 400 °C and a ramp rate of 1 °C min<sup>-1</sup> from 400 °C to 650 °C. The reduced sample was washed by HCl (1M) and HF (1 vol%) solutions more than three times, to achieve the C@SiC@Si@SiC@C composite material. At least three samples were prepared to assess the reproducibility of the results.

#### Synthesis of hollow porous pure Si nanospheres

#### (a) Synthesis of hollow porous SiO<sub>2</sub> nanospheres

PTMPM (0.3 mL) and water (9.7 mL) were mixed and stirred for 1 h. Afterwards, a NaOH solution (1 mL, 1.25 M) was dropwise added

into the above solution and stirred overnight. The suspension was centrifuged at 5000 rpm for 20 min. The precipitate was collected and washed by water until the pH reached a value of 7 - 8. The washed sample was dissolved into EtOH (8 mL), and dropwise added into a CTAB solution (20 mL, 3.75 mg mL<sup>-1</sup>). Successively, NH<sub>3</sub>·H<sub>2</sub>O (30  $\mu$ L) and TEOS (200  $\mu$ L) were thoroughly mixed into the solution. The mixed solution was heated in an oil bath at 38 °C for 24 h. The P@SiO<sub>2</sub> particles were collected by centrifugation at 9000 rpm during 20 min for 3 times. The P@SiO<sub>2</sub> sample was calcined for 2 h at 900 °C in a muffle furnace under air atmosphere. Then the sample of hollow porous SiO<sub>2</sub> was obtained.

## (b) Magnesiothermic reduction reaction

Hollow porous SiO<sub>2</sub> sample, magnesium powder, and NaCl were thoroughly mixed in an agate mortar, where the molar ratio of SiO<sub>2</sub> and Mg was 1:2.1, and the mass ratio of Mg and NaCl was 1:10. Then the mixture was sealed in a boron nitride reactor under argon. In a typical magnesiothermic reduction reaction, the reactor was heated at 650 °C for 2.5 h under argon atmosphere, with a ramp rate of 10 °C min<sup>-1</sup> below 400 °C and a ramp rate of 1 °C min<sup>-1</sup> from 400 °C to 650 °C. The reduced sample was washed by 1 M HCl and 1 vol% HF solutions more than three times, to achieve the hollow porous pure Si material.

Synthesis of C@SiC@C nanospheres

#### (a) Synthesis of PTMPM-silica composite nanospheres

PTMPM (0.3 mL) and water (9.7 mL) were mixed and stirred for 1 h. Afterwards, a NaOH solution (1 mL, 1.25 M) was dropwise added

into the above solution and stirred overnight. The suspension was centrifuged at 5000 rpm for 20 min. The precipitate was collected and washed by water until the pH reached a value of 7 - 8. The washed sample was dissolved into EtOH (8 mL), and dropwise added into a CTAB solution (20 mL, 3.75 mg mL<sup>-1</sup>). Successively, NH<sub>3</sub>·H<sub>2</sub>O (30  $\mu$ L) and TEOS (200  $\mu$ L) were thoroughly mixed into the solution. The mixed solution was heated in an oil bath at 38 °C for 24 h. The P@SiO<sub>2</sub> particles were finally collected by centrifugation at 9000 rpm during 20 min for 3 times.

#### (b) Swelling of PTMPM and *in-situ* carbonization

The P@SiO<sub>2</sub> sample was swelled in EtOH for 24 h and freeze-dried, to obtain the swollen sample, denoted as P@SiO<sub>2</sub>@P. P@SiO<sub>2</sub>@P (0.2 g) was impregnated by a H<sub>2</sub>SO<sub>4</sub> aqueous solution (0.6 mL, 10 wt%) for 2 h at room temperature, followed by 12 h at 100 °C, and finally 12 h at 160 °C. The pre-carbonized sample was calcined for 2 h at 900 °C in a tubular furnace under argon atmosphere, with a ramp rate of 2 °C min<sup>-1</sup>. The carbonized sample was obtained and denoted as C@SiO<sub>2</sub>@C.

#### (c) Magnesiothermic reduction reaction

C@SiO<sub>2</sub>@C sample, magnesium powder, and NaCl were thoroughly mixed in an agate mortar, where the molar ratio of SiO<sub>2</sub> (in C@SiO<sub>2</sub>@C) and Mg was 1:2.1, and the mass ratio of Mg and NaCl was 1:10. The mixture was then sealed in a boron nitride reactor under argon. In a typical magnesiothermic reduction reaction, the reactor was heated at 650 °C for 2.5 h under argon atmosphere, with a ramp rate of 10 °C min<sup>-1</sup> below 400 °C and a ramp rate of 1 °C min<sup>-1</sup> from 400 °C to 650 °C. The reduced sample was firstly washed by HCl (1M), and then washed by HF (1 vol%) solutions more than a week to completely remove the silicon and unreacted silica, to achieve the C@SiC@C composite material.

# Synthesis of C@SiC@Si&SiO2@SiC@C nanospheres

#### (a) Synthesis of PTMPM-silica composite nanospheres

PTMPM (0.3 mL) and water (9.7 mL) were mixed and stirred for 1 h. Afterwards, a NaOH solution (1 mL, 1.25 M) was dropwise added into the above solution and stirred overnight. The suspension was centrifuged at 5000 rpm for 20 min. The precipitate was collected and washed by water until the pH reached a value of 7 - 8. The washed sample was dissolved into EtOH (8 mL), and dropwise added into a CTAB solution (20 mL, 3.75 mg mL<sup>-1</sup>). Successively, NH<sub>3</sub>·H<sub>2</sub>O (30 µL) and TEOS (200 µL) were thoroughly mixed into the solution. The mixed solution was heated in an oil bath at 38 °C for 24 h. The P@SiO<sub>2</sub> particles were finally collected by centrifugation at 9000 rpm during 20 min for 3 times.

#### (b) Swelling of PTMPM and *in-situ* carbonization

The P@SiO<sub>2</sub> sample was swelled in EtOH for 24 h and freeze-dried, to obtain the swollen sample, denoted as P@SiO<sub>2</sub>@P. P@SiO<sub>2</sub>@P (0.2 g) was impregnated by a H<sub>2</sub>SO<sub>4</sub> aqueous solution (0.6 mL, 10 wt%) for 2 h at room temperature, followed by 12 h at 100 °C, and finally 12 h at 160 °C. The pre-carbonized sample was calcined for 2 h at 900 °C in a tubular furnace under argon atmosphere, with a ramp rate of 2 °C min<sup>-1</sup>. The carbonized sample was obtained and denoted as C@SiO<sub>2</sub>@C.

#### (c) Magnesiothermic reduction reaction

C@SiO<sub>2</sub>@C sample, magnesium powder, and NaCl were thoroughly mixed in an agate mortar, where the molar ratio of SiO<sub>2</sub> (in C@SiO<sub>2</sub>@C) and Mg was 1:2.1, and the mass ratio of Mg and NaCl was 1:10. The mixture was then sealed in a boron nitride reactor under argon. In a typical magnesiothermic reduction reaction, the reactor was heated at 650 °C for 2.5 h under argon atmosphere, with a ramp rate of 10 °C min<sup>-1</sup> below 400 °C and a ramp rate of 1 °C min<sup>-1</sup> from 400 °C to 650 °C. The reduced sample was washed by HCl (1M), to achieve the C@SiC@Si&SiO<sub>2</sub>@SiC@C composite material.

## 3.2.3 Characterizations

Transmission electron microscopy (TEM) imaging was performed on a FEI Tecnai G<sup>2</sup>20 system at an acceleration voltage of 120 kV and the layers structure of C@SiC@Si@SiC@C was investigated with a JEOL JEM-2100 (JEOL GmbH, Eching, Germany) at an acceleration voltage of 200 kV. Samples have been prepared by applying a finely grinded powder onto a carbon coated TEM grid (Quantifoil, Germany). Scanning electron microscopy (SEM) images were collected with a JEOL 7600F electron microscope. An ALV/CGS-3 compact goniometer system (ALV GmbH, Germany) was used to measure the average hydrodynamic radius of the samples using dynamic light scattering (DLS). The CONTIN algorithm available in the ALV software was used to analyze DLS data. Nitrogen sorption isotherms were measured with a Micromeritics ASAP 2020 analyzer at 77 K. X-ray diffraction (XRD) patterns were collected on a STOE Stadi P transmission diffractometer system using Cu-K $\alpha$  ( $\lambda$ =1.54 Å) or Mo-K $\alpha$  ( $\lambda$ =0.71 Å) radiation. X-band electron spin resonance (ESR) spectra were acquired on an EMXmicro CW-EPR spectrometer from Bruker, Germany (EMX micro EMM-6/1/9-VT control unit, ER 070 magnet, EMX premium ER04 X-band microwave bridge equipped with EMX standard resonator, EMX080 power unit). The powdery samples were investigated at room temperature and the data handling was done using the Bruker Xenon software package, version 1.1b86. Raman analysis was carried out using a DXR Raman microscope with laser excitation at 532 nm from Thermo Fisher Scientific. FTIR spectra were recorded with the KBr method on a Nicolet iN10 IR Microscope from Thermo Fisher Scientific. Thermogravimetric analysis (TGA) was conducted in a TGA/SDTA851 instrument from Mettler Toledo under air flow with a heating ramp of 5 °C min<sup>-1</sup>. X-ray photoelectron spectroscopy (XPS) analysis was realized at room temperature by using a SSI X-Probe (SSX 100/206) photoelectron spectrometer from FISONS equipped with a monochromatized microfocus Al-Ka X-ray source.

# 3.2.4 Electrochemical measurements

C@SiC@Si@SiC@C, super P, and PVDF (5wt% in NMP) were mixed with a mass ratio of 7:2:1 to form a slurry. After casting the

slurry onto a copper foil, the electrode was dried in a vacuum oven overnight at 70 °C. A polished lithium metal foil was used as a reference and counter electrode. A glass fiber membrane was used as a separator. The electrolyte consisted of LiPF<sub>6</sub> (1 M) in EC and DEC (1:1 v/v), with VC (1 vol%) as an additive. All coin-cells (2032) were assembled under an argon atmosphere (H<sub>2</sub>O and O<sub>2</sub> <0.1 ppm) in a MBraun glovebox. The cells were cycled galvanostatically between 0.01 V and 1.5 V vs. Li/Li<sup>+</sup> on a NEWARE system. Galvanostatic intermittent titration technique (GITT) was used after two cycles of activation at 0.02 C, wherein the current density of pulse current was 0.02 C for 10 minutes, followed by 1 hour as rest time. Electrochemical impedance spectroscopy (EIS) tests were carried out using a Bio-Logic BSC-COM instrument. Charge/discharge rates were calculated based on the theoretical capacity of silicon (C = 4200 mA g<sup>-1</sup>).

# 3.3 Results and discussion

The strategy used in this contribution for the synthesis of hollow porous C@SiC@Si@SiC@C nanospheres with 3D SiC@C coating is illustrated in Figure 3.1A and is directed by the swelling behavior of the PTMPM (structural formula in Figure 3.2) polymer template. This novel and innovating strategy is based on four successive main steps: (i) synthesis of PTMPM-silica composite nanospheres, (ii) swelling of PTMPM, (iii) *in-situ* carbonization, and finally (iv) magnesiothermic reduction.



**Figure 3.1** Synthetic pathway towards C@SiC@Si@SiC@C hollow porous nanospheres (A). TEM images of P@SiO<sub>2</sub> (B), P@SiO<sub>2</sub>@P (C), C@SiO<sub>2</sub>@C (D), and C@SiC@Si@SiC@C (E) with the corresponding high magnification inserts. Projection images of C@SiO<sub>2</sub>@C (D1-D6) and C@SiC@Si@SiC@C (E1-E6) at various tomography tilt angles ranging from -50 to 0°, with a scale bar of 100 nm.



**PTMPM** 

**Figure 3.2** Chemical structure of poly(2,2,6,6-tetramethyl-4-piperidyl methacrylate) (PTMPM).

Firstly, PTMPM-silica composite nanospheres with a porous silica shell have been synthesized, using our previously reported procedure [34]. This approach relies on a mini-emulsion process resulting in monodisperse PTMPM spherical nanoparticles stabilized bv cetyltrimethylammonium bromide (CTAB) surfactant molecules which are denoted as P@CTAB. In a further step, both PTMPM and CTAB are used as templating agents. More precisely, the condensation reaction of tetraethoxysilane (TEOS) is realized on the P@CTAB nanoparticles, and core-shell nanoparticles that consist of a PTMPM core and a porous silica shell (denoted as P@SiO<sub>2</sub>) are obtained after removal of the excess of TEOS and CTAB. The porosity in the SiO<sub>2</sub> shell originates from the partial removal of CTAB molecules and/or CTAB micelles located at the surface of the PTMPM nanoparticles, which is in agreement with our previous reports [35, 36]. The transmission electron microscope (TEM) image presented in Figure 3.1B shows that the P@SiO<sub>2</sub> composite has a regular spherical shape with a uniform diameter around 100 nm. The magnified insert image in Figure 3.1B shows the rough edges of the nanospheres resulting from the porous SiO<sub>2</sub> shells.

Secondly, the P@SiO<sub>2</sub> nanospheres have been brought into contact with ethanol, resulting in the swelling of the PTMPM polymer. The swelling of PTMPM does not result in the breaking of the porous SiO<sub>2</sub> layer but rather in swollen PTMPM polymer chain segments passing through the pores from the inside of P@SiO<sub>2</sub> nanospheres to their outside. This results in a three-dimensional wrapping of PTMPM around the porous SiO<sub>2</sub> shells, and the resulting swollen materials are denoted as P@SiO<sub>2</sub>@P. Compared to other reported synthetic methods for Si@C composites (Table 3.1), the carbon precursor in the P@SiO2@P sample originates from the PTMPM templating agent rather than from an extrinsic carbon source. Moreover, PTMPM polymer chains direct the formation of the future three-dimensional carbon outer layers obtained after calcination. The spontaneous migration of PTMPM polymer chain segments in response to the external polarity change of the solvent is at the origin of this behavior. This unique re-wrapping process of the precursor nanoparticles by PTMPM allows to get rid of additional steps in order to generate the targeted 3D structure, further saving additional material, times and energy costs. Practically, the migration of PTMPM chain segments leads to extra outer margins for the nanoparticles, as shown in Figure 3.1C. The swelling behavior of PTMPM in ethanol is further confirmed by dynamic light scattering (DLS). As shown in Figure 3.3A, the particle radius of swollen P@SiO<sub>2</sub>@P samples is 95.7 nm, which is significantly larger than that of the initial P@SiO<sub>2</sub> (78.4 nm). Besides, the polydispersity index (PD.I.) measured by DLS for P@SiO<sub>2</sub>@P (PD.I. of 0.116) is smaller than that of P@SiO<sub>2</sub> (PD.I. of 0.137), suggesting a more homogeneous size distribution for the nanoparticles after PTMPM swelling. This observation is further confirmed by TEM images before and after swelling. Compared to the rough edges of P@SiO<sub>2</sub>, P@SiO<sub>2</sub>@P nanoparticles display a smooth surface, since the porous SiO<sub>2</sub> nanospheres are wrapped by a conformal and uniform PTMPM coating layer (Figures 3.1B and C). The change in porosity of the nanoparticles associated with the swelling of PTMPM has been also tracked by N<sub>2</sub> adsorption-desorption isotherms. As shown in Figure 3.3B, P@SiO<sub>2</sub> and P@SiO<sub>2</sub>@P display isotherms of similar tendency, with a gradual increase in adsorption quantity in the relative pressure range of 0 - 0.3, and another sharp capillary condensation step in the relative pressure range of 0.9 - 1.0, indicating the co-existence of two types of pores in these two samples. The smaller pores are attributed to the porosity generated in the SiO<sub>2</sub> shell by the arrangement of CTAB molecules, while the larger pores refer to the inside of the nanospheres filled with PTMPM. The pore size distribution curves derived from the adsorption branch based on the Barrett-Joyner-Halanda model show a bimodal porous structure with highly uniform small pores centered at ~ 1 nm and larger pores with a relatively broad size distribution ranging from 40 nm to 200 nm (Figure 3.3C). Textural properties (Table 3.2) calculated from the N<sub>2</sub> sorption isotherms

indicate that, before swelling,  $P@SiO_2$  exhibits a large surface area (424 m<sup>2</sup> g<sup>-1</sup>) and large pore volume (0.34 cm<sup>3</sup> g<sup>-1</sup>). After swelling, the size of both small and large pores in the  $P@SiO_2@P$  sample decreases as well as the surface area (420 m<sup>2</sup> g<sup>-1</sup>) and the pore volume (0.32 cm<sup>3</sup> g<sup>-1</sup>) since swollen PTMPM occupies more volume and is filling the pores.

Ref	Sample	Synthetic method		Elect	rochem	ical per	forman	ce	
		1) The DTMDM polymer template constance why evalls in	Rate (C)	0.1	.0	0.20	0.40	)	1.00
This C@ work S	C@SiC@Si@	<ul> <li>1) The PTMPM polymer template spontaneously swells in –</li> <li>EtOH and forms three-dimensional outer layers.</li> <li>2) Si, C, and SiC interlayer originate from the –</li> <li>magnesiothermic reduction of SiO<sub>2</sub> at 650 °C.</li> </ul>	Rate (mA g⁻¹)	42	0	840	1680	) ,	4200
	3166931		Capacity (mAh g <sup>-1</sup> )	394	18	3419	2600	)	1214
[24]	Si core/C	1) The poly-peri-naphthalene (PPN) is wrapped on the	Rate (mA g⁻¹)	100	200	500	1000	2000	5000
[24] layer	layer	2) The PPN layer is carbonized at 800 °C.	Capacity (mAh g <sup>-1</sup> )	-	1712	1513	1402	1209	876
[4 - ]	silicon nanocrystal-	1) Solid Si clusters are encapsulated by the corn-starch and CTAB micelles by micro-emulsion method.	Rate (mA g⁻¹)	40	100 20	0 400	600 10	000 150	00 2000
[15]	[15]micro carbon2) Si particles nucleate by collision reaction at 320 °C.ball3) Carbonized under a C3H6 atmosphere at 800 °C.	Capacity (mAh g <sup>-1</sup> )	1500	in the ra	ange of	1300-14	150 ~12	50 1150	
[37]	Si@SiC@ graphite	<ol> <li>1) SiO<sub>2</sub>, Mg and graphite nanosheets (GNs) are ballmilled.</li> <li>iC@</li> <li>2) Si/SiC/GNs composites are obtained by –</li> <li>hite magnesiothermic reduction.</li> </ol>	Rate (mA g⁻¹)	100	200	500	1000	2000	5000
			Capacity (mAh g <sup>-1</sup> )	1193	1100	981	868	804	675

**Table 3.1** Comparison of the synthetic method and the electrochemical performance of various Si-based anode materials.

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[38]	hollowed carbon	hollowed carbon 2) The ZIF-8@SiO <sub>2</sub> yolk-shell structure is carbonized and		100		200	500	)	1000
	polyhedron @SiC@Si	reduced by magnesiothermic reaction at 800 °C.	Capacity (mAh g <sup>-1</sup> )	~800	) ^	~500	~30	0	~200
[20]	SiN coated	<ol> <li>The pristine porous Si is prepared via thermal nitridation of Mg<sub>2</sub>Si under N<sub>2</sub> at 750 °C.</li> </ol>	Rate (mA g <sup>-1</sup> )	100	200	500	1000	2000	5000
[39] b	Si@SiN)	2) The fresh porous Si is washed by HF and annealed under NH₃ at 860 °C to produce p-Si@SiN.	Capacity (mAh g <sup>-1</sup> )	2584	2199	2071	1899	1590	1125
	n a na na na Ci	1) Fabricate the mesoporous silica nanospheres (MSNs)	Rate (C)	0.1	0.2	. 0	).5	1	2
[40]	porous Si nanospheres /rGO	brows Si2) The MSNs and GO composite (MSNs/GO) areospheressynthesized by electrostatic self-assembly./rGO3) MSNs/GO is reduced by a modest magnesiothermicreduction with Mg2Si as the Mg vapor source.	Rate (mA g <sup>-1</sup> )	420	840	) 2:	100 4	1200	8400
			Capacity (mAh g <sup>-1</sup> )	2018	189	2 14	133	933	497



**Figure 3.3** DLS analysis of P@SiO<sub>2</sub> and P@SiO<sub>2</sub>@P (A). N<sub>2</sub> adsorption-desorption isotherms (B), and the corresponding pore size distribution curves (C) of P@SiO<sub>2</sub>, P@SiO<sub>2</sub>@P, and C@SiO<sub>2</sub>@C.

	Sper	Pore diam	Pore	
Sample	(m <sup>2</sup> g <sup>-1</sup> ) <sup>a)</sup>	small	largo	volume
	(	Silidii	laige	(cm <sup>3</sup> g <sup>-1</sup> ) <sup>c)</sup>
P@SiO <sub>2</sub>	424	1.3	114.6	0.34
P@SiO <sub>2</sub> @P	420	1.1	76.8	0.32
C@SiO₂@C	827	1.3	117.3	0.66

Table 3.2 Textural properties of P(	@SiO <sub>2</sub> , P@SiO <sub>2</sub> @P, and C@SiO <sub>2</sub> @C
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<sup>a)</sup> Surface area calculated from the adsorption branches at 0.02 - 0.2 on the basis of Brunauer-Emmet-Teller method; <sup>b)</sup> Pore diameter calculated by Barrett-Joyner-Halenda method from the adsorption branch of isotherms; <sup>c)</sup> Pore volume calculated from the adsorbed amount at  $p/p_0$  of 0.995.

Thirdly, the swollen PTMPM and remaining CTAB molecules have been transformed *in-situ* into carbon material by pretreatment with sulfuric acid followed by high-temperature carbonization. Sulfuric acid, by initiating reactions of dehydration and sulfonation, is well-known to allow the immobilization of carbonaceous substances during calcination [41, 42]. After calcination under argon atmosphere, 3D carbon layers are therefore generated in-situ on the inner and outer surface of the porous silica shell and replicate the initial templating structure of P@SiO<sub>2</sub>@P nanoparticles. Remarkably, the spherical morphology of those carbonized materials (denoted as C@SiO<sub>2</sub>@C) is highly preserved after high-temperature calcination, as a proof of the good thermal stability of the obtained composites (Figure 3.1D). The preservation of the spherical morphology is further confirmed by continual multi-angle tomographic images (Figures 3.1D<sub>1</sub>-D<sub>6</sub>). As expected, the carbonization of swollen PTMPM and CTAB molecules to thin carbon layers results in increased pore size, surface area and pore volume for C@SiO<sub>2</sub>@C nanoparticles compared to the P@SiO<sub>2</sub>@P precursor, confirming the porosity of the nanoparticles after the carbonization process (Figures 3.3B and C, and Table 3.2).

Finally, silica has been reduced to silicon by a magnesiothermic reduction reaction. Meanwhile a silicon carbide interlayer is generated at the contact region between silicon and carbon, assisted by magnesium [43-45]. Thus, the targeted hollow porous silicon nanospheres coated with a 3D SiC@C structure have been obtained and are denoted as C@SiC@Si@SiC@C (Figures 3.1E and 3.4A). Those uniform hollow nanostructures are clearly observed in tomography characterization (Figures 3.1E<sub>1</sub>-E<sub>6</sub>), and further show a large difference compared to samples before reduction. The shell thickness of the final hollow spheres is ~14 nm as measured by TEM (Figure 3.1E). Those shells are consisting of a sandwich-like structure, listed from the inside to the outside as C, SiC, Si, SiC, and C, which is further confirmed by high-resolution TEM (Figure 3.4B) and justifies the C@SiC@Si@SiC@C acronym. As a consequence, it could be inferred that the actual thickness of the inner silicon layer is less than 14 nm (Figure 3.4C). Such an ultrathin silicon layer with SiC@C functional coating is highly sought in the design of silicon-based anode materials, since it could easily accommodate severe volumetric expansion during lithium insertion and display improved electronic conductivity.



**Figure 3.4** SEM image (A) and high-resolution TEM image (B) of the C@SiC@Si@SiC@C sample, schematic diagram (C) of the sandwich structure of the composite shells.

The composition of the C@SiC@Si@SiC@C nanospheres has been further analyzed by X-ray diffraction (XRD) as shown in Figure 3.5A. As a comparison, the XRD pattern of the C@SiO<sub>2</sub>@C precursor displays only one broad peak attributed to amorphous silica. This broad peak disappears after reduction for the C@SiC@Si@SiC@C sample and is replaced by a series of intense peaks located at 28.5°, 47.5°, and 56.3°, corresponding to (111), (220), and (311) of the Fd3m silicon phase (JCPDS 77-2107), respectively. In addition, the peak at 35.3° is indexed to silicon carbide (JCPDS 74-2307). These results confirm the successful conversion of silica to silicon, as well as the consecutive reaction of silicon and carbon to form a small amount of silicon carbide. According to the existing reports and the structural characteristics of C@SiC@Si@SiC@C nanospheres, the silicon carbide formation could be attributed to the close areal contact of reactants between silicon and carbon with the assistance of magnesium [43-45]. The presence of amorphous carbon could not be detected in the XRD pattern, but will be further evidenced below by other experimental techniques.



**Figure 3.5** XRD patterns of C@SiC@Si@SiC@C and C@SiO<sub>2</sub>@C samples (A). ESR spectra of C@SiC@Si@SiC@C and Si (B). Raman spectra (C) and FTIR spectra (D) of P@SiO<sub>2</sub>, P@SiO<sub>2</sub>@P, C@SiO<sub>2</sub>@C, and C@SiC@Si@SiC@C.

In order to confirm the presence of carbon layers in the synthesized samples, electron spin resonance (ESR) has been employed to study the electron states of the Si surface with and without the carbon layer (Figure 3.5B). Under air atmosphere, strong ESR signals are detected in the C@SiC@Si@SiC@C sample, which originate from unpaired electrons on the Si surface while, without carbon coating, the signals associated to hollow porous pure Si material dramatically weaken (the synthetic process towards hollow porous pure Si is detailed in the 3.2.2 section, SEM image and XRD pattern are presented in Figure 3.6), because the unpaired electrons
on the Si surface are mostly captured by O<sub>2</sub> when silicon is exposed to air without any coating [24, 25]. These results unambiguously demonstrate that the porous Si in the C@SiC@Si@SiC@C sample is protectively encapsulated by outer carbon layers. Raman spectroscopy and Fourier-transform infrared (FTIR) spectroscopy have then been used to monitor structural and compositional changes among carbonaceous species in the four synthetic stages. In the Raman spectrum before carbonization, the C-H bands from PTMPM and CTAB in P@SiO<sub>2</sub> and P@SiO<sub>2</sub>@P are detectable (Figure 3.5C). After carbonization, all C-H bands disappear, while the two strong D band at 1331 cm<sup>-1</sup> and G band at 1588 cm<sup>-1</sup> are detected due to the formation of sp<sup>2</sup> carbon, indicating that organic matter has been completely transformed to carbon black during high-temperature calcination. After reduction, the D and G bands are both preserved. Notably, the Ig/Id ratio increases to 0.98 after reduction compared to 0.96 before reduction, indicating that the graphitization level slightly increases after reduction [46]. Furthermore, a series of characteristic Si bands appears at 292, 503, and 920 cm<sup>-1</sup> [47]. Besides, compared to the hollow porous pure silicon, the main Si band of the C@SiC@Si@SiC@C sample exhibits a blue shift from 499.0 cm<sup>-1</sup> to 502.8 cm<sup>-1</sup>. Based on the phonon confinement effect, this blue shift suggests that the size of the composite particles increases due to the presence of the outer coating layers [48]. In the corresponding FTIR spectra, both P@SiO<sub>2</sub> and P@SiO<sub>2</sub>@P show characteristic bands of the CH<sub>2</sub> and CH<sub>3</sub> stretching vibrations at 2800 – 3000 cm<sup>-1</sup>, the C=O stretching vibration at 1726 cm<sup>-1</sup>, and the C-H bending vibration at 1461 cm<sup>-1</sup>, all ascribed to the presence of PTMPM and CTAB before carbonization (Figure 3.5D) [46]. After carbonization, all above-mentioned organic bands disappear, in agreement with the complete conversion of the organic materials into carbon, echoed by the results of Raman spectra. As expected, after Mg reduction, a single band characteristic of Si-C at 822 cm<sup>-1</sup> is detected for the C@SiC@Si@SiC@C sample. As a reference, there is no characteristic carbonaceous band in the hollow porous pure Si material. These additional characterizations are further supporting the successful formation of the C@SiC@Si@SiC@C hollow porous nanostructures.



**Figure 3.6** SEM image (A) of the hollow porous pure Si sample with the corresponding enlarged insert. XRD pattern (B) of the hollow porous pure Si sample. <sup>a</sup> XRD pattern is collected by using Mo-Kα radiation.

The composition of the C@SiC@Si@SiC@C hollow porous nanoparticles was quantitively determined by combining X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA) [47]. In Figure 3.7A, before reduction, only quadrivalent Si is observed. After reduction, zero-valent Si, Si-C and a few quadrivalent Si are detected, with the corresponding percentages of 57%, 33%, and 10%, respectively. In Figure 3.7B, before reduction, there is a 4.9% of mass decrease due to the pyrolysis of carbon. In C@SiC@Si@SiC@C, there is a decrease of mass during the pyrolysis of carbon, then an increase due to the oxidization of silicon. To eliminate the influence of oxidization of silicon, the hollow porous pure silicon has been measured as a reference, and has been subtracted from C@SiC@Si@SiC@C, with the corrected curve shown as blue dotted curve [33]. The minimum of corrected curve is 52.7%, which is the mixture of Si, SiC and little remaining SiO<sub>2</sub>. Hence, the weight percentage of zero-valent Si among the C@SiC@Si@SiC@C sample is calculated to be 24%, with the detailed calculation as follows:  $wt_{Si}^{0} =$ 

 $\frac{57\%}{57\%+33\%\times40/28+10\%\times60/28}\times52.7\%=24\%.$ 



**Figure 3.7** XPS Si 2p spectra (A) of C@SiC@Si@SiC@C and C@SiO<sub>2</sub>@C. TGA curves (B) of hollow porous Si, C@SiO<sub>2</sub>@C and C@SiC@Si@SiC@C.

When employed as an anode material, the lithiation-delithiation properties of C@SiC@Si@SiC@C hollow porous nanosphere have

been investigated by galvanostatic charge-discharge measurements within a voltage range of 0.01 - 1.50 V (vs. Li/Li<sup>+</sup>). As shown in Figure 3.8, the electrode has been activated for the first five cycles at a low current rate of 0.02 C and the capacities have been normalized to the total weight of the composite materials. The C@SiC@Si@SiC@C electrode displays high specific discharge capacities up to 2625 mAh gtotal<sup>-1</sup> at the first cycle and tends to maintain stable at 1300 mAh gtotal<sup>-1</sup> <sup>1</sup> from the second cycle. The extremely large capacities are mainly due to the following reasons: i) the hollow porous nanostructure greatly shortens the conduction paths of electrons and Li<sup>+</sup> ions in the active materials, thereby improving the utilization of active materials during the cycling; ii) the additional capacities from composite components under low current density, *e.g.* Si, *C*, and SiC [49-51].



**Figure 3.8** Cycling performance (A) of C@SiC@Si@SiC@C electrode at a current rate of 0.02 C from the 1<sup>st</sup> to the 5<sup>th</sup> cycle, with the corresponding CE of Si content in the C@SiC@Si@SiC@C material. The corresponding charge/discharge curves (B) at the 1<sup>st</sup> cycle and the 2<sup>nd</sup> cycle with a rate of 0.02 C. <sup>a</sup> Specific capacity is based on the total mass of composited materials.



**Figure 3.9** Schematic illustration (A) for C@SiC@Si@SiC@C, hollow porous Si and commercial micron Si at the 4<sup>th</sup> pulse of lithiation and delithiation during GITT tests. An overview of GITT curves (B) of C@SiC@Si@SiC@C, hollow porous Si and commercial  $\mu$ m Si plotted with the voltage as a function of SOC during lithiation and delithiation, with the corresponding Li<sup>+</sup> diffusion coefficients ( $D_{Li}$ ) and overpotentials ( $\eta$ ).

**Table 3.3** Comparison of the average Li-ion diffusion coefficients calculated fromGITT tests.

50	mnlo	C@SiC@Si@Si	hollow porous	commercial		
Sample		C@C	Si	μm Si		
$\overline{D_{L\iota}}$	Lithiation	2.91×10 <sup>-14</sup>	2.31×10 <sup>-14</sup>	4.81×10 <sup>-15</sup>		
(cm³ S⁻¹)	Delithiation	8.90×10 <sup>-14</sup>	6.80×10 <sup>-14</sup>	1.21×10 <sup>-14</sup>		

To confirm the benefit of hollow porous nanostructures, the Li<sup>+</sup> diffusion coefficients (D<sub>Li</sub>) of C@SiC@Si@Si@C, hollow porous Si and commercial  $\mu$ m size Si have been compared by utilizing the galvanostatic intermittent titration technique (GITT). D<sub>Li</sub> is derived from GITT data with the following Equation (3.1):

$$D_{Li} = \frac{4}{\pi\tau} \times \left(\frac{n \times V_m}{S}\right)^2 \times \left(\frac{\Delta E_s}{\Delta E_\tau}\right)^2 \tag{3.1}$$

where  $\tau$  (s) refers to the time of current pulse; *n* (mol) and  $V_m$  ( $cm^3 mol^{-1}$ ) are the mole number and molar volume of active material of electrode, respectively; S is the surface area of the electrode;  $\Delta E_s$  is the steady-state voltage change due to the current pulse; and  $\Delta E_{\tau}$  is the voltage variation during a galvanic titration time  $\tau$ . All are illustrated in a typical analysis of one single step (Figure 3.9A) [29]. The full process is displayed in the plot of voltage as a function of state of charge (SOC), which is the level of charge of a battery relative to its capacity (Figure 3.9B). The average D<sub>Li</sub> of C@SiC@Si@Ci during lithiation or delithiation is slightly larger than that of hollow porous Si and the values measured for both nanoscale samples are obvious higher than for the commercial  $\mu$ m size Si (Table 3.3). Compared to the microscale structure, the hollow porous nanostructure obviously possesses shorter conduction pathways for

the diffusion of Li ions, further promoting the utilization of active materials. Moreover, C@SiC@Si@Si@C provides the smallest overpotential in GITT analysis among the three investigated samples, implying the optimized electrochemical reaction and electrical energy efficiency [29].

In order to further clarify the specific contribution of SiC and C components, C@SiC@C nanospheres with similar hollow porous structures have been synthesized (synthetic process shown in the section 3.2.2, SEM image and XRD pattern in Figure 3.10A and B). At a low current density of 0.02 C, the capacity of the C@SiC@C sample even reaches 1478 mAh g<sup>-1</sup> at the first discharge process with low initial coulombic efficiency (ICE) of 14.9%, and averages at 215 mAh g<sup>-1</sup> for the next 4 cycles (Figure 3.10C). However, when the charge/discharge rate increases to 0.1 C or higher, the capacity substantially decreases. This can be explained in short: the capacity of C@SiC@Si@SiC@C includes specific contributions of Si, SiC and C under low current density. When the current density increases at a higher value than 0.1 C, the capacity mainly originates from Si and the contribution from SiC@C can be considered negligible (Table 3.4). The particularly high capacity and low ICE of C@SiC@C in the first cycle indicate the generation of the SEI. Therefore, the SEI formation of Si in the composite electrode (denoted as Si-in-C@SiC@Si@SiC@C) could be estimated by eliminating the capacity contribution of C@SiC@C from that of C@SiC@Si@SiC@C, combined with the proportion of each component in the C@SiC@Si@SiC@C sample. Consequently, ICE of Siin-C@SiC@Si@SiC@C is calculated to be 64.0%, which is obviously higher than 45.7% for the C@SiC@Si@SiC@C sample. Furthermore, the CEs of the C@SiC@Si@SiC@C surpass 90% from the 2<sup>nd</sup> cycle indicating that the SEI quickly reaches stabilization. Thus, it can be hypothesized that the formation of the SEI on the SiC@C layer eventually prevents excessive SEI formation on the surface of Si and improves the stability of the composite electrode during the cycling.



**Figure 3.10** SEM image (A) of the C@SiC@C sample with the corresponding enlarged insert. XRD pattern (B) of C@SiC@C, collected by using Mo-K $\alpha$  radiation. Cycling performance(C) of C@SiC@C at various current rates, with the insets of charge/discharge curves and the differential capacity as a function of voltage (dQ/dV vs. V) of C@SiC@C at the 1<sup>st</sup> cycle and the 2<sup>nd</sup> cycle under 0.02 C rate (C = 4200 mA g<sup>-1</sup>).

	Specifi	c capacity (mA	Comparison of capacity			
Rate (C)	C@SiC@C	C@SiC@C-in -C@SiC@Si@ SiC@C ª	C@SiC@Si @SiC@C	C@SiC@C-in-C@SiC@Si@SiC@C vs. C@SiC@Si@SiC@C		
0.1	149	100	3948	3%		
0.2	131	88	3419	3%		
0.4	115	77	2600	3%		
1	96	64	1214	5%		

**Table 3.4** Comparison of capacity of C@SiC@C and C@SiC@Si@SiC@C at variouscurrent rate.

<sup>a</sup> The capacity of C@SiC@C component in C@SiC@Si@SiC@C. The weight percentage of C@SiC@C is quantified by combining XPS and TGA characterizations (Figure 3.7), as follows:  $wt_{C@SiC@C} = wt_{SiC} + wt_{C} = (33\% \times 40/28)/(57\% + 33\% \times 40/28 + 10\% \times 60/28) \times 52.7\% + (1 - 52.7\%) = 67\%$ .

Furthermore, the formation of the stable SEI in the composite electrode can also be demonstrated by electrochemical impedance spectroscopy (EIS) measurements (Figure 3.11 and Table 3.5), which have been conducted on the C@SiC@Si@SiC@C and hollow porous pure Si samples. Before cycling, the Nyquist plots of the C@SiC@Si@SiC@C and the hollow porous pure Si anodes both exhibit a depressed semicircle in the high-frequency region and a sloped line in the low-frequency region, equivalent to the circuit models shown in the insert of Figure 3.11. The surface resistance (Rsf) of the highfrequency region is equal to 60.6  $\Omega$  for the C@SiC@Si@SiC@C electrode, which is similar with the Rsf of the hollow porous pure Si anode (Table 3.5). After four cycles, the resistance of C@SiC@Si@SiC@C electrodes is equal to 75.8  $\Omega$ , which is much smaller than the value measured for the hollow porous pure Si (247.8  $\Omega$ ). Notably, after cycling, only one semicircle is detected in the curve of the C@SiC@Si@SiC@C sample, while two semicircles are observed for the hollow porous pure Si [52]. This suggests that a new interface is formed after cycling for the hollow porous pure Si, while the interface impedance of C@SiC@Si@SiC@C basically remains unchanged in agreement with the formation of a stable SEI on the surface. Besides, at low-frequency region, the steeper inclined line of C@SiC@Si@SiC@C indicates the enhanced Li<sup>+</sup> diffusion compared to hollow porous pure Si materials, which is consistent with GITT results.



**Figure 3.11** Nyquist plots of C@SiC@Si@SiC@C (in blue) and hollow porous pure Si reference electrode (in black), before cycling (plotted by hollow circles) and at the 4<sup>th</sup> cycle (plotted by solid spheres).

Sample		Equi-	R	sa)	R	sf)	R	ct <sup>c)</sup>	Sum(I	R <sub>sf+</sub> R <sub>ct</sub> )	Δ(R <sub>s</sub>	<sub>f+</sub> R <sub>ct</sub> )
		valent circuit model	Ω	Ω× cm <sup>2 d)</sup>	Ω	$\Omega \times cm^2$	Ω	Ω× cm²	Ω	Ω× cm²	Ω	Ω× cm²
C@SiC @Si@ SiC@C	Before cycling	(a)	14.1	28.3	60.6	121.8	-	-	60.6	121.8		
	At 4 <sup>th</sup> cycle	(a)	17.8	35.7	75.8	152.2	-	-	75.8	152.2	15.2	30.4
Si	Before cycling	(a)	47.3	95.1	50.6	101.7	-	-	50.6	101.7		
	At 4 <sup>th</sup> cycle	(b)	45.4	91.2	68.4	137.5	179.4	360.5	247.8	498.0	197.2	396.3

 Table 3.5 Impedance analysis of C@SiC@Si@SiC@C and Si before and after 4 cycles

<sup>a)</sup> R<sub>s</sub>: Solution resistance, when lithium ions migrated through the electrolyte towards the surface of electrode; <sup>b)</sup> R<sub>sf</sub>: Surface resistance, when lithium ions entered to the surface of electrode materials; <sup>c)</sup> R<sub>ct</sub>: Charge transfer resistance, when lithium ions migrated from the SEI layer into the surface of the anode materials; <sup>d)</sup> The area of an electrode is 2.0096 cm<sup>2</sup>.

After the activation process at 0.02 C, the rate capacity performance of the C@SiC@Si@SiC@C electrode has been tested at various current densities ranging from 0.1 to 2 C (Figure 3.12A). The composite electrode displays high utilization of Si at different current densities, up to 94.0% at 0.1 C, 81.4% at 0.2 C, 61.9% at 0.4 C, and 28.9% at 1 C, which represents outstanding rate performances compared to the previously reported samples from literature and described in Table 3.1. Notably, after running at high current density of 2 C, the capacity recovers to 93.4% of the initial value at 0.2 C, confirming the high stability of C@SiC@Si@SiC@C anodes. Such property can also be demonstrated by high CEs (close to 100%). In contrast, although the

nanostructures have been mostly maintained for the pure Si electrode before cycling (see Figure 3.6A), the utilization of Si drastically decreases with cycles due to the instable SEI and the loss of structural support from SiC@C (see Figure 3.13A and B). The charge-discharge performances of C@SiC@Si@SiC@C and pure Si are further compared, using the differential capacity as a function of voltage and the corresponding charge-discharge profiles under different current density. In Figure 3.12B, as for the C@SiC@Si@SiC@C sample during the 7<sup>th</sup> cycle at 0.2 C, two pairs of redox peaks are observed. The first cathodic peak c<sub>1</sub> is located at 0.19 V, attributed to the reduction of Si and the generation of a Li-Si alloy phase; the corresponding anodic peak a1 at 0.50 V is related to the extraction of Li ions from the Si host. The second cathodic peak c<sub>2</sub> at 0.04 V and the anodic peak a<sub>2</sub> at 0.29 V suggest the further reduction of the Li-Si alloy and the partial decomposition of the Li-Si alloy, respectively. It reflects that the lithiation mechanism is the gradual reduction process of Si, and the delithiation is the gradual oxidation of the Li<sub>x</sub>Si alloy. Besides, after running under various current rates, the two pairs of redox peaks are both maintained at the 26<sup>th</sup> cycle. In contrast, these redox peaks for the pure Si electrode become too flat to be observed after cycling (Figure 3.13C). In the charge-discharge profiles of Figure 3.12C, the C@SiC@Si@SiC@C anode exhibits the specific electrochemical platforms of silicon in the voltage range of 0.0 - 0.2 V, echoed by the cathodic lithiation peaks  $c_1$  and  $c_2$  in Figure 3.12B. Furthermore, there is almost no change among discharge curves from the 7<sup>th</sup> cycle to the

26<sup>th</sup> – 28<sup>th</sup> cycle, at the same current rate of 0.2 C. As far as the hollow porous pure Si anode is concerned, the characteristic plateau of silicon dramatically shortens (Figure 3.13D). Based on the above observations, such extreme utilization of Si in the composite electrode and highly reversible capacity values of C@SiC@Si@SiC@C could be attributed to the following reasons: i) thanks to the three-dimensional carbon coating, the electronic conductivity is enhanced compared to the pure Si material; ii) nanosized Si greatly shortens the pathways of electrons and Li<sup>+</sup> in the active materials of the composite electrodes, in which the thickness of Si layer is ultrathin compared to some previously reported Si-based materials (Table 3.1); iii) the formation of a stable SEI and the robust structure from SiC@C further improves the stability of the composite electrode. The formation of a stable SEI is also confirmed by SEM characterization of electrodes after cycling (Figure 3.14). The electrode of C@SiC@Si@SiC@C displays a smooth and uniform surface (Figure 3.14A and B), as well as the highly intact morphology of nanospheres after running (Figure 3.14C). On the contrary, the surface of hollow porous Si electrode is uneven and coarse with obvious cracks (Figure 3.14D and E), resulting from the volumetric change of bare Si without robust coating during cycles. In addition, the original spherical shape of the nanoparticles is lost since they become aggregated when covered by a thick SEI film (Figure 3.14F).



**Figure 3.12** (A) Cycling performance of C@SiC@Si@SiC@C electrode and hollow porous pure Si reference electrode at various rate from 0.1 C to 2 C. (B) The differential capacity as a function of voltage (dQ/dV vs. V) for C@SiC@Si@SiC@C measured at the 7<sup>th</sup> cycle and the 26<sup>th</sup> cycle with a rate of 0.2 C between 0 and 1.5 V. (C) Charge/discharge curves of C@SiC@Si@SiC@C at the 7<sup>th</sup> cycle and the 26<sup>th</sup> - 28<sup>th</sup> cycle with a rate of 0.2 C. (D) Long-term cycling performance of C@SiC@Si@SiC@C electrode and C@SiC@Si&SiO<sub>2</sub>@SiC@C electrode at the current rate of 0.2 C. <sup>a</sup> Normalized capacity is calculated by dividing experimental data by the theoretical capacity of Si (4200 mAh g<sup>-1</sup>).



**Figure 3.13** Cycling performance (A) of hollow porous pure Si electrode at current rate of 0.02 C from the 1<sup>st</sup> to 5<sup>th</sup> cycle. Charge/discharge curves (B) of hollow porous pure Si electrode at the 1<sup>st</sup> cycle and the 2<sup>nd</sup> cycle with a rate of 0.02 C. <sup>a</sup> Normalized capacity is calculated by dividing experimental data by the theoretical capacity of Si (4200 mA g<sup>-1</sup>). The differential capacity as a function of voltage (dQ/dV *vs.* V) for hollow porous pure Si measured at the 7<sup>th</sup> cycle and the 26<sup>th</sup> cycle with a rate of 0.2 C between 0 - 1.5 V (C). Charge/discharge curves of hollow porous pure Si at the 7<sup>th</sup> cycle and the 26<sup>th</sup> - 28<sup>th</sup> cycle with a rate of 0.2 C (D).



**Figure 3.14** SEM images of electrodes of C@SiC@Si@SiC@C (A-C) and hollow porous Si (D-F) after cycling.

The long-term cycling performance of the C@SiC@Si@SiC@C electrode has been tested at 0.2 C after the rate capacity measurement. As shown in Figure 3.12D, despite having been cycled under different current densities, the composite electrode still exhibits a capacity as high as 3200 mAh g<sup>-1</sup> (based on the content of Si) at the beginning of the long cycling. After 1000 cycles, the reversible capacity of the

C@SiC@Si@SiC@C electrode remains more than 600 mAh g<sup>-1</sup> and the CE maintains at around 100% for the entire measurement. Moreover, there is only 0.8‰ loss of capacity per cycle for the electrode during the whole cycling and, if only the last 900 cycles are considered, this value is further improved to 0.7‰. The long-term cyclability of C@SiC@Si@SiC@C electrodes could be related to two features: i) the robust SiC@C layer efficiently prevents the inner Si material from pulverization [30, 53, 54], ensuring the stability of the SEI and improving the conductivity of the composite electrode; ii) the nanoscale size of silicon is responsible for superior stability when lithium repeatedly inserts and extracts compared to large size particles [8], and allows a better utilization of Si. Nevertheless, the capacity shows a more obvious degradation for the first 100 cycles (decay rate of 0.5% per cycle at 0.2 C). This may be due to the gradual inactivation of part of the Si component. Because of the complex hierarchical nanostructure and the small size of different components in the nanoparticles, the step of removing unreduced SiO<sub>2</sub> may cause the breakage of small parts of particles (see Figure 3.1E), resulting in the exposure of Si to the electrolyte. Hence the exposed Si would become gradually inactive. To test this hypothesis, another reference sample has been synthesized in which the residual SiO<sub>2</sub> component is retained by suppressing the HF acid washing step, denoted as C@SiC@Si&SiO<sub>2</sub>@SiC@C (synthetic process shown in the section 3.2.2). Hence, the structural integrity of the particles is improved and prevented from breakage (SEM image and XRD pattern are shown in

Figure 3.15A and B). The capacity performance rate of C@SiC@Si&SiO<sub>2</sub>@SiC@C is inferior than that of the C@SiC@Si@SiC@C sample (59.0% at 0.01 C, 50.0% at 0.05 C, 40.9% at 0.1 C, 31.2% at 0.2 C, 16.4% at 0.5 C, and 7.0% at 1 C), which could be attributed to the lower conductivity of the C@SiC@Si&SiO2@SiC@C particles (Figure 3.15C). However, C@SiC@Si&SiO<sub>2</sub>@SiC@C particles display higher stability at long-term cycling (decay rate of 0.6‰ at 0.2 C for 1000 cycles and 0.5‰ per cycle at 0.2 C during last 900 cycles). It inferred that the structural integrity could be of the C@SiC@Si&SiO<sub>2</sub>@SiC@C particles is beneficial to the cycling stability.



**Figure 3.15** SEM image (A) and XRD pattern (B) of C@SiC@Si&SiO2@SiC@C nanospheres. Cycling performance (C) of C@SiC@Si&SiO<sub>2</sub>@SiC@C electrode at various rate from 0.01 C to 1 C.

## 3.4 Conclusion

The polymer-templated one-pot synthesis strategy detailed in this contribution innovatively takes advantage of the intrinsic swelling property of PTMPM in ethanol, successfully allowing the formation of a sandwiched structure in which a silica porous capsule is uniformly wrapped on both sides by polymer layers. Remarkably, those precursor structures are not only employed as template agents for the formation of two distinct types of pores, but can also be in-situ transformed into a well-defined SiC@C 3D coating surrounding the porous silicon layer after high temperature and reduction treatments, hence preventing the waste of organic components and the post-introduction of foreign carbon sources. The nano-size of the accordingly formed Si crystals guarantees the stability of Si during lithiation and improves its utilization at different current densities. This is because their size is far less than the critical breaking dimension reported for lithium insertion and the diffusion paths of Li ions and electrons through the Si active material are quite short. Lastly, the accordingly formed carbon species could admirably improve the electrical conductivity and the conformal coating provided by carbon and silicon carbide contributes strongly to the robustness of the C@SiC@Si@SiC@C nanospheres, not only providing strong structural support, but also favoring the formation of a stable SEI. This unique design contributes strongly to the ultrahigh capacity (3200 mAh g<sup>-1</sup>), the high coulombic efficiency (64.0% of ICE of Si-in-C@SiC@Si@SiC@C, above 90% from the second cycle, and

almost 100% during cycling), and the excellent long-term cycling stability (0.7‰ per cycle decay rate) of the C@SiC@Si@SiC@C anodes. Clearly, the polymer templated approach presented in the present study discloses an original design of composite Si-based hollow nanoparticles exhibiting a unique combination of C, SiC and Si materials with a well-defined 3D structure. Furthermore, those newly designed materials demonstrate outstanding electrochemical performance when used as anodes in Li-ion batteries.

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# Chapter 4

# Polymer-coated silica dual functional fillers to improve the performance of poly(ethylene oxide)-based solid electrolytes

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#### Abstract

The application of solid polymer electrolytes (SPEs) is mainly hindered by their low ionic conductivity and the limited mechanical properties. Adding functional small molecules and inorganic fillers are two of the simplest and most effective ways to improve the performance of SPEs. However, most of the time, both methods cannot be implemented concomitantly, and may even inhibit each other. Here, an original dual functional filler, consisting of hollow porous SiO<sub>2</sub> nanospheres threedimensionally wrapped by poly(2,2,6,6-tetramethylpiperidin-4-yl methacrylate) (PTMPM), is blended with poly(ethylene oxide) (PEO) and LiClO<sub>4</sub> to obtain a composite solid electrolyte (CSE). Compared to the reference PEO SPE, the room-temperature ionic conductivity of the synthesized CSE is improved by 4 orders of magnitude reaching  $1.3 \times$ 10<sup>-4</sup> S cm<sup>-1</sup>. Moreover, a lithium-ion transference number value as high as 0.81 is obtained. The CSE membrane is further assembled with a Li anode and a standard LiFePO4 cathode to obtain an all-solid-state battery showing high capacity (149.3 mAh g<sup>-1</sup> at 0.1C) and long-term stability (0.68‰ loss of capacity per cycle, over 100 cycles). The peculiar structure of the PEO/PTMPM interface is thought to be at the origin of the enhanced LiClO<sub>4</sub> dissociation and mobility of lithium ions. Remarkably, the well-known toughening effect of SiO<sub>2</sub> fillers is preserved in the CSE.

KEYWORDS: three-dimensional coating, silica filler, poly(ethylene oxide), composite solid electrolyte, lithium metal battery

#### 4.1 Introduction

Rechargeable Li-ion batteries (LIBs), which feature high energy density and long cycle life, are ubiquitously utilized in practical applications, e.g., portable devices, electronic vehicles, and grid storage for new energy sources [1, 2]. To date, considerable effort has been dedicated to develop LIB components with higher energy density and increased safety. Compared to conventional liquid electrolytes, solid-state electrolytes (SSEs) are promising candidates for nextgeneration batteries, due to their better chemical/thermal stability and higher mechanical strength, allowing their utilization in high energy density Li metal batteries [2-8].

Due to their light weight, good processability and low cost, solid polymer electrolytes (SPEs) are mainstream alternatives among SSEs. Poly(ethylene oxide) (PEO) is one of the most typical polymer materials for SPEs, since its ether oxygen can coordinate/decoordinate with Li<sup>+</sup> and then accomplish Li<sup>+</sup> transfer *via* the so-called ion-hopping mechanism [9]. Moreover, the inherent flexibility of PEO brings superior interfacial contact between electrodes and PEO-based electrolytes. Nevertheless, the primary drawback is the limited roomtemperature ionic conductivity ( $\sigma$  of 10<sup>-6</sup> - 10<sup>-8</sup> S cm<sup>-1</sup>), which originates from the high degree of crystallinity of PEO at ambient temperature, where the macromolecular chains are orderly arranged in the crystalline domains so that the segmental chain motion is restricted, hence suppressing the ionic transfer [10]. Therefore, batteries containing PEO-based SPEs need to be operated above the melting temperature of crystallites (ca. 60 °C) [11]. In addition, low Li-ion transference number ( $t_{Li^+}$  of 0.1 - 0.2), narrow electrochemical window, and inherent softness hinder the application of the PEO-based SPEs.

A tremendous amount of effort has been made to improve the  $\sigma$ of PEO-based SPEs, e.g., polymer modification, dropping functional small-molecule additives, and adding inorganic fillers. Modification of PEO-based polymers includes polymer blending, crosslinking, and copolymerization, aiming at lowering their intrinsic crystallinity degree [2, 12, 13]. Introducing functional small-molecule additives is a valuable method to promote  $\sigma$ . For example, it has been recently reported that succinonitrile as an additive simultaneously suppresses PEO crystallization and mitigates the affinity between ether oxygen in PEO and Li<sup>+</sup> [14]. Another strategy consists in adding inorganic fillers into a SPE to fabricate an organic-inorganic composite solid electrolyte (CSE), which is one of the most accessible and efficient methods to boost the electrochemical performance of SSEs. The inorganic fillers play an important role in reducing the degree of crystallinity, which is significantly beneficial for the increase of  $\sigma$ . Besides, it would be possible for Li<sup>+</sup> ions to migrate quickly through the interfacial regions between fillers and polymers, as demonstrated by recent studies [1, 7, 15-17]. In some cases, the interactions between anions and filler

particles further increase the dissociation of Li salts and  $t_{Li^+}$  values [18, 19].

Among the three strategies described hereabove, the latter two are more accessible, low-cost and practical. As far as the addition of small-molecule additives is concerned, the major obstacle is a slight or even negligible effect for a low loading amount. Conversely, when the additive amount continually increases, some properties of the SPE sacrificed, would be such as mechanical strength, and electrochemical/thermal stability. The addition of inorganic fillers is an effective option to compensate the mechanical strength, as well as reducing the crystallinity. Whereas the bottleneck is a limited addition amount since the material often becomes brittle for excessive filler amounts. Worse still, the inorganic particles tend to agglomerate along with the increased amount of fillers, resulting in a decreased contact area between polymers and fillers. Especially for inert filler species, which refers to Li<sup>+</sup> insulators, the aggregated fillers are inclined to further diminish  $\sigma$  [6, 7, 20]. Combining the latter two strategies seems to be an ideal way to solve the problem of crystallinity, while keeping both advantages of functional small molecules and inorganic fillers and even complementing each other. Furthermore, combining both approaches in a single material could be a valuable strategy to avoid the huge loading amounts required for conductivity enhancement and their detrimental effects on other properties such as mechanical properties, as described hereabove [21].

Following this idea, the present study introduces a novel and

feasible approach that creates a tailored interface between a PEObased SPE and surface-modified inorganic filler particles. Practically, our strategy is based on the design of a dual functional filler consisting of hollow porous SiO<sub>2</sub> nanospheres (i.e., the inorganic filler component) three-dimensionally wrapped by a poly(2,2,6,6-tetramethylpiperidin-4-yl methacrylate) (PTMPM) polymer coating (i.e., the functional additive component) exposing PTMPM chain segments on the surface of the SiO<sub>2</sub> nanospheres. When they are dispersed in a PEO-based SPE, we hypothesize that those peculiar fillers promote interfacial areas, which considerably inhibit the crystallinity of the PEO matrix and establishes Li<sup>+</sup> fast transport pathways. Meanwhile, the interactions between PTMPM segments and PEO allow the uniform dispersion of the fillers in the polymer matrix, significantly enhancing the mechanical properties of the accordingly obtained CSE membranes.

#### 4.2 Experimental section

#### 4.2.1 Materials

2,2,6,6-Tetramethyl-4-piperidyl methacrylate (TMPM,  $C_{13}H_{23}NO_2$ ) was supplied by TCI. Ethanol (EtOH, 99.97%), hydrochloric acid (HCl, 37%), ammonia (NH<sub>3</sub>·H<sub>2</sub>O, 32%), sodium hydroxide (NaOH), acetonitrile (ACN, CH<sub>3</sub>CN) were supplied by VWR. 2,2'-Azobis(2methylpropionamidine) dihydrochloride (C<sub>8</sub>H<sub>18</sub>N<sub>6</sub>·2HCl) was supplied by Acros Organics. Cetyltrimethylammonium bromide (CTAB, C<sub>19</sub>H<sub>42</sub>BrN) was supplied by Carl Roth. Tetraethyl orthosilicate (TEOS) and PEO (Mv 600K) were supplied by Sigma-Aldrich. Lithium perchlorate (LiClO<sub>4</sub>, anhydrous, 99.5%) was supplied by Alfa Aesar. Nmethylpyrrolidone (NMP) was supplied by Fisher. Lithium iron phosphate (LFP), super P and lithium metal foils were supplied by XIAMEN TOB. All chemicals were used as received without any further treatment. Milli-Q water was used.

### 4.2.2 Characterizations

Transmission electron microscopy (TEM) investigations were performed on a FEI Tecnai G<sup>2</sup>20 system at an acceleration voltage of 120 kV. Samples have been prepared by applying finely grinded powders onto carbon coated TEM grids (Quantifoil, Germany). Scanning electron microscopy (SEM) images were collected with a JEOL 7600F electron microscope. Nuclear magnetic resonance (NMR) spectroscopy was conducted using a Bruker 300 UltraShield spectrometer and the investigated CSE was completely dissolved in deuterated dimethyl sulfoxide. High-resolution Raman spectra were collected on a DXR Raman microscope with laser excitation at 532 nm from Thermo Fisher Scientific. Fourier transform infrared (FTIR) spectra were collected on a Nicolet iN10 IR Microscope from Thermo Fisher Scientific. Thermogravimetric analysis (TGA) was conducted in a TGA/SDTA851 instrument from Mettler Toledo under air flow with a heating ramp of 5 °C min<sup>-1</sup>. Differential scanning calorimetry (DSC) was conducted using a Mettler Toledo DSC1 equipped with STARe software. Samples were placed in a 40  $\mu$ L sealed aluminum pan. The temperature profile was swept from -80 to 100 °C at a heating rate of 10 °C min<sup>-1</sup> under a nitrogen atmosphere. Dynamic mechanical analysis (DMA) was performed on Mettler Toledo DMA/SDTA861 by the shear deformation mode, in which the viscoelasticity response of a sample under oscillating load was monitored at temperatures ranging from -70 to 60 °C. The diameter and thickness of samples were (4 - 5) mm × (0.16 - 0.20) mm, repectively. A tube furnace (Nabertherm R 50/250/13 with Controller C450) was applied to calcine samples.

#### 4.2.3 Sample synthesis

#### Synthesis of TMPM-Cl

TMPM (5 g) was dissolved in EtOH (25 ml) at room temperature (RT), and further stirred for 30 min. Then a HCl solution (6.5 mL, 4.1 M) was added into the solution, at a syringe speed of 13 mL  $h^{-1}$ , and stirring was continued for 1 h. The dry TMPM-Cl was obtained by removing the solvent with a rotary evaporator followed by drying in a vacuum oven at 40 °C overnight.

#### • Synthesis of PTMPM

TMPM-Cl (1 g) was dissolved into a mixture of water (3 mL) and EtOH (3 mL). Then 2,2'-Azobis(2-methylpropionamidine) dihydrochloride (50 mg) was added into the above solution. After thoroughly degassing with argon, the mixed solution was put in an oil
bath of 70 °C for 3 h to obtain PTMPM.

#### Synthesis of P@SiO<sub>2</sub>@P fillers

PTMPM (0.3 mL) and water (9.7 mL) were mixed and stirred for 1 h. Afterwards, a NaOH solution (1 mL, 1.25 M) was dropwise added into the above solution and stirred overnight. The suspension was centrifuged at 5000 rpm for 20 min. The precipitate was collected and washed by water until the pH reached a value of 7 - 8. The washed sample was dissolved into EtOH (8 mL), and dropwise added into a CTAB solution (20 mL, 3.75 mg mL<sup>-1</sup>). Successively, NH<sub>3</sub>·H<sub>2</sub>O (30 µL) and TEOS (200 µL) were thoroughly mixed into the solution. The mixed solution was heated in an oil bath at 38 °C for 24 h. The PTMPM-silica (denoted as P@SiO<sub>2</sub>) particles were finally collected by centrifugation at 9000 rpm for 20 min. The P@SiO<sub>2</sub> sample was swelled in EtOH for 24 h and collected by centrifugation at 8000 rpm for 20 min to obtain the swollen sample, denoted as P@SiO<sub>2</sub>@P.

#### Preparation of P@SiO<sub>2</sub>@P-PEO-LiClO<sub>4</sub>

PEO (300 mg) and ACN (6 mL) were mixed overnight to obtain a homogeneous solution. A certain amount of P@SiO<sub>2</sub>@P (2.5 wt% - 15 wt% of the weight of PEO) was dispersed in ACN (1 mL), and afterwards dropwise added into the above PEO solution and stirred for 2 h. Then a certain amount of LiClO<sub>4</sub> (the molar ratio of Li<sup>+</sup>/ethylene-oxide from 1/20 to 1/5, in 1 ml of ACN) was added into the above PEO solution. The mixed solution was continuously stirred at RT for 24 h, subsequently casted on a Teflon mold, and dried at RT for 24 h and followed by 24 h at 80 °C in a vacuum oven to obtain a P@SiO<sub>2</sub>@P-PEO- LiClO<sub>4</sub> membrane.

### Preparation of PEO-1/8LiClO<sub>4</sub>

PEO (300 mg) and ACN (7 mL) were mixed overnight to obtain the homogeneous PEO solution. Then LiClO<sub>4</sub> (91 mg in 1 ml of ACN) was added into the above PEO solution. The mixed solution was continuously stirred at room temperature (RT) for 24 h, subsequently casted on a Teflon mold, and dried at RT for 24 h and followed by 24 h at 80 °C in a vacuum oven. The dry membrane was finally obtained as a PEO-1/8LiClO<sub>4</sub> sample.

#### Preparation of PTMPM-PEO-1/8LiClO<sub>4</sub>

PEO (300 mg) and ACN (6 mL) were mixed overnight to obtain the homogeneous PEO solution. Then PTMPM (2.517 ml, 3.87 mg ml<sup>-1</sup> in ACN) and LiClO<sub>4</sub> (91 mg in 1 ml of ACN) were added into the above PEO solution. The mixed solution was continuously stirred at RT for 24 h, subsequently casted on a Teflon mold, and dried at RT for 24 h and followed by 24 h at 80 °C in a vacuum oven. The dry membrane was finally obtained as a PTMPM-PEO-1/8LiClO<sub>4</sub> sample.

#### Preparation of SiO<sub>2</sub>-PEO-1/8LiClO<sub>4</sub>

PTMPM (0.3 mL) and water (9.7 mL) were mixed and stirred for 1 h. Afterwards, NaOH (1 mL, 1.25 M) solution was dropwise added into the above solution and stirred overnight. The suspension was centrifuged at 5000 rpm for 20 min. The precipitate was collected and washed by water until the pH reached a value of 7 - 8. The washed sample was dissolved into EtOH (8 mL), and dropwise added into a CTAB solution (20 mL, 3.75 mg mL<sup>-1</sup>). Successively, NH<sub>3</sub>·H<sub>2</sub>O (30 µL) and

TEOS (200  $\mu$ L) were thoroughly mixed into the solution. The mixed solution was heated in an oil bath at 38 °C for 24 h. The PTMPM-silica (denoted as P@SiO<sub>2</sub>) particles were collected by centrifugation at 9000 rpm during 20 min. The P@SiO<sub>2</sub> sample was calcined for 2 h at 900 °C in a tube furnace under air atmosphere. Then the sample of hollow porous SiO<sub>2</sub> was obtained.

PEO (300 mg) and ACN (7 mL) were mixed overnight to obtain a homogeneous PEO solution. Then hollow porous SiO<sub>2</sub> (12.758 mg) and LiClO<sub>4</sub> (91 mg in 1 ml of ACN) were added into the above PEO solution. The mixed solution was continuously stirred at RT for 24 h, subsequently casted on a Teflon mold, and dried at RT for 24 h and followed by 24 h at 80 °C in a vacuum oven. The dry membrane was finally obtained as a SiO<sub>2</sub>-PEO-1/8LiClO<sub>4</sub> sample.

## 4.2.4 Electrochemical Measurements

Electrochemical impedance spectroscopy (EIS) was conducted on the SSE assembled into a symmetric stainless steel (SS) configuration for measuring  $\sigma$ . EIS was measured in the frequency range from 7 MHz to 100 mHz and the temperature range from 90 to 20 °C on a Bio-Logic VMP-300 instrument. Temperature was controlled by a climate chamber with a ramp rate of 0.33 °C min<sup>-1</sup>, besides there is a period of 30 min for each 10 °C as an equilibration time for measurement. Linear sweep voltammetry (LSV) measurement was used to determine the electrochemical stability window and was performed in the potential range from 0.1 to 6.0 V with a scanning rate of 1 mV s<sup>-1</sup> at 60 °C, in a Li/SSE/SS configuration, with SS as a working electrode and Li metal as a reference and counter electrode. Galvanostatic cycling experiments in a Li symmetric cell were applied to evaluate the interface stability between electrodes and electrolytes. At each cycle, cells were charged and discharged at 60 °C under a certain currency density of 0.025 - 0.20 mA cm<sup>-2</sup> for 1 h, respectively. The  $t_{Li^+}$  was measured by a combination of direct current (DC) polarization and EIS techniques, in a cell configuration of Li/SSE/Li at 60 °C. DC polarization was performed with a bias of 10 mV until the response current reached stability; EIS measurement was as the same as above. To assemble an all-solid-state battery, LFP, super P, and PEO-LiClO<sub>4</sub> solution (in NMP, Li<sup>+</sup>/EO ratio of 1/8) were vigorously mixed in a mixing machine (Thinky ARE-250) with the mass ratio of 30:30:40. The obtained slurry was coated onto a carbon-coated aluminum foil, then dried at RT overnight, followed by 70 °C in a vacuum oven for 24 h to obtain working electrodes. A polished lithium metal foil was used as a reference and counter electrode. All coin cells (2032 type) were assembled under an argon atmosphere (H<sub>2</sub>O and O<sub>2</sub> <0.1 ppm) in a MBraun glovebox. The cells were galvanostatically cycled between 3.0 V and 3.8 V vs. Li/Li<sup>+</sup> at 60 °C. Charge and discharge rates were calculated based on the theoretical capacity of LFP (C = 170 mA  $g^{-1}$ ).

## 4.3 Calculation section

4.3.1 Ionic conductivity calculated by electrochemical impedance spectroscopy

Ionic conductivity ( $\sigma$ ) of a solid-state electrolyte (SSE) is converted from the impedance measured by electrochemical impedance spectroscopy (EIS) in a cell configuration of stainless-steel symmetric electrodes from 20 °C to 90 °C. The calculation follows Equation (4.1):

$$\sigma = \frac{l}{RA} \tag{4.1}$$

where  $\sigma$  (S cm<sup>-1</sup>) is the ionic conductivity of the SSE sample, l (cm) is the thickness of the membrane-like SSE sample, R ( $\Omega$ ) is the bulk impedance measured by EIS, and A (cm<sup>2</sup>) is the contact area between the SSE and the stainless steel [8].

# 4.3.2 Activation energy fitted by the Vogel-Fulcher-Tammann equation

Above melting temperature  $T_m$ , the segmental movement of polymer chains also helps Li<sup>+</sup> ions transfer among the coordination sites. The composite Li-ion transfer mechanism is suitable to be simulated by the Vogel-Fulcher-Tammann (VFT) equation. The relationship of temperature and  $\sigma$  is interpreted as Equation (4.2):

$$\sigma = A_{VFT} T^{-\frac{1}{2}} \times e^{-\frac{E_a}{R(T-T_0)}}$$
(4.2)

where  $\sigma$  (S cm<sup>-1</sup>) is the ionic conductivity of samples,  $A_{VFT}$  (S cm<sup>-1</sup> K<sup>0.5</sup>) is the VFT pre-exponential factor, T (K) is the absolute temperature,  $E_a$  (J mol<sup>-1</sup>) is the activation energy, R (J mol<sup>-1</sup> K<sup>-1</sup>) is the gas constant, and  $T_0$  (K) is the reference temperature, related to the glass transition temperature T<sub>g</sub> of sample [22].

Equation (4.2) is transformed into Equation (4.3).

$$\ln\left(\sigma T^{\frac{1}{2}}\right) = \frac{E_a}{R(T - T_0)} \tag{4.3}$$

By plotting the  $\ln \left(\sigma T^{\frac{1}{2}}\right)$  vs.  $(T - T_0)^{-1}$ ,  $E_a$  can be determined related to the slope. Noticeably, for better meeting VFT simulation conditions and improving the fitting accuracy, the temperature-dependent  $\sigma$  data from 50 °C to 90 °C is chosen to be simulated.

### 4.3.3 Li-ion transference number calculation

Li-ion transference number  $(t_{Li^+})$  is defined as the ratio of the current from cations to the total current, which is characterized by current detection under an applied voltage of 10 mV in the cell configuration of Li symmetric electrodes, with detailed calculation Equation (4.4):

$$t_{Li^+} = \frac{I_{ss}(\Delta V - I_0 R_0)}{I_0(\Delta V - I_{ss} R_{ss})}$$
(4.4)

where  $t_{Li^+}$  is the Li-ion transference number of the SSE sample,  $I_0$ (A) and  $I_{ss}$  (A) are the initial and steady-state current, respectively;  $R_0$  ( $\Omega$ ) and  $R_{ss}$  ( $\Omega$ ) are the initial and steady-state interfacial impedances measured by EIS, respectively;  $\Delta V$  (V) is the applied voltage, which is set as 0.010 V [8].

## 4.4 Results and discussion

# 4.4.1 Synthesis and characterization of P@SiO<sub>2</sub>@P dual functional fillers

The dual functional fillers designed in this contribution are composed of hollow porous SiO<sub>2</sub> nanospheres three-dimensionally wrapped by PTMPM, which are denoted as P@SiO<sub>2</sub>@P. Those fillers have been prepared according to a synthetic strategy previously reported by us [23]. In short, a mini-emulsion process is used to fabricate monodisperse PTMPM nanospheres stabilized by CTAB. Those nanospheres are further used as templates for the fabrication of SiO<sub>2</sub> shells, whose nanoporosity relies on the presence of CTAB micelles on the surface of the PTMPM nanospheres. The exposure of those nanospheres to ethanol allows the migration of PTMPM chain segments through the nanopores and the re-wrapping of the nanospheres by a PTMPM layer leading to the P@SiO2@P nanoobjects [19]. TEM imaging (Figure 4.1A) confirms that the accordingly synthesized P@SiO2@P sample is characterized by a regular spherical morphology with a uniform diameter (~100 nm). The corresponding magnified inset shows the smooth surface of the nanoparticles, resulting from the conformal PTMPM coating layer. SEM imaging

(Figure 4.1B) reveals the high uniformity of P@SiO<sub>2</sub>@P nanoparticles and the inset illustrates their hierarchical structure. The FTIR spectrum recorded for the P@SiO<sub>2</sub>@P sample (Figure 4.1C) shows the presence of characteristic signals associated to the C=O and C-H vibration bands that are attributed to the PTMPM segments wrapping the P@SiO<sub>2</sub>@P nanospheres. The TGA under air atmosphere (Figure 4.1D) displays a remaining weight of 56.7% ascribed to the SiO<sub>2</sub> component after the pyrolysis of PTMPM-dominant organic matter.



**Figure 4.1** (A) TEM image of P@SiO<sub>2</sub>@P with the corresponding magnified inset. (B) SEM image and the structural schematic of P@SiO<sub>2</sub>@P. (C) FTIR spectrum and (D) TGA curve of P@SiO<sub>2</sub>@P.

4.4.2 Synthesis and characterization of P@SiO<sub>2</sub>@P-PEO-LiClO<sub>4</sub> composite solid electrolytes

The synthetic process towards P@SiO<sub>2</sub>@P-PEO-LiClO<sub>4</sub> CSE is depicted in Figure 4.2. CSE membranes are obtained by casting a mixture of P@SiO<sub>2</sub>@P, PEO and LiClO<sub>4</sub> dispersed in ACN, followed by extensive evaporation of ACN in a vacuum oven. The absence of residual ACN in the dried membranes is confirmed by NMR since no characteristic peak of ACN within the range of ~2 ppm is observed (Figure 4.3). In the following, the samples will be designated as x%P@SiO<sub>2</sub>@P-PEO-yLiClO<sub>4</sub>, where x stands for the weight percentage of P@SiO<sub>2</sub>@P fillers in a CSE and y refers to the molar ratio of Li<sup>+</sup> ion for 8 ether groups.



Figure 4.2 Synthetic pathway towards a P@SiO<sub>2</sub>@P-PEO-LiClO<sub>4</sub> sample.



**Figure 4.3** <sup>1</sup>H NMR spectrum of the 10%P@SiO<sub>2</sub>@P-PEO-1/8LiClO4 sample dissolved in deuterated dimethyl sulfoxide, with the corresponding enlarged image of the 2 ppm, where ACN signals are to be expected.



**Figure 4.4** (A) Self-standing behavior of the  $7.5\%P@SiO_2@P-PEO-1/8LiClO_4$  sample. (B) Optical photo of a  $7.5\%P@SiO_2@P-PEO-1/8LiClO_4$  sample, with corresponding (C) cross-sectional SEM image and further (D) enlarged image. Elemental mapping of the overview of  $7.5\%P@SiO_2@P-PEO-1/8LiClO_4$  with various elements of C, O, Si and Cl (E, F, G, and H), and (I) corresponding energy dispersive X-ray spectrum.

The prepared self-standing composite membranes have been then easily cut into disks for further use in electrochemical cells (Figures 4.4A and B). When observing the cross section (Figures 4.4C and D) of the membrane by SEM, a uniform dispersion of the P@SiO2@P fillers in the PEO-LiClO4 matrix is noted and credited to the hydrogen bonds between amine groups of PTMPM and ether groups of PEO [7]. This is confirmed by the homogenous distribution of Si in energy dispersive X-ray-mapping (Figure 4.4E-I). Besides, the dispersion of Cl from perchlorate anions is also uniform in the sample and is thought to result from hydrogen bonds between perchlorate anions of LiClO<sub>4</sub> and amine groups of PTMPM [24]. DSC measurements have been carried out to survey thermal transitions of the 7.5%P@SiO<sub>2</sub>@P-PEO-1/8LiClO<sub>4</sub> sample (Figure 4.5 and Table 4.1) and have been further compared to the PEO-1/8LiClO<sub>4</sub>, SiO<sub>2</sub>-PEO-1/8LiClO<sub>4</sub> and PTMPM-PEO-1/8LiClO<sub>4</sub> control samples. These control samples contain the same amount of SiO<sub>2</sub> or PTMPM than that of the 7.5%P@SiO<sub>2</sub>@P-PEO-1/8LiClO<sub>4</sub> sample, respectively, in order to ensure comparability (their synthesis is detailed in the Supporting Information section). The PEO-1/8LiClO<sub>4</sub> sample reveals a glass transition temperature  $T_g$  of -28.8 °C and a melting temperature  $T_m$  of 55.6 °C. The degree of crystallization  $\chi_c$  is calculated as high as 51.8%. In the PTMPM-PEO-1/8LiClO<sub>4</sub> sample, the presence of PTMPM does not influence much T<sub>g</sub>, T<sub>m</sub> and  $\chi_c$  compared to the PEO-1/8LiClO<sub>4</sub> system. For the SiO<sub>2</sub>-PEO-1/8LiClO<sub>4</sub> sample, both  $T_g$  and  $T_m$  slightly decrease to lower temperatures compared to the PEO-LiClO<sub>4</sub> sample,

and  $\chi_c$  declines to 42.9%, since SiO<sub>2</sub> particles are well-known to decrease PEO crystallinity [3, 6, 18]. As far as the 7.5%P@SiO<sub>2</sub>@P-PEO-1/8LiClO<sub>4</sub> sample is concerned, T<sub>g</sub> and T<sub>m</sub> drop to -37.4 °C and 35.4 °C, respectively, and the measured  $\chi_c$  of 5.4% is the smallest among the four investigated samples.



**Figure 4.5** DSC curves of PEO-1/8LiClO<sub>4</sub>, SiO<sub>2</sub>-PEO-1/8LiClO<sub>4</sub>, PTMPM-PEO-1/8LiClO<sub>4</sub> and 7.5%P@SiO<sub>2</sub>@P-PEO-1/8LiClO<sub>4</sub> samples.

**Table 4.1** Thermal properties characterized by DSC for PEO-1/8LiClO<sub>4</sub>, PTMPM-PEO-1/8LiClO<sub>4</sub>, SiO<sub>2</sub>-PEO-1/8LiClO<sub>4</sub>, and 7.5%P@SiO<sub>2</sub>@P-PEO-1/8LiClO<sub>4</sub> samples as well as the corresponding degrees of crystallization.

Samples	T <sub>g</sub> (°C)	T <sub>m</sub> (°C)	$\chi_c^a$
PEO-1/8LiClO <sub>4</sub>	-28.8	55.6	51.8%
PTMPM-PEO-1/8LiClO <sub>4</sub>	-24.4	61.4	51.5%
SiO <sub>2</sub> -PEO-1/8LiClO <sub>4</sub>	-31.9	54.2	42.9%
7.5%P@SiO2@P-PEO-1/8LiClO4	-37.4	35.4	5.4%

<sup>a</sup> The degree of crystallization  $\chi_c$  is calculated by  $\chi_c = (\Delta H_m)/(\omega \times \Delta H_0)$ , wherein  $\Delta H_m$  (Jg<sup>-1</sup>) is the specific heat of fusion, from the integration of the T<sub>m</sub> peak from the DSC curve;  $\Delta H_0$  (Jg<sup>-1</sup>) is the enthalpy of fusion of 100 % crystalline PEO, 205 Jg<sup>-1</sup> [24];  $\omega$  is the mass fraction of PEO in the composite material.

The characterization of the mechanical properties of the samples has been then achieved by DMA in the shear deformation mode. In shear mode, two samples are clamped within a sandwich holder, comprising two fixed parts and a movable part (Figure 4.6A). Apply a force to slide one part of the sample past another. The applied force, displacement of the sample and the corresponding modulus are recorded. In Figure 4.6B, compared to the PEO-1/8LiClO<sub>4</sub> and SiO<sub>2</sub>-PEO-1/8LiClO<sub>4</sub> control samples, the 7.5%P@SiO<sub>2</sub>@P-PEO-1/8LiClO<sub>4</sub> sample displays a larger slope in relation to a higher stiffness, demonstrating the superior ability of this material to resist shear deformation among the investigated samples. In Figure 4.6C, along with the increase of temperature from -70 °C to 60 °C, the shear storage modulus G' of the 7.5%P@SiO2@P-PEO-1/8LiClO4 sample is obviously always larger than that of the other control samples. Furthermore, the higher G' of 7.5%P@SiO2@P-PEO-1/8LiClO4 compared to SiO<sub>2</sub>-PEO-1/8LiClO<sub>4</sub> clearly highlights the importance of the PTMPM coating layers on the mechanical properties, since all the other parameters are kept constant. The superior mechanical properties of the 7.5%P@SiO<sub>2</sub>@P-PEO-1/8LiClO<sub>4</sub> sample are further highlighted by the damping factor tan  $\delta$ , defined as the ratio of the loss modulus G" to the storage modulus G', and which reflects the dissipation energy of a material (Figure 4.6D). Indeed, tan  $\delta$  declines to 0.4 at -35 °C for the 7.5%P@SiO2@P-PEO-1/8LiClO4 sample compared to the tan  $\delta$  of the PEO-1/8LiClO<sub>4</sub> (1.6 at -29 °C) and SiO<sub>2</sub>-PEO-1/8LiClO<sub>4</sub> (1.5 at -27 °C) samples. Reinforced stiffness, superior

shear storage modulus and small damping factor suggest that the P@SiO<sub>2</sub>@P functional fillers improve the mechanical properties of the PEO-LiClO<sub>4</sub> system.



**Figure 4.6** (A) Illustration of a shear deformation holder for DMA. (B) Forcedisplacement curves, (C) storage modulus-temperature curves and (D) Tan  $\delta$ temperature curve of PEO-1/8LiClO<sub>4</sub>, SiO<sub>2</sub>-PEO-1/8LiClO<sub>4</sub> and 7.5%P@SiO<sub>2</sub>@P-PEO-1/8LiClO<sub>4</sub> samples.



**Figure 4.7** (A) FTIR spectra of PEO, PTMPM and 7.5%P@SiO<sub>2</sub>@P-PEO-1/8LiClO<sub>4</sub> samples. (B) Raman spectra in the range from 600 to 660 cm<sup>-1</sup> of 7.5%P@SiO<sub>2</sub>@P-PEO-LiClO<sub>4</sub> samples with various Li<sup>+</sup>/EO ratios, 7.5%P@SiO<sub>2</sub>@P-PEO without LiClO<sub>4</sub>, LiClO<sub>4</sub>, PEO-1/8LiClO<sub>4</sub>, SiO<sub>2</sub>-PEO-1/8LiClO<sub>4</sub> and PTMPM-PEO-1/8LiClO<sub>4</sub> samples. (C) Raman spectra in the range from 1588 to 1750 cm<sup>-1</sup> of 7.5%P@SiO<sub>2</sub>@P-PEO-LiClO<sub>4</sub> samples with various Li<sup>+</sup>/EO ratios, 7.5%P@SiO<sub>2</sub>@P-PEO without LiClO<sub>4</sub> and PTMPM-PEO-1/8LiClO<sub>4</sub> samples with various Li<sup>+</sup>/EO ratios, 7.5%P@SiO<sub>2</sub>@P-PEO-LiClO<sub>4</sub> samples with various Li<sup>+</sup>/EO ratios, 7.5%P@SiO<sub>2</sub>@P-PEO without LiClO<sub>4</sub> and PTMPM-PEO-1/8LiClO<sub>4</sub> samples with various Li<sup>+</sup>/EO ratios, 7.5%P@SiO<sub>2</sub>@P-PEO without LiClO<sub>4</sub> and PTMPM-PEO-1/8LiClO<sub>4</sub> samples.

In order to obtain further information on the chemical groups and their possible mutual interactions in the investigated CSEs, FTIR and Raman characterizations have been carried out. Figure 4.7A displays the FTIR spectra of the PEO, PTMPM, and 7.5%P@SiO<sub>2</sub>@P-PEO-1/8LiClO<sub>4</sub> samples. In the spectrum recorded for PEO, two bands at 839 and 1340 cm<sup>-1</sup> are ascribed to CH<sub>2</sub> bending vibration, a band at 1099 cm<sup>-1</sup> is attributed to the C-O-C stretching vibration and a band at 2881 cm<sup>-1</sup> is ascribed to CH<sub>2</sub> stretching vibration. In the PTMPM sample, the C=O stretching vibration band located at 1718 cm<sup>-1</sup>, the CH<sub>3</sub> stretching vibration band at 2958 cm<sup>-1</sup> and the N-H stretching vibration band at 3319 cm<sup>-1</sup> have to be pointed out. In the FTIR spectrum of the 7.5%P@SiO<sub>2</sub>@P-PEO-1/8LiClO<sub>4</sub> sample, a red shift of the C-O-C vibration band to 1081 cm<sup>-1</sup> is observed compared to the original PEO, suggesting that the ether groups of PEO possibly coordinate with Li<sup>+</sup>. Likewise, compared to the original PTMPM, a blue shift of the N-H vibration band and a red shift of the C=O vibration band, both illustrate that the amine and ester groups are likely coordinated with Li<sup>+</sup> ions in the 7.5%P@SiO<sub>2</sub>@P-PEO-1/8LiClO<sub>4</sub> sample [7]. Such specific interactions are strengthening our hypothesis about the formation of Li<sup>+</sup> ion transport pathways on the PTMPM-rich surface of the P@SiO<sub>2</sub>@P fillers and have been further verified by high-resolution Raman spectroscopy [26-28]. Samples containing various amounts of LiClO<sub>4</sub> and other control samples have been investigated by Raman spectroscopy (Figures 4.7B-C and 4.8) and all PEO-containing samples have been normalized by the CH<sub>2</sub> peak of 1478 cm<sup>-1</sup>, guaranteeing the comparability among samples. Figure 4.7B displays the deconvolution of the perchlorate peak which is composed of a ClO<sub>4</sub><sup>-</sup> anion peak at ~623 cm<sup>-1</sup> and a Li<sup>+</sup>/ClO<sub>4</sub><sup>-</sup> ion pair peak at ~634 cm<sup>-1</sup>. As the amount of

Li<sup>+</sup> ion gradually increases from the Li<sup>+</sup>/EO molar ratio of 1/20 to 1/8, the ratio of ClO<sub>4</sub><sup>-</sup> anions increases until it reaches a value as high as 93% for the 1/8 Li<sup>+</sup>/EO molar ratio, indicating that the majority of the LiClO<sub>4</sub> salt has been dissociated. Such high degree of dissociation may originate from two factors [3, 7]. Firstly, the binding between Li<sup>+</sup> ions and coordination sites is ameliorated by the addition of P@SiO<sub>2</sub>@P fillers, including the inhibition of crystallization, the enhancement of segmental chain motion, and the introduction of Li-ion coordination sites with low binding energy. Secondly, hydrogen-bonds establishing (i) between ClO<sub>4</sub><sup>-</sup> and amine of PTMPM and (ii) between ClO<sub>4</sub><sup>-</sup> and terminal hydroxide of PEO help to fix ClO<sub>4</sub><sup>-</sup>. The former factor enhances the transport of Li<sup>+</sup> cations and the latter immobilizes ClO<sub>4</sub><sup>-</sup> anions, both of which promote LiClO<sub>4</sub> salt dissociation [3, 7]. When the Li<sup>+</sup>/EO molar ratio further increases to 1/5, the proportion of ClO<sub>4</sub><sup>-</sup> anions decreases to 88% and the formation of Li<sup>+</sup>/ClO<sub>4</sub><sup>-</sup> ion pairs is favored, confirming the optimum 1/8 Li<sup>+</sup>/EO molar ratio to maximize free Li<sup>+</sup> ion transport [29]. In order to decipher the contributions of the different components of the P@SiO2@P-PEO-LiClO4 system, control samples have been investigated in the bottom of Figure 4.7B. While pure LiClO<sub>4</sub> only contains 20% of ClO<sub>4</sub><sup>-</sup> anions, this percentage increases to a value as high as 81% for the PEO-1/8LiClO<sub>4</sub> sample. This clearly demonstrates that Li<sup>+</sup> ions are interacting with the ether oxygen of PEO freeing a substantial amount of ClO4<sup>-</sup> anions. The addition of SiO2 particles in the SiO<sub>2</sub>-PEO-1/8LiClO<sub>4</sub> sample further increases the proportion of ClO<sub>4</sub><sup>-</sup> anions to 90% since silicon hydroxyl is reported to

form hydrogen bonds with ClO<sub>4</sub><sup>-</sup> anions hence anchoring them and promoting the dissociation of Li salts [30-34]. The presence of a small amount of blended PTMPM polymer in the PTMPM-PEO-1/8LiClO<sub>4</sub> sample only increases this proportion to 84%, demonstrating that "diluted" PTMPM has little effect on the LiClO<sub>4</sub> dissociation. In sharp contrast, when the same amount of PTMPM three-dimensionally coats SiO<sub>2</sub> particles in the P@SiO<sub>2</sub>@P fillers, a PTMPM-rich interface is built between the filler and the PEO matrix, further promoting hydrogenbonding between PTMPM and ClO<sub>4</sub><sup>-</sup>. This further releases free Li<sup>+</sup> ions and creates preferred Li<sup>+</sup> ion pathways.

In the next step, the region of the Raman spectra corresponding to amine and carbonyl groups has been investigated in Figure 4.7C. Before the addition of LiClO<sub>4</sub>, the 7.5%P@SiO<sub>2</sub>@P-PEO sample shows two main peaks, a first at 1633 cm<sup>-1</sup> ascribed to secondary amine groups and a second at 1734 cm<sup>-1</sup> corresponding to carbonyl groups. The further addition of LiClO<sub>4</sub> results in a blue shift from 1633 cm<sup>-1</sup> to 1654 cm<sup>-1</sup> for the amine groups and a red shift from 1734 cm<sup>-1</sup> to 1673 cm<sup>-1</sup> for the carbonyl groups, owing to the interactions between those groups and Li<sup>+</sup> ions [26-28]. However, when the Li<sup>+</sup>/EO molar ratio raises from 1/8 to 1/5, a blue shift is observed for the carbonyl peak instead of a red shift, pointing towards a decreased coordination. This could indicate preferential binding of Li<sup>+</sup> ions to amine groups rather than carbonyl groups at high Li<sup>+</sup> concentration [7]. Since the binding energy between the amine groups and Li<sup>+</sup> ions, Li<sup>+</sup> ions can rapidly and smoothly transfer on the PTMPM-rich interface between the fillers and the polymer matrix, paving the way to fast Li<sup>+</sup> ion transport pathways [7]. As far as the PTMPM-PEO-1/8LiClO<sub>4</sub> control sample is concerned, similar amine and carbonyl peaks have been observed compared with the 7.5%P@SiO<sub>2</sub>@P-PEO-1/8LiClO<sub>4</sub> sample, but with lower intensities (Figure 4.7C bottom). This difference in peak intensities between 7.5%P@SiO<sub>2</sub>@P-PEO-1/8LiClO<sub>4</sub> and PTMPM-PEO-1/8LiClO<sub>4</sub> samples containing the same amount of PTMPM strengthens our hypothesis about the accumulation of free Li<sup>+</sup> ions in the PTMPM interfacial layer of P@SiO<sub>2</sub>@P fillers. Finally, Figure 4.8 focuses on the ether groups of the investigated samples. The specific peak associated to the ether groups, highlighted in green in Figure 4.8, shows a red shift from 874 cm<sup>-1</sup> to 863 cm<sup>-1</sup> along with the increase of Li<sup>+</sup>/EO ratio, which results from the coordination between ether oxygen and Li<sup>+</sup>.

Finally, Figure 4.8 focuses on the ether groups of the investigated samples. The specific peak associated to the ether groups, highlighted in green in Figure 4.8, shows a red shift from 874 cm<sup>-1</sup> to 863 cm<sup>-1</sup> along with the increase of Li<sup>+</sup>/EO ratio, which results from the coordination between ether oxygen and Li<sup>+</sup>.



**Figure 4.8** Raman spectra in the range from 770 to 880 cm<sup>-1</sup> of 7.5%P@SiO<sub>2</sub>@P-PEO-LiClO<sub>4</sub> samples with various Li<sup>+</sup>/EO ratios, 7.5%P@SiO<sub>2</sub>@P-PEO without LiClO<sub>4</sub>, PEO-1/8LiClO<sub>4</sub>, SiO<sub>2</sub>-PEO-1/8LiClO<sub>4</sub> and PTMPM-PEO-1/8LiClO<sub>4</sub> samples.

# 4.4.3 Performance of P@SiO<sub>2</sub>@P-PEO-LiClO<sub>4</sub> CSEs

The performance of  $P@SiO_2@P-PEO-LiClO_4$  as a CSE has been subsequently investigated. The  $\sigma$  of samples has been investigated in

the temperature range of 20 to 90 °C and different parameters have been varied. The first parameter to be tested was the mass loading of P@SiO<sub>2</sub>@P fillers in CSEs. As shown in Figure 4.9A, the P@SiO<sub>2</sub>@P filler amount has been varied from 2.5 wt% to 15 wt% and all samples show an increasing  $\sigma$  along with the temperature. Besides, at each temperature, the  $\sigma$  gradually increases until reaching the optimal filler amount of 7.5 wt%. In the control sample without fillers, there is a dramatic drop of  $\sigma$  in the range of 30 to 60 °C caused by the crystallization of the PEO matrix (see thermal properties in Figure 4.5), which is not observed in any filler-containing samples in agreement with their low degree of crystallinity. The PTMPM-PEO-1/8LiClO<sub>4</sub> and SiO<sub>2</sub>-PEO-1/8LiClO<sub>4</sub> control samples also show an obvious drop of  $\sigma$ below 60 °C because of the presence of PEO crystalline domains (Figure 4.9B).

The room-temperature  $\sigma$  of the best performing 7.5%P@SiO<sub>2</sub>@P-PEO-1/8LiClO<sub>4</sub> sample reaches a remarkable value of  $1.3 \times 10^{-4}$  S cm<sup>-1</sup> at 20 °C corresponding to almost 4 orders of magnitude amelioration compared to the PEO control sample ( $1.6 \times 10^{-8}$  S cm<sup>-1</sup> of PEO-1/8LiClO<sub>4</sub> in Figure 4.9A), and outperforming the other recently reported PEO-based CSEs listed in Table 4.2. Noticeably, although  $\sigma$  measurements have been conducted at temperatures as high as 90 °C, there are almost no changes in the shape and thickness of the sample before and after measurement at high temperature (Figure 4.10).



**Figure 4.9** Temperature-dependent  $\sigma$  of (A) P@SiO<sub>2</sub>@P-PEO-1/8LiClO<sub>4</sub> CSEs with various filler amounts in the range of 0% - 15%, (B) PTMPM-PEO-1/8LiClO<sub>4</sub> and SiO<sub>2</sub>-PEO-1/8LiClO<sub>4</sub> CSEs. (C) VFT plots for the  $\sigma$  of 7.5%P@SiO<sub>2</sub>@P-PEO-1/8LiClO<sub>4</sub>, PEO-1/8LiClO<sub>4</sub>, PTMPM-PEO-1/8LiClO<sub>4</sub>, and SiO<sub>2</sub>-PEO-1/8LiClO<sub>4</sub> CSEs. (D) Temperature-dependent  $\sigma$  of 7.5%P@SiO<sub>2</sub>@P-PEO-LiClO<sub>4</sub> CSEs with various Li<sup>+</sup>/EO ratio in the 1/20 - 1/5 range.



**Figure 4.10** Photograph of  $7.5\%P@SiO_2@P-PEO-1/8LiClO_4$  sample before (A) and (B) after high temperature ionic conductivity measurement.

Furthermore, the temperature-dependent  $\sigma$  data (Figure 4.9C) of

the 7.5%P@SiO<sub>2</sub>@P-PEO-1/8LiClO<sub>4</sub>, PEO-1/8LiClO<sub>4</sub>, PTMPM-PEO-1/8LiClO<sub>4</sub> and SiO<sub>2</sub>-PEO-1/8LiClO<sub>4</sub> samples are nicely fitted by the Vogel-Fulcher-Tammann (VFT) equation corresponding to segmental motion of polymer chains allowing Li<sup>+</sup> ions to transfer between coordination sites [10, 22, 45]. The accordingly calculated activation energies (E<sub>a</sub>) are plotted in the inset of Figure 4.9C and show the highest value for the PEO-1/8LiClO<sub>4</sub> sample (7.81 KJ mol<sup>-1</sup>). With the addition of PTMPM or SiO<sub>2</sub>, E<sub>a</sub> has been slight reduced to either 6.96 KJ mol<sup>-1</sup> or 6.15 KJ mol<sup>-1</sup>, respectively. Only in the presence of the P@SiO<sub>2</sub>@P fillers, E<sub>a</sub> can be significantly dropped to 3.96 KJ mol<sup>-1</sup>. This points out again towards the fact that the transport of Li<sup>+</sup> ion is facilitated in the P@SiO<sub>2</sub>@P filler containing samples, because of the formation of preferential Li<sup>+</sup> ion pathways in the PTMPM interfacial layer on P@SiO<sub>2</sub>@P fillers and the considerable reduction of crystallinity in the P@SiO<sub>2</sub>@P containing samples allowing enhanced segmental motion of PEO chains. Moreover, the  $\sigma$  of a CSE closely depends on the concentration of LiClO<sub>4</sub> in the system (Figure 4.9D), the 7.5%P@SiO<sub>2</sub>@P-PEO-1/8LiClO<sub>4</sub> sample displaying the optimal  $\sigma$ . In the other two samples with lower amounts of LiClO<sub>4</sub>, namely the 7.5%P@SiO<sub>2</sub>@P-PEO-1/15LiClO<sub>4</sub> and 7.5%P@SiO<sub>2</sub>@P-PEO-1/20LiClO<sub>4</sub> samples, PEO crystallization is observed leading to a sharp  $\sigma$  decrease below 60 °C. For the sample with a higher amount of LiClO<sub>4</sub> (i.e., 7.5%P@SiO<sub>2</sub>@P-PEO-1/5LiClO<sub>4</sub>), the  $\sigma$  decreases because of the formation of more immobilized Li<sup>+</sup>/ClO<sub>4</sub><sup>-</sup> ion pairs as shown before by Raman spectroscopy (Figure 4.7B).

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 Tables 4.2 Comparison of ionic conductivities of various PEO-based CSE materials.

Ref	Sample	Molecular weight of PEO	Additives	lonic conductivity		
This work	7.5%P@SiO2@P-PEO-1/8LiClO4	600K	7.5% P@SiO <sub>2</sub> @P	1.3 × 10 <sup>-4</sup> S cm <sup>-1</sup> @ 20 °C		
[3]	PEO-MUSiO <sub>2</sub> composite polymer electrolyte	600K	~10% SiO <sub>2</sub>	$4.4 \times 10^{-5} \text{ S cm}^{-1} @ 30 \text{ °C}$		
[4]	Graphene oxide-PEO	600K	1% Graphene oxide	1.54 × 10 <sup>-5</sup> S cm <sup>-1</sup> @ 24 °C		
[35]	Hydroxyapatite-PEO hybrid solid electrolyte	600K	36% Hydroxyapatite	$1.05 \times 10^{-5} \mathrm{S  cm^{-1}} @ 25 ^\circ\mathrm{C}$		
[6]	SiO <sub>2</sub> -PEO-LiTFSI	600K	~9% SiO <sub>2</sub>	1.3 × 10 <sup>-4</sup> S cm <sup>-1</sup> @ 30 °C		
[36]	PEO/LiClO <sub>4</sub> /walnut-like SiO <sub>2</sub> -15	600K	15 wt % walnut-like SiO <sub>2</sub> nanoparticles	6.31 × 10 <sup>-6</sup> S cm <sup>-1</sup> @ 30 °C		
[37]	CPE-(SiO <sub>2</sub> @PMMA)	1000K	4 wt% nano-SiO <sub>2</sub> @PMMA particles	8.54 × 10 <sup>-5</sup> S cm <sup>-1</sup> @ 60 °C		
[38]	PEO-Li <sub>2</sub> O. SiO <sub>2</sub> . TiO <sub>2</sub> . P <sub>2</sub> O <sub>5</sub> (LSTP) composite electrolyte	1000K	25 wt% nm size LSTP particle	5.44 × 10 <sup>-4</sup> S cm <sup>-1</sup> @ 60 °C		

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	PEO/LiTFSI/oxyethyl containing poly(ionic liquid) modified			
[39]	graphene oxide nanoparticles (ox-PIL@GO) composite electrolyte	600K	5 wt% ox-PIL@GO	1.01 × 10 <sup>-4</sup> S cm <sup>-1</sup> @ 40 °C
[18]	PEO-LiClO <sub>4</sub> @SiO <sub>2</sub> NP	600K	10% in situ SiO $_{2}$	1.1 × 10 <sup>-4</sup> S cm <sup>-1</sup> @ 30 °C
[40]	PEO/Mg-Al Layer-double-hydroxides (LDH) electrolyte	600K	5 wt% 2D LDH nanosheets	1.1 × 10 <sup>-5</sup> S cm <sup>-1</sup> @ 30 °C
[14]	PEO <sub>18</sub> -LiTFSI-5%SiO <sub>2</sub> -5%succinonitrile	600K	5 wt% SiO <sub>2</sub> and 5% succinonitrile	3.3 × 10 <sup>-4</sup> S cm <sup>-1</sup> @ 60 °C
[41]	Flyash-treated submicro/micron particles and PEO composite polymer electrolyte	600K	10 wt% flyash	10 <sup>-6</sup> - 10 <sup>-5</sup> S cm <sup>-1</sup> @ 20 °C
[42]	Li-doping high entropy oxide (Li <sub>0.25</sub> HEO) ceramic powder as the filler for the PEO-based composite solid electrolyte	600K	15 wt% Li <sub>0.25</sub> HEO	8.9 × 10 <sup>-5</sup> S cm <sup>-1</sup> @ 30 °C
[42]	PEO <sub>20</sub> /LiTFSI/tungsten trioxide	2000K	5% WO <sub>3</sub>	7.4 × 10 <sup>-4</sup> S cm <sup>-1</sup> @ 60 °C
[43]	PEO-LiTFISI-Li <sub>1.3</sub> Al <sub>0.3</sub> Hf <sub>1.7</sub> (PO <sub>4</sub> ) <sub>3</sub> (LAHP) powder	600K	20 wt% LAHP	$1.3 \times 10^{-4} \mathrm{S \ cm^{-1}} @ 30 ^{\circ}\mathrm{C}$
[44]	PEO/LiTFSI/Aminopropyltriethoxy silane (KH550)-Fe <sub>3</sub> O <sub>4</sub> - Sepiolite (KFSEP) composite particles	1000K	10% aligned KFSEP	2.0 × 10 <sup>-5</sup> S cm <sup>-1</sup> @ 20 °C

Li-ion transference number  $(t_{Li^+})$  is defined as the ratio of the cationic current to the total current, which is an important parameter to characterize the transport of Li<sup>+</sup> ions. The  $t_{Li^+}$  of the PEO-1/8LiClO<sub>4</sub> sample is only 0.19 (Figure 4.11A), which is in agreement with the literature [21]. Notably, the 7.5%P@SiO<sub>2</sub>@P-PEO-1/8LiClO<sub>4</sub> sample rapidly achieves steady state within 2500 s, with a  $t_{Li^+}$  of 0.81 (Figure 4.11B). Such a high  $t_{Li^+}$  could originate from the immobilization of perchlorate anions, which further allows to free the associated Li<sup>+</sup> cations. This has been here evidenced before by Raman spectroscopy (Figure 4.7B) and is confirmed now by  $t_{Li^+}$  determination.



**Figure 4.11** Polarization curves for PEO-1/8LiClO<sub>4</sub> (A) and 7.5%P@SiO<sub>2</sub>@P-PEO-1/8LiClO<sub>4</sub> (B) CSEs at 60 °C under an applied voltage of 10 mV, with the corresponding impedance diagram at the initial and the steady state (insets). LSV curves for PEO-1/8LiClO<sub>4</sub> (C) and 7.5%P@SiO<sub>2</sub>@P-PEO-1/8LiClO<sub>4</sub> (D) CSEs at 60 °C with a scan rate of 1 mV s<sup>-1</sup>.

In a further step, LSV has been used to probe the electrochemical stability window of samples. The LSV curve of the PEO-1/8LiClO<sub>4</sub> sample shows a plateau and afterwards an obvious rise starting from

3.8 V (Figure 4.11C), since PEO is easily oxidized at high voltage [21]. In sharp contrast, the 7.5%P@SiO<sub>2</sub>@P-PEO-1/8LiClO<sub>4</sub> sample displays a wide electrochemical stability window, since the oxidation peak occurs only after 5 V, demonstrating that the oxidation of PEO is effectively inhibited in the filler-containing system (Figure 4.11D) [21].



**Figure 4.12** (A) Galvanostatic cycling curve of a Li symmetric cell built with a 7.5%P@SiO<sub>2</sub>@P-PEO-1/8LiClO<sub>4</sub> CSE at 60 °C under various current densities of 0.025, 0.05, 0.10, 0.15, 0.20 mA cm<sup>-2</sup>. (B) Long-term galvanostatic cycling curves of Li symmetric cells built with 7.5%P@SiO<sub>2</sub>@P-PEO-1/8LiClO<sub>4</sub> and PEO-1/8LiClO<sub>4</sub> CSEs at 60 °C under current density of 0.10 mA cm<sup>-2</sup>, with enlarged views of details.

Galvanostatic cycling experiments in Li symmetric cell configurations aim at probing the interfacial stability between SSEs and Li electrodes. Here, a symmetric cell built with the 7.5%P@SiO<sub>2</sub>@P-PEO-1/8LiClO<sub>4</sub> sample has been charged and discharged for 1 h respectively under various current densities ranging from 0.025 to 0.20 mA cm<sup>-2</sup>, for 5 cycles at each density (Figure 4.12A). The investigated sample reaches stable and symmetric overpotential platforms during charging and discharging: ~14 mV at 0.025 mA cm<sup>-2</sup>, ~28 mV at 0.05 mA cm<sup>-2</sup>, ~50 mV at 0.10 mA cm<sup>-2</sup>, ~72 mV at 0.15 mA cm<sup>-2</sup>, ~92 mV at 0.20 mA cm<sup>-2</sup>. Afterwards, the overpotential even returns to ~12 mV at 0.025 mA cm<sup>-2</sup> after high current running, revealing the high stability under the various currents. For a long-term cycling at 0.10 mA cm<sup>-2</sup>, the overpotential of the 7.5%P@SiO<sub>2</sub>@P-PEO-1/8LiClO<sub>4</sub> sample starts to decline due to the gradual formation of interfaces, and subsequently stabilizes at ~58 mV during the 50<sup>th</sup> – 60<sup>th</sup> cycle, ~57 mV during the 150<sup>th</sup> – 160<sup>th</sup> cycle, and ~58 mV during the 250<sup>th</sup> – 260<sup>th</sup> cycle (Figure 4.12B). In the whole cycles, the overpotential almost remains the same over 300 h, evidencing the excellent interfacial stability between the CSE and Li electrodes, while for the PEO-1/8LiClO<sub>4</sub> control sample, a hard short occurs within the first hour under the 0.1 mA cm<sup>-2</sup> current (Figure 4.12B inset). Subsequently, the interfaces between SSEs and Li electrodes have been investigated by SEM after cycling. The cross section of the Li electrode and the 7.5%P@SiO<sub>2</sub>@P-PEO-1/8LiClO<sub>4</sub> sample displays a uniform interface (Figure 4.13A) and the top surface of the Li electrode is relatively smooth (Figures 4.13C and E). On the contrary, Li electrode reveals an uneven and coarse interface with PEO-1/8LiClO<sub>4</sub> (Figure 4.13B) and obvious cracks on the surface (Figure 4.13D, highlighted by arrows), due to the instability of Li electrodes. Worse still, Li dendrites are formed (Figure 4.13B inset and Figure 4.13F, circled by curves). The formation of a stable interface and the reinforced mechanical modulus

of the  $7.5\%P@SiO_2@P-PEO-1/8LiClO_4$  sample are beneficial to mitigate the instability of the Li electrode.



**Figure 4.13** Cross-sectional SEM images of interfaces (A) between Li electrode and 7.5%P@SiO<sub>2</sub>@P-PEO-1/8LiClO<sub>4</sub> and (B) between Li electrode and PEO-1/8LiClO<sub>4</sub> after cycling. SEM images of the surface of the Li electrode contacting with 7.5%P@SiO<sub>2</sub>@P-PEO-1/8LiClO<sub>4</sub> (C and E) and PEO-1/8LiClO<sub>4</sub> (D and F).

# 4.4.4 Application in all-solid-state battery

Finally, the  $7.5\%P@SiO_2@P-PEO-1/8LiClO_4$  sample has been tested as a CSE in an all-solid-state battery, using lithium iron

phosphate (LFP) as a cathode and metal Li as an anode. The accordingly assembled solid-state battery has been tested at 60 °C. With respect to the rate performance, after activation for the first three cycles, the specific capacity rapidly stabilizes at 149.3 mAh g<sup>-1</sup> at 0.1 C, 139.4 mAh g<sup>-1</sup> at 0.2 C, 116.9 mAh g<sup>-1</sup> at 0.5 C, 90.6 mAh g<sup>-1</sup> at 1 C, and even 67.3 mAh g<sup>-1</sup> at 2 C high current density (Figure 4.14A). The capacity finally recovers to 141.6 mAh g<sup>-1</sup> at 0.1 C after high current density, with a capacity retention as high as 95%. Besides, the corresponding charge/discharge curves from 0.1 to 2 C all display the characteristic charge and discharge plateaus of LFP (Figure 4.14B). Moreover, in the long-term cycling, the specific capacity is rapidly stabilized at 147.7 mAh g<sup>-1</sup> at 0.1 C and the decay rate is only 0.068% after 100 cycles (Figures 4.14C and D). Compared to the other PEO-based materials listed in Table 4.3, the 7.5%P@SiO<sub>2</sub>@P-PEO-1/8LiClO<sub>4</sub> sample shows outstanding capacity and cyclability.



**Figure 4.14** (A) Rate performance and (B) charge/discharge profiles of LFP/7.5%P@SiO<sub>2</sub>@P-PEO-1/8LiClO<sub>4</sub>/Li at 60 °C under various current rates. (C) Long-term cycling performance and (D) charge/discharge profiles of LFP/7.5%P@SiO<sub>2</sub>@P-PEO-1/8LiClO<sub>4</sub>/Li at 60 °C at 0.1 C.

Ref	Sample	Mole- cular weight of PEO	lonic conductivity	Opera	ation	<u>م</u>	Applicat	tion per	formance		Long-te	erm cycling
				cond	condition Rate performance					performance		
This	7.5%P@SiO₂@ P-PEO-	600K	1.3 × 10 <sup>-4</sup> S cm <sup>-1</sup> @	Tempera- ture (°C)	Voltage (V)	Rate (C)	0.1	0.2	0.5 1	2	Rate (C)	0.1
WOLK	1/8LiClO4		20 °C	60	3 - 3.8	Capacity (mAh g <sup>-1</sup> )	149.3	139.4 1	.16.9 90.6	67.3	decay rate	0.068%/cy at 100 cycles
	PEO-MUSiO <sub>2</sub>		4.4 × 10⁻⁵ S			Rate (C)	0.1	0.25	0.5	1	Rate (C)	1
[3]	composite polymer electrolyte	600K	cm⁻¹ @ 30 °C	60	2.5 - 4.1	Capacity (mAh g <sup>-1</sup> )	~148	~130	) ~116	100	decay rate	0.3%/cy at 65 cycles
	GO-PEO hvbrid		1.54 × 10 <sup>-5</sup> S			Rate (C)	0.1	0.2	0.5	1	Rate (C)	1
[4]	solid electrolyte	600K	cm <sup>-1</sup> @ 24 °C	60	2.5 - 4	Capacity (mAh g <sup>-1</sup> )	160	152	146	92	decay rate	0.09%/cy at 100 cycles
[35]	Hydroxyapatite-	600K	1.05 × 10⁻⁵ S	160	2.5 - 4	Rate (C)			4		Rate (C)	4

Tables 4.3 Comparison of performance of various PEO-based CSE materials with LFP cathodes and Li anodes.

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	PEO hybrid solid polymer electrolyte		cm <sup>-1</sup> @ 25 °C			Capacity (mAh g <sup>-1</sup> )	137			decay rate	0.08%/cy at 300 cycles	
			$1.1 \times 10^{-4}$ S			Rate (C)	0.3	0.5	1	2	Rate (C)	0.2
[18]	@SiO <sub>2</sub> NP	600K	cm <sup>-1</sup> @	90	2.5 - 4.2	Capacity	~1/6	~1/1	130	110	decay	0.3%/cy at
			30 °C			(mAh g <sup>-1</sup> )	140	141	130		rate	100 cycles
	PEO/Mg-Al		1 1 × 10 <sup>-5</sup> S			Rate (C)	0.1	0.2	0.5	1	Rate (C)	0.2
[40]	Layer-double- hydroxides electrolytes	600K	cm <sup>-1</sup> @ 30 °C	60	2.8 - 4.2	Capacity (mAh g <sup>-1</sup> )	~142	~139	~122	~104	decay rate	0.1%/cy at 100 cycles

# 4.5 Conclusion

Composite solid electrolytes consisting of P@SiO<sub>2</sub>@P dualfunctional fillers highly dispersed in a PEO matrix loaded with LiClO<sub>4</sub> have been synthesized and investigated in this contribution. We have demonstrated that the peculiar design of the P@SiO<sub>2</sub>@P filler allows the formation of a PTMPM-rich interface which is highly beneficial for the Li<sup>+</sup> ion transport properties of our electrolytes. The benefits have been ascribed to the following aspects: firstly, PTMPM interacts with PEO via hydrogen bonding, improving the dispersion of SiO<sub>2</sub> in the PEO matrix and further inhibiting its crystallinity of PEO; secondly, the amine groups of PTMPM are weakly coordinated with Li<sup>+</sup> ions, weakening the strong affinity between Li<sup>+</sup> ions and other polar groups, and thus Li<sup>+</sup> ions can rapidly and smoothly transfer; lastly, the hydrogen bonds between amine groups and perchlorate anions further promote the dissociation of LiClO<sub>4</sub> salt and the release of free Li<sup>+</sup> ions. Based on its unique structure, the 7.5%P@SiO<sub>2</sub>@P-PEO-1/8LiClO<sub>4</sub> CSE achieves excellent room-temperature  $\sigma$  as high as 1.3 × 10<sup>-4</sup> S cm<sup>-1</sup>, broad electrochemical stability window, outstanding  $t_{Li^+}$  of 0.81, and interfacial stability facing Li anodes. Finally, the LFP/7.5%P@SiO2@P-PEO-1/8LiClO<sub>4</sub>/Li all-solid-state battery achieves high capacity ~150 mAh g<sup>-1</sup> at 0.1 C, with outstanding long-term cycling stability (only 0.68‰ loss of capacity per cycle) and fully demonstrates the potential of our composite solid electrolytes.

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# Chapter 5

# One-pot synthesis of long-range aligned

nanochannels for Li-ion transfer highways

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#### Abstract

Limited ionic conductivity ( $\sigma$ ) of solid polymer electrolytes (SPEs) is a bottleneck for their wide practical application. Constructing ordered ionic transfer pathways is a prospective direction to promote  $\sigma$ . This can be achieved by e.g. immersing SPEs in porous molds. As an alternative to this cumbersome process, we propose here a straightforward one-pot synthesis strategy for the obtention of longrange aligned nanochannels, which is based on the evaporation of the solvent to induce the self-assembly of F127 Pluronic<sup>™</sup>-resol micelles. Dicyandiamide (DCD) and LiClO<sub>4</sub> are then uniformly dispersed in the F127-resol nanochannels. Compared to the random counterpart, the accordingly synthesized channel-aligned sample significantly improves room-temperature  $\sigma$  by 2 orders of magnitude reaching 1.65 × 10<sup>-4</sup> S/cm at 20 °C. The FTIR spectra further demonstrate that the best performing sample possesses more Li<sup>+</sup> ions coordinated to cyano groups and less coordinated to ether moieities, diminishing the Li<sup>+</sup> conduction energy since cyano groups have lower binding energy. Both aligned nanostructures and beneficial coordinating groups synergistically accelerate and smooth the ionic transport, contributing to the formation of Li-ion transfer highways.

KEYWORDS: Pluronic<sup>™</sup> F127, cyano, long-range, aligned, nanochannel, solid polymer electrolyte

#### 5.1 Introduction

With the ever-growing requirement for increased safety and high energy density, solid-state batteries (SSBs) are promising candidates for next-generation batteries [1]. More specifically, SSBs are based on solid-state electrolytes (SSEs) which should be highly safe and capable to face with high-capacity Li anodes [2]. SSEs include three main classes: inorganic solid electrolytes (ISEs), solid polymer electrolytes (SPEs) and their hybrids [3]. Among them, SPEs composed of Li<sup>+</sup>conducting polymers and Li salts, have garnered great interest thanks to their high flexibility, good processability, light weight and low cost [4-6]. Nevertheless, their limited room-temperature ionic conductivity ( $\sigma$ ) caused by the high crystallinity of polymers, especially in the case of poly(ethylene oxide) which is the main polymer used in SPEs, is a main challenge, which hinders the practical application [7].

To date, considerable effort has been devoted to promote the  $\sigma$  of SPEs and constructing Li-ion transfer pathways is a prospective direction [2, 3, 7]. Through the introduction of fillers (e.g., nanoparticles [8], nanowires [7, 9], nanochannels [3, 4, 10-12]) into polymer matrixes, Li-ion transfer pathways can be established along with the interfaces between polymers and fillers, efficiently promoting ionic conduction. This enhanced effect has been demonstrated in Chapter 4. The reason for the reinforced Li-ion conductive behavior can be summarized by the three following points: (i) incorporated fillers

suppress the crystallinity of polymers, and also boost the amorphous volume of the system, especially for the regions surrounding fillers; (ii) interactions between fillers and anions of Li salts are beneficial to disassociate Li salts, and meanwhile release more free Li<sup>+</sup> ions to transfer; (iii) some modified surfaces of fillers allow Li<sup>+</sup> ions to fast coordinate/decoordinate, as a consequence to speed up ionic transport, such as grafted groups with low binding energy [8], loaded ionic liquids [10] and plasticizers [13].

Drawing inspiration from Chapter 4, the shape and orientation of fillers influence the enhancement effect of  $\sigma$ , as the formation of Li-ion transfer paths is accordingly affected. Figure 5.1 shows the schematic of conducting paths using various fillers, with the functional filler P@SiO<sub>2</sub>@P discussed in Chapter 4 as a representative example. In terms of geometrical shape, the enhancement on  $\sigma$  by nanoparticles is inferior to that by nanowires. The reason is assigned to the Li-ion transfer pathways provided by nanoparticles which are short-range, isolated and not prone to continuous Li-ion transport. In sharp contrast, the transfer routes provided by nanowires are long-range, relatively uninterrupted and beneficial for Li-ion migration. As far as the orientation is concerned, the randomly oriented fillers show poorer electrochemical performance than the aligned ones, since the random orientation of fillers leads to the formation of tortuous and indirect Liion transfer pathways. Besides, the random stack of fillers inevitably generates crossing junctions. Conversely, the aligned structures can avoid the tortuosity and crossing junctions of ionic transfer pathways.

Moreover, when the orientation of aligned channels is perpendicular to electrodes, the Li-ion conduction can be further promoted [2, 3, 7].



**Figure 5.1** Schematics of Li-ion transfer paths for various geometrical structures in solid-state electrolytes.

It has been reported that aligned ionic channels can be provided by preformed frameworks with ordered pores, such as porous inorganic films [2] and porous polymer films [3]. However, their synthesis process is complicated, firstly preparing a porous framework as a mold, followed by immersion in polymer solutions. Besides, in some cases of ionically insulating frameworks, the  $\sigma$  of bulk SSEs can rapidly fade when the inert content excessively increases. To address those bottlenecks, a simple and straightforward synthesis method towards prolonged, aligned channels in SSEs is highly pursued.

In the present work, we develop a novel approach towards the one-pot synthesis of long-range well-aligned nanochannels in SPEs. Induced by the evaporation of EtOH solvent, prolonged ordered nanochannels based on Pluronic<sup>TM</sup> F127-resol micelles are gradually self-assembled with uniform dispersion of dicyandiamide (DCD) and LiClO<sub>4</sub> in those channels. Due to the peculiar fabrication of aligned nanochannels containing an optimal amount of DCD additive, the accordingly synthesized SPE exhibits an outstanding  $\sigma$  of 1.65 × 10<sup>-4</sup> S/cm at 20 °C, which is improved by 2 orders of magnitude compared to the random-structure reference. Furthermore, we attempt to elucidate the mechanism of fast Li-ion migration from the two aspects of composition and structure.

#### 5.2 Experimental section

#### 5.2.1 Materials

Phenol was supplied by Acors Organics. Formaldehyde (37 wt%) was supplied by TCI. Dicyandiamide (DCD) was supplied by Thermo Scientific. Pluronic<sup>™</sup> F127 was supplied by BASF. Ethanol (EtOH), hydrochloric acid (HCl, 37%), sodium hydroxide (NaOH), dimethylformamide (DMF) were supplied by VWR. Ammonium hexafluorophosphate (NH<sub>4</sub>PF<sub>6</sub>) was supplied by Sigma-Aldrich. Lithium perchlorate (LiClO<sub>4</sub>, anhydrous, 99.5%) was supplied by Alfa Aesar. All

chemicals were used as received without any further treatment. Milli-Q water was used.

#### 5.2.2 Characterizations

Fourier transform infrared (FTIR) spectra were collected on a Nicolet iN10 IR Microscope from Thermo Fisher Scientific using a diamond attenuated total reflection (ATR) technique. Differential scanning calorimetry (DSC) was conducted using a Mettler Toledo DSC1 equipped with STARe software. Samples were placed in 40 μL sealed aluminum pans. The temperature profile was swept from –80 to 100 °C at a heating rate of 10 °C min<sup>-1</sup> under a nitrogen atmosphere. Scanning electron microscopy (SEM) images were collected by a Zeiss Auriga FIB-SEM. A tube furnace (Nabertherm R 50/250/13 with Controller C450) was used to calcine samples for SEM measurements. Molar masses of polymers were measured on a Polymer Standards Service size exclusion chromatography (SEC) system with the calibration by a PEO standard curve. The samples were dissolved in a NH<sub>4</sub>PF<sub>6</sub> solution (2.5 mM in DMF).

#### 5.2.3 Sample synthesis

#### • Synthesis of resol

Resol, also known as phenolic resin, with low molecular weight was prepared from phenol and formaldehyde assisted by a base catalyst [14, 15]. For a typical synthesis of resol, phenol (8.0 g) was melted in a flask at 45 °C. A NaOH aqueous solution (0.279 ml, 20 wt%) was mixed into the melted phenol and stirred for 10 min. Then formaldehyde (4.805 ml, 37 wt%) was dropwise added into the above mixture. Successively, the whole mixture was heated in an oil bath at 70 °C for 1 h. After cooling to RT, the pH value of the mixture was adjusted to ~7 by a HCl solution (2M). The remaining water of the mixture was further removed by rotary evaporator at 40 °C. The resulting product, namely resol, was dissolved in EtOH at the weight ratio of 20 wt%, for further use.

#### Synthesis of F127-channel-aligned-DCD-LiClO<sub>4</sub>

In a typical process for a F127-channel-aligned-DCD-LiClO<sub>4</sub> sample, certain amounts of DCD (the molar ratio of DCD/ethylene-oxide from 0 to 1/4) and LiClO<sub>4</sub> (the molar ratio of Li<sup>+</sup>/ethylene-oxide from 1/25 to 1/8) were dissolved in EtOH (2 ml) at room temperature (RT) and mixed at 40 °C. Then a resol solution (0.615 ml, 20 wt% in EtOH) was added into the above mixture drop by drop. Besides, Pluronic<sup>TM</sup> F127 (0.1 g) was dissolved in EtOH (1 ml) at 40 °C and then added into the above mixture. After stirring for 30 min at 40 °C, the liquid mixture was dropwise casted on stainless-steel (SS) spacers of coin cells. After evaporating the EtOH at RT overnight, these samples were further heated at 100 °C for 24 h in a vacuum oven. The dry membrane was finally obtained as a F127-channel-aligned-xDCD-yLiClO<sub>4</sub> sample, where x refers to the molar ratio of DCD to ethylene oxide (EO) in a sample, ranging from 0, 1/64, 1/32, 1/16, 1/8 to 1/4; y stands for the molar ratio of Li<sup>+</sup> to EO in a sample, ranging from 1/25, 1/20, 1/15, 1/10

to 1/8.

#### Synthesis of F127-random-structure-DCD-LiClO<sub>4</sub>

A mixture of DCD (0.1 mmol) and LiClO<sub>4</sub> (0.08 mmol) was dissolved in EtOH (2 ml) at RT. Then a resol solution (0.615 ml, 20 wt% in EtOH) was added into the above mixture drop by drop. Besides, Pluronic<sup>™</sup> F127 (0.1 g) was dissolved in EtOH (1 ml) at 40 °C and then added into the above mixture. After stirring of 30 min, the liquid mixture was dropwise casted on SS spacers of coin cells. After evaporating the EtOH at RT under intensive ventilation, these samples were further heated at 100 °C for 24 h in a vacuum oven. The dry membrane was finally obtained as a F127-random-structure-1/16DCD-1/20LiClO<sub>4</sub> sample.

#### 5.2.4 Electrochemical Measurements

Electrochemical impedance spectroscopy (EIS) was conducted on a SPE assembled into a symmetric SS configuration for measuring the ionic conductivity. EIS was measured in the frequency range from 7 MHz to 100 mHz and in the temperature range from 90 to 20 °C on a Bio-Logic VMP-300 instrument. Temperature was controlled by a climate chamber with a ramp rate of 0.33 °C/min, besides a period of 30 min was applied for each 10 °C as an equilibration time for measurement.

#### 5.3 Calculation section

5.3.1 Ionic conductivity calculated by electrochemical impedance spectroscopy

The  $\sigma$  of a SPE is converted from the resistance measured by EIS in a cell configuration of SS symmetric electrodes from 20 °C to 90 °C. The calculation formula is as Equation (5.1):

$$\sigma = \frac{l}{RA} \tag{5.1}$$

Where  $\sigma$  (S cm<sup>-1</sup>) is the ionic conductivity of the SPE sample, l (cm) is the thickness of the membrane-like SPE sample, R ( $\Omega$ ) is the bulk resistance measured by EIS, and A (cm<sup>2</sup>) is the contact area between the SPE and SS [16].

# 5.3.2 Activation energy fitted by the Vogel-Fulcher-Tammann equation

Above the melting temperature  $T_m$ , the segmental movement of polymer chains helps Li<sup>+</sup> ions transfer among the coordination sites. The Li-ion transfer mechanism is suitable to be simulated by the Vogel-Fulcher-Tammann (VFT) equation. The relationship between temperature and  $\sigma$  is interpreted as Equation (5.2):

$$\sigma = A_{VFT} T^{-\frac{1}{2}} \times e^{-\frac{E_a}{R(T-T_0)}}$$
(5.2)

Where  $\sigma$  (S/cm) is the ionic conductivity of samples,  $A_{VFT}$  (S

cm<sup>-1</sup> K<sup>0.5</sup>) is the VFT pre-exponential factor, T (K) is the absolute temperature,  $E_a$  (J mol<sup>-1</sup>) is the activation energy, R (J mol<sup>-1</sup> K<sup>-1</sup>) is the gas constant, and  $T_0$  (K) is the reference temperature, related to the glass transition temperature T<sub>g</sub> of a sample [17].

Equation (5.2) is transformed into Equation (5.3):

$$\ln\left(\sigma T^{\frac{1}{2}}\right) = \frac{E_a}{R(T - T_0)} \tag{5.3}$$

By plotting  $\ln \left(\sigma T^{\frac{1}{2}}\right)$  vs.  $(T - T_0)^{-1}$ ,  $E_a$  can be related to the slope. In order to better meet VFT simulation conditions and to improve the fitting accuracy, the temperature-dependent  $\sigma$  data from 50 °C to 90 °C are chosen to be simulated.

#### 5.4 Results and discussion

Using Pluronic<sup>™</sup> F127 triblock copolymer as a template agent, resol as a channel matrix, DCD as a nitrogen source, LiClO<sub>4</sub> as a Li salt, the F127-channel-aligned-DCD-LiClO<sub>4</sub> sample is synthesized based on evaporation-induced self-assembly of F127 in EtOH solvent. The synthetic pathway is illustrated in Figure 5.2. Pluronic<sup>™</sup> F127 is a triblock copolymer consisting of poly(ethylene oxide) (PEO) blocks and poly(propylene oxide) (PPO) blocks, and is characaterized by a molecular weight of ~12000 g/mol (Figures 5.3). In a polar solvent, the PEO blocks tend to dissolve in the solvent, while PPO blocks perform oppositely, leading to the formation of F127 micelles with PPO as a core and PEO as a shell (micelle as shown in Figure 5.2). The evaporation of EtOH solvent induces the ordered stacking of F127 micelles following the evaporation front and construct the aligned nanosized channels vertical to the surface of the substrate (i.e., spacers of coin cells). Thanks to the non-covalent interactions formed between resol, DCD and PEO blocks, resol participates in establishing nanochannels surrounding the F127 micelles, accompanied by dispersed DCD molecules [15]. Because of the coordination (i) between Li<sup>+</sup> ions and EO groups and (ii) between Li<sup>+</sup> ions and cyano groups, Li<sup>+</sup> ions are also distributed in the aligned nanochannels. After adequate drying, the F127-resol aligned nanochannels incorporating DCD and LiClO<sub>4</sub> are achieved and denoted as F127-channel-aligned-DCD-LiClO<sub>4</sub> for further usage as SPEs.



**Figure 5.2** Synthetic pathway towards SPEs consisting of long-range aligned nanochannels.



Figure 5.3 SEC curve (B) of commercial Pluronic<sup>™</sup> F127 triblock copolymers.

The morphology, structure, thermal properties, and ionic conductivity of F127-channel-aligned-1/16DCD-1/20LiClO<sub>4</sub> have been investigated. Besides, a control sample, denoted as F127-randomstructure-1/16DCD-1/20LiClO<sub>4</sub>, has also been investigated for the sake of comparison. This control sample contains the same composition as the channel-aligned sample but in a random arrangement. The primary distinction between their synthesis processes lies in the evaporation conditions. The morphology of both samples has been detected by SEM. It should be noted that samples for SEM characterization have been calcined under an inert atmosphere before observation in order to increase contrast, since polymers and organic matter have been transformed into stable carbonaceous material. The calcined F127channel-aligned-1/16DCD-1/20LiClO<sub>4</sub> sample exhibits prolonged and straight stripe-like nanochannels with diameters of ~10 nm; moreover, most of them are aligned (Figure 5.4A). Oppositely, in the calcined F127-random-structure-1/16DCD-1/20LiClO<sub>4</sub> sample, a randomly stacked and even locally aggregated structure is observed, without continuous channels (Figure 5.4B). The SAXS pattern (Figure 5.4C) of the F127-channel-aligned-1/16DCD-1/20LiClO<sub>4</sub> sample reveals five scattering peaks with q-values of 0.44, 0.76, 1.16, 1.32 and 1.58  $nm^{-1}$ , The q-value ratios of these peaks correspond precisely to  $1:\sqrt{3}:\sqrt{7}:\sqrt{9}:\sqrt{13}$  and can be indexed to the 10, 11, 21, 30 and 31 planes of a 2D hexagonal mesostructure [18]. The unit cell parameter is calculated to be about 16.5 nm, which is slightly larger than the TEM result (Figure 5.4 A). This difference is reasonable because the sample used for TEM is calcined, resulting in framework shrinkage [18]. Conversely, the SAXS pattern of the F127-random-structure-1/16DCD-1/20LiClO<sub>4</sub> sample reflects a disorder structure. Differential scanning calorimetry (DSC) has been conducted to survey thermal transitions of the investigated samples (Figure 5.4D and Table 5.1). The F127random-structure-DCD-LiClO<sub>4</sub> sample shows a glass transition temperature T<sub>g</sub> of -46 °C and a melting temperature T<sub>m</sub> of 37 °C. The presence of a T<sub>m</sub> is attributed to the crystallization of PEO coronal chains from the F127 micelles and the integration of the T<sub>m</sub> peak is calculated to be as high as -17.3 J/g. For F127-channel-aligned- $1/16DCD-1/20LiClO_4$ , T<sub>g</sub> and T<sub>m</sub> values remain similar but the integration of  $T_m$  dramatically decreases to -0.5 J/g. This suggests that the structure of the aligned channels has a great influence on the crystallization behavior of samples. The PEO coronal chains in randomly stacked F127 micelles show tendency to crystallize while in the channel-aligned sample, the conformation adopted by PEO coronal blocks obviously does not favor crystallization.



**Figure 5.4** Comparison of samples with channel-aligned and random structures. SEM images of (A) calcined F127-channel-aligned-1/16DCD-1/20LiClO<sub>4</sub> sample (with an inset of structure diagram) and (B) calcined F127-random-structure-1/16DCD-1/20LiClO<sub>4</sub> sample. SAXS patterns (C) of F127-channel-aligned-1/16DCD-1/20LiClO<sub>4</sub> and F127-random-structure-1/16DCD-1/20LiClO<sub>4</sub> samples. DSC curves (D) of F127-channel-aligned-1/16DCD-1/20LiClO<sub>4</sub> and F127-random-structure-1/16DCD-1/20LiClO<sub>4</sub> and F127-random-structure-dependent  $\sigma$  of F127-channel-aligned-1/16DCD-1/20LiClO<sub>4</sub> and F127-random-structure-1/16DCD-1/20LiClO<sub>4</sub> and F127-random-structure-1/16DCD-1/20LiClO<sub>4</sub> samples. (E) Temperature-dependent  $\sigma$  of F127-channel-aligned-1/16DCD-1/20LiClO<sub>4</sub> and F127-random-structure-1/16DCD-1/20LiClO<sub>4</sub> samples. (F) VFT fitting plots for the  $\sigma$  of F127-channel-aligned-1/16DCD-1/20LiClO<sub>4</sub> and F127-random-structure-1/16DCD-1/20LiClO<sub>4</sub> samples, with an inset of E<sub>a</sub> diagram.

lable 5.1 The	rmal properties cha	aracterized by DSC fo	or F127-channel-aligned-
1/16DCD-1/20	LiClO4 and F127-ran	dom-structure-1/16D	OCD-1/20LiClO <sub>4</sub> samples.

Samples	T <sub>g</sub> (°C)	T <sub>m</sub> (°C)	Integration of $T_m$ (J/g)
F127-channel-aligned- 1/16DCD-1/20LiClO₄	-45	40	-0.5
F127-random-structure- 1/16DCD-1/20LiClO <sub>4</sub>	-46	37	-17.3

performances of the F127-channel-aligned-1/16DCD-The 1/20LiClO<sub>4</sub> sample as a SPE have been subsequently investigated. The temperature-dependent  $\sigma$  is presented in Figure 5.4E in the range of 90 to 20 °C. Noticeably, the F127-channel-aligned-1/16DCD-1/20LiClO<sub>4</sub> sample achieves a room-temperature  $\sigma$  as high as 1.65 × 10<sup>-4</sup> S/cm at 20 °C, corresponding to almost 2 orders of magnitude amelioration compared to the random-structure control sample (2.99 × 10<sup>-6</sup> S/cm @ 20 °C). Such excellent performance at RT also outperforms most of previously reported SSEs equipped with ionic transfer pathways (see Table 5.2). The temperature-dependent  $\sigma$  data have been further simulated Vogel-Fulcher-Tammann by the (VFT) equation corresponding to segmental motion of polymer chains allowing Li<sup>+</sup> ions to transfer between coordination sites [17, 19, 20]. The fitting results and the accordingly calculated activation energies (E<sub>a</sub>) are displayed in Figure 5.4F. The E<sub>a</sub> of the F127-channel-aligned-1/16DCD-1/20LiClO<sub>4</sub> (3.31 KJ/mol) is smaller than that of the random-structure sample (3.83 KJ/mol). Compared to the random-structure counterpart, the channel-aligned sample exhibits increased  $\sigma$  and minimal E<sub>a</sub>, suggesting that the channel-aligned structure is promoting Li-ion migration. It is hypothesized that those long-range aligned channels can be considered as Li-ion transfer routes and are diminishing the crossing junctions during transport.

**Tables 5.2** Comparison of the ionic conductivity of various solid-state electrolytesequipped with ionic transfer pathways

Ref	Sample	Formation of Li <sup>+</sup> pathway	lonic conductivity (S/cm)	Temperat ure (°C)
This work	F127-channel-aligned-1/16DCD- 1/20LiClO <sub>4</sub> solid polymer electrolyte	Aligned channels by F127 micelles	1.65 × 10 <sup>-4</sup>	20
[5]	PEO-MUSiO <sub>2</sub> composite polymer electrolyte	~12 nm SiO <sub>2</sub>	4.4 × 10 <sup>-5</sup>	30
[3]	Polyimide/PEO/LiTFSI solid polymer electrolyte	Nanoporous polyimide film	2.3 × 10 <sup>-4</sup>	30
[6]	SiO <sub>2</sub> -PEO-LiTFSI electrolyte	SiO <sub>2</sub> nanofibre framework	1.3 × 10 <sup>-4</sup>	30
[7]	LLTO-PAN-LiClO <sub>4</sub> electrolyte	Aligned LLTO nanowires	6.05 × 10 <sup>-5</sup>	30
[8]	P-P-A@=SiO <sub>2</sub> solid polymer electrolyte	Modified nanosilica	2.6 × 10 <sup>-4</sup>	RT
[9]	Composite solid-state polymer electrolyte based on ceramic nanowires	Ceramic nanowires	10 <sup>-3</sup> -10 <sup>-5</sup>	RT
[10]	PEO-100ZrO <sub>2</sub> @ ionic liquids	Framework of ZrO <sub>2</sub> loading ionic liquids	4.06 × 10 <sup>-4</sup>	60
[11]	LLTO nanotubes/PAN composite solid electrolyte	LLTO nanotubes	3.6 × 10 <sup>-4</sup>	RT
[12]	Polyamide/PEO/LiTFSI electrolyte	Porous polyamide film	2.05 × 10 <sup>-4</sup>	30



**Figure 5.5** Ionic conductivity and FTIR characterizations of F127-channel-aligned-DCD-LiClO<sub>4</sub> SPEs. Temperature-dependent  $\sigma$  (A) and FTIR spectra (B) of F127-channel-aligned-1/16DCD-LiClO<sub>4</sub> SPEs with various Li<sup>+</sup>/EO molar ratios in the range of 1/25 – 1/8. Temperature-dependent  $\sigma$  (C) and FTIR spectra (D) of F127-channel-aligned-DCD-1/20LiClO<sub>4</sub> SPEs with various DCD/EO molar ratios in the range of 0 – 1/4.

In addition to the structural analysis, the influence of different compositions on electrochemical properties has been investigated. Firstly, the influence of Li salt concentration on  $\sigma$  has been probed by varying the Li<sup>+</sup>/EO molar ratio of samples from 1/25 to 1/8. Among the investigated samples, the best performing one is F127-channel-aligned-1/16DCD-1/20LiClO<sub>4</sub>, suggesting that 1/20 is the optimal Li<sup>+</sup>/EO molar ratio (Figure 5.5A). This sample has been further explored by FTIR spectroscopy (Figure 5.5B). Note that the coordination between Li<sup>+</sup> and ether leads to a red shift of the band corresponding to the stretching vibration of C-O-C, as demonstrated in Chapter 4. The C-O-C band experiences a larger red shift when the Li<sup>+</sup>/EO molar ratio increases from 1/25 to 1/8 (except for 1/20). Interestingly, an opposite shift trend is observed for the sample with the 1/20 Li<sup>+</sup>/EO molar ratio, indicating that the ether groups in this sample have a decreased coordination with Li<sup>+</sup> ions compared to the other investigated samples.

The impact of the DCD component on  $\sigma$  of samples has been evaluated by measuring samples with various DCD concentration in which the DCD/EO molar ratio changes from 0 to 1/4. Figure 5.5C demonstrates that  $\sigma$  increases until reaching an optimal DCD/EO molar ratio of 1/16. In the case of the absence of DCD, the  $\sigma$  is inferior at each temperature compared to DCD-containing samples. Note that there is a dramatic drop of  $\sigma$  beginning at 30 °C. This plunge may be related to a thermal transition in the sample, caused by the crystallization of the polymer component (see thermal properties in Figure 5.6 and Table 5.3). This result sheds light on the important role of the DCD component in dramatically decreasing polymer crystallinity. The coordination between DCD and Li<sup>+</sup> was analyzed by FTIR spectroscopy (Figure 5.5D). In DCD-containing samples, a characteristic band of cyano group locates at ~2158 cm<sup>-1</sup>, which experiences a red shift when coordinating with Li<sup>+</sup>. Among all investigated samples, the sample with the 1/16 DCD/EO molar ratio exhibits the largest red shift, indicating the highest degree of coordination of C=N…Li<sup>+</sup>.



**Figure 5.6** DSC thermogram of F127-aligned channel-0DCD-1/20LiClO<sub>4</sub>. **Tables 5.3** Thermal properties characterized by DSC of F127-aligned channel-0DCD-1/20LiClO<sub>4</sub>.

Sample	T <sub>g</sub> (°C)	T <sub>m</sub> (°C)	Integration of $T_m$ (J/g)
F127-aligned channel-	-48	39	-27.3
0DCD-1/20LiClO <sub>4</sub>			

As reported, ether groups have relatively high affinity to Li<sup>+</sup> ions while cyano groups possessing weak binding energy to Li<sup>+</sup> are promising alternatives to lower the energy barrier during transport [21]. Based on the above FTIR analysis, the F127-channel-aligned-1/16DCD-1/20LiClO<sub>4</sub> sample shows less C-O-C···Li<sup>+</sup> and more C=N···Li<sup>+</sup>, compared to the other investigated samples. This further confirms that the Li<sup>+</sup> ions in this sample are apt to coordinate with cyano groups, suppressing the strong interaction between ether and Li<sup>+</sup>, and diminishing the coordination/decoordination energy, which is beneficial for Li-ion fast and smooth migration [8]. It is worth mentioning that the advantage of C-O-C···Li<sup>+</sup> vs C=N···Li<sup>+</sup>coordination is efficiently evidenced in the channel-aligned structure, as proven by the comparison between the aligned and random structures (Figure 5.4E and F). Indeed, for the same composition, the random structure without any continuous channels leads to worse  $\sigma$ , compared to the channel-aligned sample. In conclusion, the highly efficient Li-ion transport is realized by the collaborative contributions from the continuous channel-aligned structure and the low-binding-energy coordination sites from the DCD component.



**Figure 5.7** The illustration of Li-ion migration in long-range aligned nanochannels of F127-channel-aligned-DCD-LiClO<sub>4</sub> SPEs

On the basis of the above electrochemical performance and characterization findings, and in agreement with previously reported literature [2, 7, 10, 11, 13], the Li<sup>+</sup> ion migration mechanism in the F127-channel aligned-DCD-LiClO<sub>4</sub> SPE is understood as follows (Figure 5.7). Some Li<sup>+</sup> ions, derived from LiClO<sub>4</sub> salt, coordinate with ether

groups of F127 copolymers and migrate among the coordination sites assisted by the segmental chain motions. Meanwhile, other Li<sup>+</sup> ions coordinate to cyano groups of DCD with whom the binding energy is relatively low [21]. More importantly, DCD is distributed in the alignedchannels framework. Hence, DCD attracts Li<sup>+</sup> ions to the locations of nanochannels, and allows them to smoothly and quickly transport across the SPE. Both of the peculiar structure and optimal composition synergistically establish the Li-ion transfer highways.

#### 5.5 Conclusion

The long-range aligned sample F127-channel-aligned-DCD-LiClO<sub>4</sub> has been fabricated by a straightforward one-pot strategy. The construction of nanochannels is induced by the EtOH solvent evaporation and the self-assembly of the F127-based micelles. The accordingly synthesized samples achieve continuous and aligned nanochannels with the reduced crystallinity of polymers. When investigated as a SPE, the channel-aligned sample exhibits the striking  $\sigma$  of 1.65 × 10<sup>-4</sup> S/cm at 20 °C and decreased E<sub>a</sub> of 3.31 KJ/mol, reflecting the structural benefit for Li-ion migration. The compositional analysis by FTIR demonstrates that the optimal sample possesses more Li<sup>+</sup> ions coordinated to cyano groups and less Li<sup>+</sup> ions coordinated to the relatively low binding energy of cyano to Li<sup>+</sup>, the SPE mitigates the strong interaction between Li<sup>+</sup> and ether, diminishing the energy of

coordination/decoordination. The beneficial coordinating groups and directional nanochannels both synergistically enable Li<sup>+</sup> to rapidly and smoothly transport across SPEs.

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# Chapter 6

### Conclusions and perspectives

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#### 6.1 Conclusions

This thesis aimed to design and synthesize innovating nanostructured materials for LIBs, to boost the electrochemical performances and overcome the shortcomings of bulk structures. Three different creatively designed nanostructured systems have been proposed and utilized for electrodes and electrolytes. The accordingly synthesized nanostructured materials have dramatically enhanced electrochemical properties, in comparison with the bulk counterparts.

In Chapter 3, hollow porous C@SiC@Si@SiC@C nanospheres have been synthesized by the polymer-templated one-pot synthetic strategy. Taking advantage of the intrinsic swelling property of PTMPM in ethanol, the silica porous capsules have been uniformly wrapped on both sides by polymer layers, leading to the formation of a sandwiched structure. The designed materials have demonstrated outstanding electrochemical performance when used as anodes in LIBs and prevented the Si fracture issues to guarantee the stability of Si during lithiation. Besides, the Si nanoparticles have obviously shortened the diffusion paths of Li<sup>+</sup> ions and electrons through electrodes, further improving their utilization at different current densities. Lastly, the accordingly formed nanometer-thick SiC@C coating have admirably improved the electrical conductivity and the robustness of nanospheres, favoring the formation of a stable SEI.

In Chapter 4, P@SiO<sub>2</sub>@P nanostructured fillers highly dispersed in

a PEO matrix have been synthesized and formed CSEs after LiClO<sub>4</sub> loading. The large interface between hollow porous SiO<sub>2</sub> nanospheres and the PTMPM coating has contributed to Li-ion fast transport. The high dispersion of fillers, the mitigation of the strong interactions between Li<sup>+</sup> ions and coordination groups and the dissociation of LiClO<sub>4</sub> salts have been also improved. Based on the unique structure, the synthesized CSE samples achieved excellent RT ionic conductivity, broad electrochemical stability window, outstanding  $t_{Li}^+$ , interfacial stability, high capacity and long-term cycling stability.

In Chapter 5, the long-range well-aligned F127-channel-aligned-DCD-LiClO<sub>4</sub> samples have been fabricated by a straightforward one-pot method. The synthesized aligned samples exhibited enhanced RT ionic conductivity and diminished activation energy, compared to the counterparts of a random structure. Beneficial cyano coordinating groups and prolonged aligned nanochannels synergistically promoted fast and smooth Li-ion transfer highways in those samples.

From Chapter 3 to Chapter 5, three uniquely designed materials have been presented as examples of nanostructured materials for LIBs. In comparison with their bulk counterparts, the nanosized features of the synthesized materials have significantly ameliorated the electrochemical properties. Besides, the *in-situ* and one-pot synthetic methods have considerably saved the raw material sources and simplified the tedious processes, paving the way for large-scale production of nanostructured materials.
## 6.2 Perspectives

While there are limitations and opportunities for improvement in our nanostructured materials.

• In Chapter 3, hollow porous C@SiC@Si@SiC@C nanospheres with ultrathin shells are presented, offering benefits for fast ionic and electronic diffusion. However, a bottleneck arises due to occasional breakage of the nanospheres' shells, inevitably exposing the active materials to electrolytes. Therefore, achieving high-precision control steps becomes crucial, such as adjusting the quantities and types of Si and C precursors, and controlling the experimental steps of magnesiothermic reduction and acid washing, to enhance the integrity of the synthesized materials and consequently improve the performance of the corresponding battery [1, 2].

• In Chapter 4, the P@SiO<sub>2</sub>@P-LiClO<sub>4</sub>-PEO composite solid electrolytes demonstrate outstanding ionic conductivities at room temperature. However, assembling them into an all-solid-state battery brings challenges, particularly with the catholyte on the cathode side limiting ionic conduction at room temperature. Therefore, there is promise in optimizing the catholyte and/or anolyte, including their compositions and component proportions, to enable the operation of an all-solid-state battery at room temperature.

 In Chapters 4 and 5, high-resolution Raman and FTIR techniques are used to characterize the ionic pathways by localizing the coordinating groups with Li ions. Moreover, advanced characterization techniques are necessary to precisely detect the ionic transfer behavior, e.g. operando Raman [3-6], *in-situ* infrared nanospectroscopy [7], *in-situ* nuclear magnetic resonance [8-11] and atomic probe tomography [12].

• From Chapter 3 to Chapter 5, we progress from inorganic to composite materials, and then to organic materials. If this progress continues, it may become possible to develop an all-organic all-solid-state battery. This type of battery is considered a green and promising candidate due to each organic component being metal-free, less toxic, and environmentally friendly. Additionally, the raw materials are naturally abundant, and the production has less carbon footprint with less energy consumption. Moreover, with all components in a solid state, there is no risk of leakage. In the case of polymer-based materials, the battery can be flexible while retaining its mechanical strength. Solid-state materials are also easy to shape and process for practical applications. To achieve this battery design, a possible strategy involves combining conjugated materials as electrodes with solid polymer electrolytes [13].

## 6.3 References

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## Acronyms

- 0D zero-dimensional
- 1D one-dimensional
- 2D two-dimensional
- 3D three-dimensional
- AAO anodized aluminum oxide
- AC alternating current
- ACN acetonitrile
- CNT carbon nanotube
- CSE composite solid electrolyte
- CTAB cetyltrimethylammonium bromide
- CV cyclic voltammetry
- CVD chemical vapor deposition
- DCD dicyandiamide
- DEC diethyl carbonate
- DLS dynamic light scattering
- DMA dynamic mechanical analysis
- DMC dimethyl carbonate
- DSC differential scanning calorimetry
- EC ethylene carbonate
- EIS electrochemical impedance spectroscopy
- EMC ethylmethyl carbonate
- EO ethylene oxide
- ESR electron spin resonance
- ESW electrochemical stability window

EtOH	ethanol
FTIR	fourier-transform infrared
GITT	galvanostatic intermittent titration technique
ICE	initial coulombic efficiency
ISE	inorganic solid electrolyte
LCO	lithium cobalt oxide (LiCoO <sub>2</sub> )
LFP	lithium iron phosphate (LiFePO <sub>4</sub> )
LIB	lithium-ion battery
LiFSI	lithium bis(fluorosulfonyl)imide
LiTFSI	lithium bis(trifluoromethanesulfonyl)imide
LMO	lithium manganese oxide (LiMn <sub>2</sub> O <sub>4</sub> )
LSV	linear sweep voltammetry
NMC	lithium nickel manganese cobalt oxide (LiNiMnCoO <sub>2</sub> )
NMP	n-methylpyrrolidone
NMR	nuclear magnetic resonance
PAN	polyacrylonitrile
РС	propylene carbonate
PD.I.	polydispersity index
PEO	poly(ethylene oxide)
РРО	poly(propylene oxide)
РТМРМ	poly(2,2,6,6-tetramethylpiperidin-4-yl methacrylate)
PVDF	polyvinylidene difluoride
Rsf	surface resistance
SEI	solid electrolyte interphase
SEM	scanning electron microscopy
SOC	state of charge
SPE	solid polymer electrolyte

- SS stainless steel
- SSE Solid-state electrolyte
- TEM transmission electron microscopy
- TGA thermogravimetric analysis
- TMPM 2,2,6,6-Tetramethyl-4-piperidyl methacrylate
- VFT Vogel-Fulcher-Tammann
- XPS X-ray photoelectron spectroscopy
- XRD X-ray diffraction
- ZIF zeolitic imidazolate framework