"Polymer/Zinc Hybrid-Flow Battery Using Block Copolymer Micelles featuring a TEMPO Corona as Catholyte"

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The amount of electric energy, produced from renewable sources like wind power and solar radiation, increases globally every year.[1-3] Therefore, intelligent energy storage systems have to be developed. Interesting candidates for the storage of electric energy from renewable sources are redox-flow batteries (RFBs).[4-9] In contrast to “classical” batteries, the active material of RFBs does not form solid electrodes, but is dissolved in an electrolyte. Besides the all-vanadium RFB,[10-14] hybrid-flow batteries, which combine a zinc anode with a halogen cathode, have attained much attention, e.g., zinc-bromine and zinc-polyiodide batteries.[15-18] The special characteristic of a hybrid-flow battery is that at least one redox state of one active species is insoluble. Typically Zn^{2+} is reduced to Zn^{0} during the charging process forming a solid anode. Inherent of a halogen cathode is the toxicity of I_{2} and particularly of bromine, which are generated during battery cycling.\[17,19,20\] Expensive comple- xing agents are required to maintain the solubility of bromine and to increase the safety of halogen-based RFBs.\[20,21\] In recent years research on organic active materials experienced a significant upturn;\[5,22-26\] e.g., Zhao et al. reported a polyaniline-particle/zinc flow battery.\[27\] With the polymer-based redox-flow battery (pRFB), a new, metal-free concept was demonstrated recently. Organic polymers were used as redox-active materials in combination with a simple size exclusion membrane as separator.\[7\] The pRFB tries to reduce acquisition costs and the environmental impact of RFBs, by replacing toxic and expensive heavy metal salts, the critical sulfuric acid electrolyte, and also expensive Nafion membranes by more cost-efficient and less corrosive components. Both, the zinc-halogen and the pRFB system still have potential for further improvements. Combining the benefits of both systems by applying a 2,2,6,6-tetramethylpiperidinyl-N-oxyl (TEMPO) containing polymer as catholyte and a Zn^{2+}/Zn^{0} anode, together with an inexpensive size exclusion membrane, leads to a new type of a semi-organic hybrid-flow battery. TEMPO containing polymers show a lower toxicity compared with other ionic polymers (e.g., poly-L-lysine and poly(ethylene imine)) as well as vanadium salts.\[7\] Various zinc compounds, e.g., zinc chloride, -gluconate, and -oxide, are approved as nutrients and dietary supplements by the US Food and Drug Administration. Therefore, a better environmental sustainability of a TEMPO/zinc hybrid-flow battery against state-of-the-art RFB technologies is evident. Nishide and co-workers investigated TEMPO containing polymers, mainly with the focus as cathode-active material for semi- and all-organic thin-film batteries;\[28-30\] TEMPO containing catholytes for application in RFBs were previously investigated;\[31,33-35\] however, all of these systems suffered from considerable drawbacks. For instance they rely on lithium anodes strictly limited to organic solvents and anhydrous conditions. From an economic and ecological point of view lithium represents an unfavorable active material for RFB applications, due to its high price and serious safety issues. The requirement of strictly anhydrous and oxygen-free conditions results in low applicable current densities and high manufacturing efforts and costs.

With regard to the standard redox-potentials of the two redox couples, a TEMPO/zinc battery should exhibit a cell-potential of about 1.69 V.\[36,37\] Considering thermodynamics, such high voltages are not attainable in aqueous solution, as water electrolysis would initiate above 1.2 V. However, the application of a zinc-anode with a very high overpotential for hydrogen evolution expands the applicable potential window up to 2 V. An additional benefit is the robustness of the novel battery system. The presence of oxygen, commonly causing self-discharge, does not lead to any side reactions and, therefore, an elaborate inertization of the battery is not required.

The hybrid-flow battery consists of two half cells separated by a size-exclusion membrane derived from regenerated cellulose. The membrane is permeable for small ions like Zn^{2+}, chloride, and perchlorate, as well as the solvent (water), but retains the polymeric active material. The main advantages of this membrane are the high stability in many solvents as well as the low cost compared to state-of-the-art Nafion membranes. The catholyte contains a Zn^{2+}-salt as active species, which acts simultaneously as supporting electrolyte. The catholyte is basically the same solution as the anolyte, but comprises additionally the polymeric TEMPO cathode active material (Figure 1).
In this study, three types of different TEMPO copolymers were investigated (Table 1). Each polymer was designed in particular for either application in organic or aqueous media and was used as active material in a corresponding electrolyte solution (Table 2). Detailed description of the polymer synthesis and characterization can be found in the Supporting Information.

The catholytes can be divided into two groups: organic carbonate-based (A and B) and water-based (C and D) catholytes. Organic carbonates are widely used solvents in various battery applications, because of the good electrochemical stability and low vapor pressures. For this study a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC), and diethyl carbonate (DEC) was utilized showing a good ion conductivity compared with other carbonate-based electrolytes (Table S1, Supporting Information). Zn(ClO$_4$)$_2$·6H$_2$O served as supporting electrolyte and anode active material, respectively.

Water-based electrolytes reveal the highest ionic conductivity and are, therefore, used with preference (Table S1, Supporting Information). The group of aqueous catholytes employs P2 and P3. Zinc chloride was used as supporting electrolyte and anode active material. The chloride salt was selected because of its superior solubility and electrochemical stability compared to other zinc salts. To prevent the formation of zinc hydroxide, ammonium chloride was added. Solutions of P3 precipitated in zinc chloride solutions above 0.1 M, therefore, sodium chloride was utilized as main supporting electrolyte.

Cyclic voltammetry (CV) measurements of 0.1 M Zn(ClO$_4$)$_2$·6H$_2$O dissolved in a carbonate mixture (EC/DMC/DEC, v:v:v, 1:1:1) were performed to determine potentials of the Zn$^{2+}$/Zn$^0$ transition.

Table 1. Polymers used in this study.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_w$ [kg mol$^{-1}$]</th>
<th>PDI</th>
<th>Molar ratio (TEMPO:Comonomer)</th>
<th>Radical content$^f$ [mole fraction $x$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>70$^a$</td>
<td>1.3</td>
<td>3.5:1$^d$</td>
<td>0.77$^g$ (theoretical value 0.77)</td>
</tr>
<tr>
<td>P2</td>
<td>54$^a$</td>
<td>2.6</td>
<td>1:1$^d$</td>
<td>0.49$^g$ (theoretical value 0.5)</td>
</tr>
<tr>
<td>P3</td>
<td>37$^b$</td>
<td>2.4</td>
<td>1:1$^d$</td>
<td>0.28$^g$ (theoretical value 0.5)</td>
</tr>
</tbody>
</table>

$^a$SEC DMAc + 0.21 wt-% LiCl, poly(styrene) standard; $^b$Asymmetric flow field flow fractionation (AF4); comonomers: $^c$Poly(ethylene glycol) methacrylate $M_w = 450$ g mol$^{-1}$; $^d$Poly(ethylene glycol) methacrylate $M_w = 950$ g mol$^{-1}$; $^e$[2-(methacryloyloxy)ethyltrimethylammonium chloride; $^f$Calculated from EPR spin count (see Figure S4, Supporting Information, for EPR spectra).
redox couple. Zinc precipitation at potentials lower than −1.25 V versus AgNO₃/Ag and dissolution at potentials above −1.0 V versus AgNO₃/Ag were observed on a glassy carbon electrode (Figure 2a, dashed line). The special shape of the voltammogram is typical for zinc electrodeposition and illustrates a large peak split of 1.8 V. Likely, a limited ionic conductivity going along with finite diffusion of zinc cations in the carbonate electrolyte is the reason for the large peak split. As far as a battery application is concerned, this effect is disadvantageous as it decreases the cell potential. The cyclic voltammogram of P1 shows the quasi-reversible oxidation and reduction of the radical TEMPO moiety to the oxammonium cation (TEMPO⁺) at 0.4 V versus AgNO₃/Ag with a peak split of 120 mV in the previously investigated electrolyte (Figure 2a, solid line). Rotating disc electrode (RDE) measurements were performed to investigate the redox properties of P1. Levich-analysis reveals a diffusion-controlled behavior of P1 in zinc perchlorate solution and a diffusion coefficient of 1.65 × 10⁻⁷ cm² s⁻¹

Table 2. Polymeric catholytes used in this study

<table>
<thead>
<tr>
<th>Catholyte</th>
<th>Polymer</th>
<th>Solvent</th>
<th>Supporting electrolyte</th>
<th>Energy density [Wh L⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>P1</td>
<td>EC/DMC/DEC⁴</td>
<td>0.75 M Zn(ClO₄)₂ × 6H₂O</td>
<td>8.1</td>
</tr>
<tr>
<td>B</td>
<td>P1</td>
<td>EC/DMC/DEC⁴</td>
<td>0.5 M Zn(ClO₄)₂ × 6H₂O</td>
<td>1.2</td>
</tr>
<tr>
<td>C</td>
<td>P2</td>
<td>Water</td>
<td>1.0 M ZnCl₂, 1.0 M NH₄Cl</td>
<td>4.1</td>
</tr>
<tr>
<td>D</td>
<td>P3</td>
<td>Water</td>
<td>0.71 M NaCl, 0.08 M ZnCl₂, 0.08 M NH₄Cl</td>
<td>1.9</td>
</tr>
</tbody>
</table>

⁴Mixture (v:v:v 1:1:1); ⁵energy density as product of capacity and OCV at 50% SOC (carbonate-based electrolytes: 1.3 V, aqueous electrolyte: 1.7 V, see Figure S7 (Supporting Information) for OCVs depending on SOC).

Figure 2. a) Cyclic voltammogram of 0.1 M Zn(ClO₄)₂ × 6H₂O (dashed line) and 0.01 M P1 (solid line) in EC/DMC/DEC (v:v:v, 1:1:1), scan rate 50 mV s⁻¹, b) charging/discharging curve of a poly(TEMPO)/zinc hybrid-flow battery, catholyte: A 0.75 M Zn(ClO₄)₂ × 6H₂O EC/DMC/DEC (v:v:v, 1:1:1), 8 mL electrolyte per half-cell, 6.1 Ah L⁻¹, current density 1 mA cm⁻², flow rate 20 mL min⁻¹, c) long-term cycling of a static poly(TEMPO)/zinc hybrid-flow battery utilizing catholyte B with constant current of 1.4 mA cm⁻², cycles 2–501, after 500 cycles 81% of initial discharge capacity were retained, coulombic efficiency above 99.7%, and d) capacity, coulombic, voltage-, and energy efficiency depending on the current density, catholyte B with a capacity of 0.91 Ah L⁻¹, 8 mL electrolyte per half-cell, flow rate adjusted to 20 mL min⁻¹.
charging process, zinc-cations are reduced at the anode to Zn\textsuperscript{0} (s) and a transfer coefficient \(\alpha\) of 0.443, which is close to the value of an ideal reversible redox reaction of 0.5, were derived by Tafel analysis (Figure S3c,d, Supporting Information).

A hybrid-flow battery was setup by utilizing zinc-foil as anode, a 0.75 m \text{Zn(ClO$_4$)$_2$} × \text{H$_2$O} solution in EC/DMC/DEC (v:v:v, 1:1:1) as anolyte, and catholyte A with a capacity of 6.1 Ah L\textsuperscript{−1}. This configuration leads to a theoretical energy density of 8.1 Wh L\textsuperscript{−1}. Both half-cells were separated by a dialysis membrane (regenerated cellulose, molecular weight cut-off (MWCO) of 1,000 g mol\textsuperscript{−1}; see Figure S8b, Supporting Information, for a representative setup). A simple charging/discharging experiment (Figure 2b) illustrates reversible charging and discharging, but also shows a potential drop of 350 mV between the charging and discharging plateau. The cell resistance, determined by electrochemical impedance spectroscopy (EIS), was 27.3 \text{M}\Omega prior to charging. After 227 charging/discharging cycles a second EIS measurement revealed the formation of a semi-circle, which indicates a charge transfer resistance of 79 \text{M}\Omega and implies an evidence for the internal resistance drop (Figure S5b, Supporting Information). Also the kinetically restricted redox reaction of Zn(II)/Zn(0) in the carbonate-based electrolyte, determined prior via CV, and a low ionic conductivity of 6.9 mS cm\textsuperscript{−1} substantiate this observation. Continuous cycling of a static nonpumped battery with steady current (Figure 2c) revealed very slow capacity decay of only 0.04% per cycle and high coulombic efficiencies (>99.7%). Investigations of the battery performance at various current densities were conducted with catholyte B, with a capacity of 0.91 Ah L\textsuperscript{−1} (Figure 2d). Various current densities were applied and the charging/discharging capacity as well as the potentials of the corresponding plateau were determined. A material activity of 99% for current densities of 0.5 mAh cm\textsuperscript{−2} was reached. For higher current densities the discharge capacity drops to a plateau level of around 6 mAh (82% activity). Charging was possible up to 4 mAh cm\textsuperscript{−2}. The coulombic efficiency stayed always above 89% with a peak efficiency of 99% at a current density of 1.5 mAh cm\textsuperscript{−2}. A linear decline of the voltage efficiency was observed with increasing current densities. This behavior was probably caused by the restricted ion conductivity in the applied electrolytes and the consequential increasing potential gap between charging and discharging plateaus. Charging times for catholytes A and B are summarized in Tables S2 and S3 in the Supporting Information.

In conclusion, poly(TEMPO)/zinc hybrid-flow batteries based on organic carbonate electrolytes could be established successfully. Energy densities of up to 8.1 Wh L\textsuperscript{−1} were achieved with catholyte A, due to the high solubility of P1 in organic carbonates. In comparison, energy densities of water insensitive redox-flow batteries already reported in literature range from 5 to 16 Wh L\textsuperscript{−1}.\textsuperscript{[5,40]} Also, a good long-term stability with 300 consecutive charging/discharging cycles was obtained. In the charging process, zinc-cations are reduced at the anode to Zn\textsuperscript{0} and a deposit is formed on the electrode. The long-term cycling tests revealed the formation of dendrites (Figure S8a, Supporting Information), which can potentially limit the long-term stability. In order to prevent shortenings by dendrite growth through the pores of the membrane, additional space for the Zn\textsuperscript{0} deposit was established in the anode half-cell. Carbon paper is used to increase the surface area of the anode and allows the application of higher current densities. According to the limited ionic conductivity of organic electrolytes applicable current densities are limited to 4 mA cm\textsuperscript{−2}. Higher current densities can be applied in aqueous electrolytes.

Polymer P3 shows low solubility in concentrated solutions of various zinc salts, independent of the applied anion (chloride, perchlorate, sulfate, and nitrate). Therefore, the amount of zinc chloride was reduced to a twofold molar excess related to TEMPO units and sodium chloride was employed as essential supporting electrolyte. Ammonium chloride was added to suppress the formation of zinc hydroxide during battery cycling.\textsuperscript{[30]} CV analysis revealed an improved behavior of the Zn\textsuperscript{2+}/Zn\textsuperscript{0} redox couple in water-based electrolytes compared to organic carbonates (Figure 3a). The peak separation of the redox couple is reduced to 0.53 V at a scan rate of 50 mV s\textsuperscript{−1}. Determination of the diffusion coefficient for P3 by RDE analysis was not possible, due to a nonlinear curve in the Levich-plot (see Figure S3a,b, Supporting Information, for voltammograms and Levich-plot).\textsuperscript{[41]}

A water-based hybrid-flow battery with catholyte D showed an excellent battery cycling. Well-defined flat charging/discharging plateaus with a narrow potential drop were achieved. Current densities up to 12 mA cm\textsuperscript{−2} could be applied and, thus, increased by factor three compared to organic electrolytes. Varying the current density did not have a significant effect on the capacity (Figure 3d). The discharging capacity maintained stable for current densities between 1 and 10 mA cm\textsuperscript{−2}. Starting from 12 mA cm\textsuperscript{−2}, a decrease in capacity was observed. Catholyte D showed 73% of the theoretical discharging capacity. The coulombic efficiency remained always above 90% with a maximum of 99% at 12 mA cm\textsuperscript{−2}; the energy efficiency never dropped below 80%. Charging times for different current densities are summarized in Table S5 in the Supporting Information. The improved battery performance is caused by the accelerated reaction of the zinc redox couple in aqueous media and by a substantially reduced cell resistance of 1.35 \text{M}\Omega (see Figure S5a, Supporting Information, for impedance spectrum). A long-term cycling test revealed good stability (Figure 3c). After 1,000 consecutive charging/discharging cycles 78.6% of initial discharging capacity was retained, which indicates a stable redox behavior of the active species. Water electrolysis or the formation of gaseous chlorine did not occur.

A precipitation of P2 in zinc chloride solutions could not be observed up to salt concentrations of 1 \text{M}. Thus, zinc chloride could be used as supporting electrolyte without the additional usage of sodium chloride. As noted before, the addition of ammonium chloride improved the cycling stability due to the suppression of zinc hydroxide formation. Higher concentrations of P2 could be achieved in water compared to P3, so that a capacity of 2.39 Ah L\textsuperscript{−1} was reached with catholyte C. Current densities of up to 20 mA cm\textsuperscript{−2} were applicable; however, going along with a significantly reduced capacity (Figure S6c, Supporting Information). Charging times depending on the applied current density are summarized in Table S4 in the Supporting Information. In general, a linear decrease of the capacity was observed with increasing current density. This is induced
by a limited mass transport to the electrode and leads to an increasing overpotential. Nevertheless, the system benefits significantly from the increased Zn\(^{2+}\) concentration in catholyte C compared to catholyte D, as the applicable current density was nearly doubled. A maximum material activity of 87.6% was reached at 2 mA cm\(^{-2}\), which also is a significant improvement compared to catholyte C. The coulombic efficiency was not affected by the decreasing behavior of the capacity and stayed mostly above 90%. Charging/discharging curves, long-term stability test, cycling of a static cell, catholyte D, and d) electrical performance: capacity, coulombic-, voltage-, and energy efficiency depending on the applied current density.

Figure 1. a) Cyclic voltammogram of an aqueous 0.1 M zinc chloride 0.01 M P3 solution. Scan rate 50 mV s\(^{-1}\), b) exemplary charging/discharging curves at a current density of 2 mA cm\(^{-2}\), aqueous catholyte D: P3 solution in NaCl, ZnCl\(_2\), NH\(_4\)Cl with a capacity of 1.1 Ah L\(^{-1}\), flow rate 20 mL min\(^{-1}\), c) long-term stability test, cycling of a static cell, catholyte D, and d) electrical performance: capacity, coulombic-, voltage-, and energy efficiency depending on the applied current density.

In reference to the investigated hybrid-flow batteries utilizing carbonate-based electrolytes, the electrical performance could be increased by the use of an aqueous electrolyte. Thus, the environmental impact could be reduced as well. Despite of the high cut-off voltage of 2 V, no water electrolysis could be detected and stable battery cycling was performed. Particular worth mentioning is the difference between the two open circuit voltage (OCV) curves (Figure S7a,b, Supporting Information). In the aqueous system an OCV of 1.7 V at 50% state of charge (SOC) was observed, in contrast to the organic system, where an OCV of 1.3 V at 50% SOC was reached.

A novel type of zinc hybrid-flow battery was successfully implemented. The application of several TEMPO-containing polymers, as active cathode material, leads to significant improvements concerning corrosion and environmental impact compared to already known zinc-halogen hybrid-flow batteries. The different applied catholytes comprised P(TEMPO-co-PEGMA)s, synthesized via RAFT polymerization and P(TEMPO-co-METAC), which was designed particularly for aqueous solutions. To the best of our knowledge, it is the first reported type of flow battery, which enables a stable potential window of up to 2 V in aqueous media, without utilization of toxic and expensive heavy metals. Furthermore, a contamination with oxygen is unproblematic rendering the expensive inertization of the battery unnecessary. In carbonate-based electrolytes, high-energy densities of 8.1 Wh L\(^{-1}\) were achieved, while water-based electrolytes allow application of higher current densities of up to 20 mA cm\(^{-2}\), as well as a stable energy efficiency of over 80%. Furthermore, water-based TEMPO/zinc HFBs feature an elevated OCV of 1.7 V compared to organic-based ones with an OCV of 1.3 V. Both systems showed very good
long-term stability of 500 and 1,000 consecutive charging and discharging cycles, respectively. When comparing the investigated TEMPO-copolymers with one another, p(TEMPO-co-PEGMA)s are the copolymers of choice for poly(TEMPO)/zinc hybrid-flow batteries. The reported poly(TEMPO)/zinc HFB features high applicable current densities, compared to previously reported TEMPO containing RFBs, low acquisition costs and, in general, to low intrinsic hazards. This enables the suitability as energy storage system in large scales.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements
The authors acknowledge the European Regional Development Fund (EFRE), the Thüringer Aufbaubank (TAB), the Thuringian Ministry for Economic Affairs, Science and Digital Society (TMWWdG), and the Fonds der Chemischen Industrie (FCI), as well as the support from JenaBatteries GmbH. G.H. is grateful to FRIA for financial support. J.-F.G. acknowledges the CIB for support in the frame of the ARC 14/19-057 BATTAB.

Received: October 11, 2015
Revised: December 5, 2015
Published online: