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Ternary salt – solvent electrolytes for 5 V-class anode-less Li-metal batteries

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Abstract. The 'anode-less' lithium-metal battery stands out due to the lowest electrochemical reduction potential of lithium, highest capacity, and lightweight nature, making it an optimal choice for constructing rechargeable metal batteries. We explored a distinctive ternary salts-solvents electrolyte formulation to demonstrate an 'anode-less' 5 V Li-metal battery. Salt and solvent components were fine-tuned to synergistically alleviate aluminum dissolution and extend the oxidative stability up to 5.2 V (vs. Li/Li⁺) with the Li-metal interface stabilization. In a 5 V-class cobalt-free LiNi_{0.5}Mn_{1.5}O₄ – Li 'anode-less' cell, we attained 65 cycles within 20% capacity loss by keeping 40% Li-reservoir, touted as a potential next-generation battery design. The dynamical behavior of lithium metal interfaces with cycling has been analyzed through a series of surface and bulk analysis techniques. We correlate the influence of salt formulation with the composition in the negative electrode and show that the LiF-dense interface is the main cause of long cycle life.

Despite the significant advancements in various energy storage systems over the past few decades, current technologies fall short of meeting the demanding requirement for high energy density, specifically aiming for the elusive 500 Wh kg⁻¹ or 1000 Wh L⁻¹ storage metrics.¹ State-of-the-art batteries operate on the principle of storing Li-ion on the negative electrode, typically composed of graphite, but their limited intrinsic capacity constrains these.² However, a departure from the conventional battery-making approach — one that involves eliminating graphite — could revolutionize the fundamental working principle and enhance the energy density. In this scenario, metallic lithium would be electrochemically deposited instead of remaining as intercalated Li-ion. While this opens the possibility of significantly boosting the total energy density and reducing manufacturing costs, a major concern arises regarding the stability of the deposited lithium.³ This concern is rooted in its thermodynamic instability or high reactivity to most organic liquid electrolytes and salt anions. For instance, the widely used electrolyte of 1 M LiPF₆ (M = moles/liter) in ethylene carbonate (EC): dimethyl carbonate (DMC) (1:1 v:v) or LP30 operates efficiently in Li-ion batteries with graphite anodes over 2000 cycles but fails within less than 20 cycles in a zero-excess Li-metal cell.⁴ A cell with excess lithium metal or graphite as a negative electrode can yield more cycles versus an "anode-less" configuration. Yet, due to the relatively high cost of lithium metal, and safety requirements when handling it, the cost and energy density of a lightweight "anode-less" cell would be much more interesting for commercialization. Parallelly, effective lithium passivation approaches are highly intriguing, and achievable only by availing suitable electrolytes. Additional consideration must be given to the anodic stability required by state-of-the-art positive electrode materials. Given the high price of solving the challenges, considerable efforts have been dedicated to electrolyte development in recent years.⁵

The excitement surrounding the "anode-less" cell design began with the initial report in 2016 by Qian et al., who utilized a 4 M lithium bis(fluorosulfonyl)imide (LiFSI) electrolyte in monoglyme (DME) within a 3.5 V (vs. Li/Li⁺) lithium iron phosphate (LFP) based anode-less cell (LFP|Cu). Recently Fan *et al.* have demonstrated 10 M LiFSI in carbonate solvent to gain 99.2% coulombic efficiency with lithium metal albeit with its impracticality.⁶ Usually, high salt concentration can lead to more coordinated solvents rather than keeping them as free solvents and increasing the number density (or chemical potential) of anion to build up inorganic solid electrolyte interphase (SEI). The free solvent is often reduced cathodically to give poor lithium passivation and hence, low coulombic efficiency. A significant number of cycles are achieved as reported as 60 cycles within 50% retention for 1.6 mAh cm⁻² capacity.⁷ Subsequently, a variety of electrolyte formulations with LiFSI/TFSI salt in ether-based solvents have been

investigated notably with additives like lithium nitrate (LiNO₃), chemically modified etherderived solvents, addition of sacrificial agent in the positive electrode, etc.⁸ It has been shown that such salt/solvent can passivate Li-metal and reach practically high coulombic efficiencies (>99%). However, ether solvents have limited anodic stability around 4 V vs. Li/Li⁺, hampering their integration with higher voltage cathode materials (>4.5 V).⁹ In 2019, Dahn's group put forward the concept with 4.5 V lithium nickel cobalt oxide (NMC111) in the presence of 0.2 M lithium tetrafluoroborate (LiBF₄) – 1.0 M lithium difluoro(oxalato)borate (LiDFOB) mixed dual salt in a carbonate solvent.¹⁰ The versatility was demonstrated over 90 cycles with 80% capacity retention when operated at a temperature of 40 °C in the presence of Li-reservoir, further improved under constant stack pressure on the cell. Despite these promising results, there are merely any attempts with LiTFSI/FSI salt using carbonate solvent beyond 4.5 V. However high energy gain is possible only using high voltage positive electrode chemistries, such as 5 V generation-LNMO.¹¹ A 5 V positive material is seen as a highly promising in the industry due to their high energy density, and potentially low cost (driven by the abundance of manganese instead of nickel and cobalt) but their potential remains commercially untapped due to the lack of electrolytes operating at this voltage. To put into perspective, one can estimate the theoretical capacity of an LNMO|Cu "anode-less" commercial pouch cell to easily surpass the 355 Wh kg⁻¹ mark in energy density, in comparison to an NMC811|graphite (the most performing of today's mass-market chemistries) of similar architecture and calculated with the same methodology reaching ~236 Wh kg⁻¹, around more than 50% increase without further cell design optimization.12

In this work, we fine-tune the ratio of a ternary salt electrolyte based on LiTFSI, LiDFOB, and LiPF₆, at a total salt concentration of 1.2 M in mixed carbonate solvents (fluoroethylene carbonate – FEC / ethyl methyl carbonate – EMC, 1:9 v:v) to overcome the challenges mentioned above. The design principle of the ternary salt electrolyte relies on the following rationale: the onset for Al corrosion in single salt LiTFSI (1.2 M) is around 4 V vs. Li/Li⁺ in carbonate solvent, prohibiting the implementation in a 5 V-cell.¹³ In addition, this composition also displays poor lithium plating/stripping stability on copper (as noted in this work, see next). With LiDFOB as a secondary constituent, the Al-metal corrosion is effectively eliminated through the formation of a passivation layer on the aluminum surface.¹⁴ The dual LiTFSI - LiDFOB system however remains anodically unstable when operated at 5 V, given fast consumption of LiDFOB at elevated potentials, with the remaining LiTFSI composition not being able to passivate lithium metal, like in single salt LiTFSI constituent formulation. The addition of LiPF₆ leads to improved anodic stability of up to 5.2 V, significative enrichment of

the SEI with lithium fluoride (LiF), and fewer organic compounds. The best performance in zero-excess Li-metal cell with 5 V-class LNMO positive electrode is attained with an optimized and balanced composition of 0.5 M LiTFSI, 0.5 M LiDFOB and 0.2 M LiPF₆ in FEC/EMC (1:9 v:v) carbonate solvent (denoted hereafter as HVE552) which yielded to a 50% capacity retention within 60 cycles with 0.3 mA cm⁻² current density and 1.5 mAh cm⁻² nominal capacity. By limiting the active material capacity utilization, the cycling lifetime is extended to 65 cycles with 80% capacity retention at a higher current density of 0.5 mA cm⁻². Owing to this improvement, the practical application of a better battery can be realized by its hitherto stable cycling performance at 5 V.¹⁵

Lithium metal stabilization in carbonate solvent, and parallelly ensuring oxidation stability (>5 V vs. Li/Li⁺) of an electrolyte is a pragmatic way to successfully advance high voltage Li-metal battery. Usually, glyme-based electrolyte with LiTFSI/FSI have been investigated due to their interfacial stability with lithium metal.¹⁶ Unfortunately, glymes are not anodically stable above 4 V (vs. Li/Li⁺), and hence, carbonates are preferred solvents for highvoltage electrolyte formulations (>4 V vs. Li/Li⁺).¹⁷ In addition, LiTFSI salt induces aluminum dissolution above 4 V (vs. Li /Li⁺) in carbonate solvent.¹⁸ Hence, single salt LiTFSI (1.2 M concentration) in carbonate solvent (FEC/EMC, 1:9 v:v) prevents practical battery application. Furthermore, it exacerbates the lithium metal-electrolyte interface. At best, a high concentration (>2 M) of LiTFSI salt in glyme solvent is shown to passivate the lithium surface.¹⁹ Introducing second salt LiDFOB with equimolar of LiTFSI, hereafter noted as HVE660, one can passivate the aluminum surface, protecting it from Al-corrosion. It was reported earlier that LiDFOB acts as a corrosion inhibitor by decomposing below 4.5 V (vs. Li /Li⁺) as well as it can be reduced on negative electrode surfaces like graphite to form a stable solid electrolyte interface (SEI).^{20,} ²¹ The reduction potential of LiDFOB salt is observed earlier compared to other (LiTFSI, LiPF₆) and there is no preferential effect from the anion diffusion (Fig. S3, Supplementary Table T1).²² Certainly, dual salt combination gets rid of Al-dissolution, faster diminution of LiDFOB occurs when operated at 5 V.²¹ Unquestionably, it highlights the requisite of a third salt to acquire a longer stability of the electrolyte. Accompanying the third salt LiPF₆ (HVE552), one can not only extend the electrolyte oxidation stability but also stabilize lithium metal effectively by yielding a metal-fluoride shielding layer.²³ Complex interplay of anions in blended ternary salts in carbonate solvents makes lithium metal stabilization more feasible, augments aluminum passivation, and provides prolonged cycle life.²⁴ The design principle is depicted in Figure 1a. The details of the molecular effect with three salts and solvents are described in the supplementary information (Fig. S4 and S5). Lithium cation coordinates mostly with carbonyl

groups. For better reproducibility of the HVE552 electrolyte, the water level is measured below 10 ppm via KF-titration (Fig. S6).

The experimental verification of oxidation stability and metal passivation has been demonstrated by electrochemically polarizing aluminum electrode with respect to lithium metal electrode, conducting scanning electron microscopy (SEM) analysis of aluminum surface, and directly observing lithium metal plating/stripping on the copper current collector. The electrolyte oxidation onset potential is estimated by measuring anodic current density while sweeping the potential of the aluminum electrode linearly up to 6.5 V. We performed two scans while allowing a resting period of 12 hours or under conditions where the rate of change of open-circuit potential (OCP) was less than 1 mV h⁻¹ (d(OCP)/dt < 1 mV h⁻¹). In the first scan, the native aluminum oxide layer can either be broken, leading to continuous dissolution, or it can be passivated depending on the composition of the electrolyte. During the relaxation period, the system reaches an equilibrium potential, which depends on the surface state after the initial scan. The second scan provides insight into whether effective passivation occurs. The detailed information on the second scan is available in the supporting documentation (Fig. S7).

The single salt electrolyte formulation with LiTFSI (1.2 M) in carbonate solvent (FEC: EMC, 1:9 v:v) displays an anodic onset around 4.5 V during the initial scan (Fig. 1b). However, during the subsequent scan, aluminum dissolution was observed around 4 V (Fig. S7), indicating its highly corrosive nature and its unsuitability for a 5 V-cell. A dual salt solution comprising 0.6 M LiTFSI and 0.6 M LiDFOB (HVE660) is found to suppress aluminum dissolution above 4.5 V, however the electrolyte decomposition is noted at 5 V. Nevertheless, it demonstrates the capability to passivate the aluminum interface during the subsequent scan, with minimal anodic current observed at 5 V, unlike the single salt LiTFSI (Fig. S7). Assimilating LiPF₆ into the HVE XYZ formulation as HVE552 extends the anodic stability up to 5.2 V, further suppressing corrosion in the successive scan (Fig S7). Following two consecutive scans, the aluminum electrode is examined via scanning electron microscopy (SEM) to observe the corrosion effect on the aluminum metal surface. Profound pit-corrosion is evident on a micro-scale when using a single salt LiTFSI (1.2 M), as depicted in Fig. 1d. SEM surface analyses of polarized aluminum electrodes with LiTFSI salt align with LSV findings, revealing patches of significant pitting due to inadequate passivation. Conversely, in the case of the dual (HVE660) or ternary compositions (HVE552), there is minimal evidence of such pit corrosion (Fig. 1d). The presence of rolling lines in pristine aluminum foil, evident during industrial metal processing, remains undistorted in the case of HVE660 and HVE552 electrolytes, indicating efficient passivation of aluminum.

Following anodic stability confirmation, lithium metal stabilization during deposition/dissolution is assessed through coulombic efficiency measurements on a copper working electrode devoid of lithium (Cu|Li cell). In the case of single salt LiTFSI, unstable cycling performance with a sluggish activation process is observed (Fig. 1c), leading to cell failure within 40 cycles. Upon the addition of LiDFOB, (HVE660) the cycling performance of Cu|Li improves significantly to 65 cycles. Further enhancement in cycling stability is achieved with HVE552, extending the cycle life to approximately 88 cycles. The first cycle coulombic efficiency (CE) of HVE552 is approximately 96.8%, reaching an average CE of 98.2% over 88 cycles, comparable to the highest reported CE of liquefied gas electrolyte, which exhibits an initial CE of 93.6% and reaches 98.6% within the first 100 cycles.²⁵ To accurately assess CE on the bare copper metal electrode, the Aurbach method is applied, revealing a CE of 97.2% for HVE660 and 97.9% for HVE552, indicative of improved lithium passivation and enhanced cycling stability (Fig. S8).^{26, 27}



Figure 1. (a) Strategy to develop the high voltage electrolyte (HVE) using LiTFSI-corrosive salt in carbonate solvents for 5 V-class cell application. (b) Aluminum corrosion analysis using

LiTFSI, dual 0.6M LiTFSI + 0.6 M LiDFOB (HVE660), and ternary salt composition 0.5 M LiTFSI+ 0.5 M LiDFOB+ 0.2 M LiPF₆ (HVE552). Single salt LiTFSI is highly corrosive while addition of LiDFOB (HVE660) helps to protect it but decomposes around 5 V. HVE552 electrolyte comes out as anodically stable up to 5.2 V. The scan range is OCP to 6.5 V (vs Li/Li⁺). (c) Cu - Li half-cell, cycling at current density 0.3 mA cm⁻². The plating capacity is 1.5 mAh cm⁻², and the stripping potential is 1 V (vs Li/Li⁺). HVE552 electrolyte shows stable lithium plating/stripping compared to LiTFSI and HVE660. (d) Observation of aluminium surface through scanning electron microscopy (SEM) after 2nd LSV-scan. The electrolyte composition is mentioned in the inset. Pit corrosion is noted for HVE660 and HVE552 formulations.

With the observed benefits of higher anodic stability and improved coulombic efficiency of the Li metal plating/stripping process, the HVE552 electrolyte is explored for the implementation of anode-less full-cells with 5 V-class cathodes (LNMO|Cu).²⁸ However, it is essential to acknowledge that such cells, lacking a lithium source, will inevitably experience discharge capacity loss compared to conventional half-cells with a huge Li excess. This loss is attributed to the consumption of active lithium during the solid electrolyte interface (SEI) and cathode electrolyte interphase (CEI) formation in each cycle. With the baseline electrolyte of LiTFSI salt in FEC/EMC, stable cycling is unattainable, leading to immediate failure due to the combined effects of aluminum corrosion and inefficient lithium plating/stripping on copper (Figure 1b, 1c, Fig. S7 and S8). Conversely, mixing LiDFOB with LiTFSI in equal molar ratios (HVE660) enabled up to 50 cycles in anode-less cells, albeit with sudden fading thereafter. Additionally, half-cells utilizing lithium metal with HVE660 (or HVE550) result in abrupt failure within a limited cycle count, typically around 30 cycles (Fig. S9). Interestingly, irrespective of the lithium source on the negative electrode, HVE660 consistently leads to sudden failure, underscoring the need for a third salt to enhance cycling stability. A single salt LiPF₆ (1.2 M) fails to provide stable cycling, despite its non-corrosive nature towards aluminum as also observed earlier.²¹ The inadequacy is attributed to insufficient passivation of lithium metal (Fig. S10).

The addition of 0.2 M LiPF₆ i.e. HVE552 is found to significantly improve the cycling stability, yielding more than 100 cycles with over 95% capacity retention in half-cells (Fig. S9) and nearly 60 cycles with approximately 50% capacity in anode-less cells with a nominal charge capacity of around 1.5 mAh cm⁻² at C/5 (\sim 0.3 mA cm⁻²) as this current density is matching in

Cu|Li cell (Fig. S11) with low coulombic inefficiency. Various symmetric and asymmetric discharge current modes have been tested, with C/5-symmetric cycling yielding the best results, showing current density comparable to the Cu|Li system with a lower coulombic inefficiency (Figs. S12-S14).²⁹ It's noteworthy that the commercial electrolyte LP30, which exhibits excellent cycling stability in common Li-ion cells, fails drastically within 20 cycles in an anodeless configuration (Figs. S15 and S16). These inferior performances stem from inefficient passivation due to the EC solvent and the inadequacy of single salt LiPF₆ to passivate lithium metal, as observed here (Fig. S17). Also, LiFSI in the HVE_XYZ formulation does not improve the cycling performance but rather corrodes the aluminium current collector (Fig. S18). Finally, the HVE552 formulation outperforms individual single-salt and dual-salt combinations.²⁷ The ionic conductivity of HVE552 also ranges within the typical battery electrolytes with 2.4 mS cm⁻¹ (Fig. S19). It is noteworthy to highlight that the HVE552 formulation here reported shows better cycling stability compared to the recently developed formulation of 1.0 M LiDFOB + 0.2 M LiBF₄ in FEC/DEC as given in the supporting information (Fig. S20).

To further elucidate the rationale behind the use of such a salt combination in HVE552, several tests have been conducted with different concentrations of LiPF₆ salt, while maintaining a total salt concentration of 1.2 M. Low LiPF₆ concentration (0.02 M), or higher concentration (0.4 M, HVE444) consistently result in poor performance, with the cell failure within 50 to 80 cycles, respectively (Fig. 2b). This suggests that low salt concentration fails to provide uniform or homogeneous passivation, while high concentration formulation predominantly behaves as single-salt LiPF₆ after a certain number of cycles, leading to failure, as depicted in Figure 2a. Throughout cycling, irreversible products accumulate on the negative electrode, potentially leading to their gradual growth over time and impacting ionic conduction or electronic resistivity.

The electrolytes are also analyzed in a 3-electrode (3E) cell configuration to monitor the rise of negative electrode oxidation potential over various discharge timescales (Fig. 2c). The top-performing electrolyte, HVE552, exhibits a negative electrode oxidation potential of around 1 V during the final discharge, achieving 92% CE in the first cycle.²⁵ In contrast, the electrolyte containing single salt LiPF₆ failed immediately after 5 cycles, with an oxidizing potential of nearly 1.6 V vs. Li/Li⁺ (Fig. 2d). Conversely, in HVE660, the oxidation potential rises from approximately 1 V to 1.6 V after 10 cycles, while for HVE552, this occurs after 20 cycles. HVE552 delays the rise of the oxidation potential despite containing LiPF₆ salt. Furthermore, the effect of different discharge potentials is investigated at 3.0 V and 4.4 V (Fig. S21). When the discharge cut-off potential is set to 4.4 V in full cells, the rise of the oxidation

potential is dramatically suppressed, remaining below 0.2 V vs. Li/Li⁺ (Fig. S21). This observation is crucial for the development of high-voltage anode-less batteries, where the electrochemical stability of the negative electrode is paramount. The increase of the final oxidation potential of the negative electrode follows an approximately parabolic nature in the case of 4.4 V discharge, unlike the growth observed during harsh conditions of 3.0 V discharge.³⁰ Porous lithium metal deposition is observed while the cell is discharged to 4.4 V (Fig. S22). Cells subjected to 3.0 V discharge are collected after 3E measurements to investigate surface compositions.



Figure 2. (a) Cycling stability of LNMO|Cu anode-less cells with studied electrolyte formulations. The nominal charge capacity of the electrode is 1.5 mAh cm⁻² and cycling is performed at a rate of C/5, symmetric condition between 4.9 V to 3.0 V. The first two formation cycles consisted of two charge-discharge cycles at a rate of C/10. (b) The effect of LiPF₆ amount in HVE_XYZ formulation with similar experimental conditions in LNMO|Cu cell. (c) Three-electrode (3E) measurement with HVE552; 1st cycle CE is around 92%. 13 mm positive electrode has active mass loading of 11 mg cm⁻². The cell is cycled between 4.9 V to 3.0 V at a C/5 rate. (d) The evolution of negative electrode final oxidation potential after discharge is followed with LiPF₆-single salt, HVE660, and HVE552; Discharge and charge potential are 3.0 V and 4.9 V respectively for the full cell at C/5.

Irreversible surface compounds on negative electrodes are analyzed through ToF-SIMS and results illustrated in Figure 3(a-g).³¹ The composition contains organic and inorganic fragments along with dead Li. The samples are investigated with different discharge cycles such as 5 cycles for LiPF₆ (1.2 M), 5 cycles and 50 cycles for HVE660, 5 cycles, 50 cycles, and 100 cycles for HVE552. The acronym of the corresponding samples is named e.g. HVE552-5cyc, HVE552-50cyc, HVE552-100cyc for HVE552 electrolyte-based cells, respectively. A similar abbreviation is applied for other samples. We have recorded the fractional intensity of Li⁻ ion to correlate the creation of dead lithium over depth and discharge cycles.³² A significant amount of Li⁻ ion is detected for LiPF₆ single salt, and it increases with depth. This implies the formation of a large amount of irreversible metallic lithium during the beginning of cycles and the morphology appears highly inhomogeneous and needle-like structures compared to HVE660 and HVE552 electrolytes (Fig.S23). Conversely, HVE552 produces very negligible Li⁻ content compared to LiPF₆ and dual salt HVE660. This indicates that the ternary salt formulation provides highly reversible lithium deposition and dissolution, less dead lithium which is potentially associated with the lack of improper passivation. The presence of organic compounds is traced with the C⁻ ion profile. In the case of single salt LiPF₆, the C⁻ intensity rises at the proximity of the outer surface. Thus, one can assume that solvent reduction occurs during the failure of LiPF₆-electrolyte due to the non-availability of reversible lithium and insufficient passivation. Similarly, C⁻ ions are identified with equal fractions in the case of HVE660-5cyc. This can be regarded as the reduction of either the organic solvent or the organic part of LiDFOB/LiTFSI salts. Unlike LiPF₆, the C⁻ ion intensity of HVE660-50cyc decreases during cell failure, which can be attributed to a shortage of salts or solvents in the electrolyte. Throughout cycling, HVE552 exhibits a lower fraction of C⁻ ions, mostly due to thin organic layer formation or less solvents/salts decomposition.

In addition to the observation of dead lithium and organic compounds, we have also focused on inorganic components. One of the major components studied is LiF_2^- ion, attributed to the presence of fluorine-containing salts/solvents (Fig. S24). Notably, single salt LiPF₆-5cyc, HVE660 after 5 cycles and 50 cycles each exhibit a very low amount of LiF₂⁻ on the surface compared to HVE552-5cyc. The intensity of LiF₂⁻ is found to increase with cycling for HVE552-electrolyte, resulting in a LiF-rich composition. Other essential components such as BO₂⁻ and LiS⁻, solely indicate the decomposition of LiDFOB and LiTFSI salts respectively. These salts are prominently present in HVE660 and HVE552 electrolytes (Fig. S25 and S26). A high amount of BO₂⁻ ion is observed during the initial cycling of HVE660-5cyc due to the

decomposition of LiDFOB (Fig. S3, Supplementary Table T1). However, it sharply decreases on the outermost surface by the end of 50 cycles, indicating the depletion of LiDFOB salt in the HVE660 electrolyte. Alongside the BO₂⁻ ion, LiS⁻ is also investigated, primarily related to LiTFSI degradation. With cycling, the LiS⁻ ion appears to increase for HVE660-50cyc, and it rises abruptly on the outer surface. This can be attributed to the unavailability of LiDFOB, as indicated by the BO2⁻ profile, and the decomposition of the remaining LiTFSI salt in the HVE660 electrolyte. The consumption of LiTFSI leads to sulfurous compounds such as Li_nStype, as observed in XPS measurements (Fig. S26).³¹ Indeed, after 50 cycles with HVE552 electrolyte, a significant amount of BO₂⁻ is present. Eventually, it completely diminishes on the surface after 100 cycles. In the case of HVE552, initially, the LiS⁻ ion intensity increases with cycling from 5 cycles to 50 cycles, while a decrease is noted afterward. Unlike HVE660, it coexists more with a LiF-containing interface rather than LinS-containing moieties due to the presence of LiPF₆. Moreover, it results in the formation of oxygenated sulfur (SO_x -species) due to sulfur oxidation rather than lithium sulfide (LinS) complexes. This is evident from the intensity of S 2P_{3/2} in the XPS data around 168 eV (Fig. S26). Overall, the evolution of the interface has been depicted for various electrolytes in Figure 3g, summarized as follows. Upon examining the single salt 1.2 M LiPF₆ in FEC/EMC, it is evident that the electrode completely failed within 5 cycles. ToF-SIMS analysis reveals a composition characterized by dead lithium, organic moieties, and notably lacking LiF element. In contrast, the dual salt HVE660 shows initial coverage with boron-based compounds like BO2⁻, along with trace amounts of organic components and isolated lithium after 5 cycles. By 50 cycles, HVE660 exhibits failure, with the surface now covered in lithium sulfide (e.g., LiS⁻) based compounds, small quantities of SO₃⁻ elements, organic molecules, and dead lithium. The failure of HVE660 can be attributed to the deposition of sulfurous compounds on the negative electrode, potentially blocking ion and electron transport. In contrast, the HVE552 electrolyte results in a negative electrode composition of LiF2⁻, BO2⁻, and SO3⁻ components, with minimal dead lithium and organic compounds after initial cycling. Over subsequent cycles, the electrode evolves to include LiF₂, BO₂⁻, and LiS⁻ after 50 cycles, and ultimately becomes enriched with LiF₂⁻ after 100 cycles. Thus, the negative electrode cycled in HVE552 electrolyte enriches with LiF and sulfurous oxide $(L_xS_yO_z)$ compounds, with negligible organic moieties and dead lithium.



Figure 3. ToF-SIMS depth-profile measurement of the negative electrode after final discharge in 3E measurement at 3.0 V and C/5 rate. The corresponding species have been analyzed: (a) Li^{-} (b) C⁻ (c) LiF_2^{-} (d) BO₂⁻ (e) LiS^{-} (f) SO₃⁻. (g) Schematic representation based on the summary of compositional analysis using ToF SIMS profile of the negative electrode cycled with different electrolytes and discharge time between 4.9 V to 3.0 V in full cell at C/5 rate. Electrolyte with LiPF₆ (after 5 cycles) shows more dead lithium and organic compounds. HVE660 is initially composed of BO₂⁻ (after 5 cycles) and later LiS⁻ deposition occurs (after 50 cycles). Whereas in the case of HVE552 containing cell, the electrode is full of BO₂⁻ at the beginning and later it is enriched with LiF₂⁻. (h) Quantification of salts using NMR for HVE660 and HVE552 electrolytes. The pouch cells (2.5 mAh cm⁻² cap. electrode) are given 1, 5, and 20 cycles at C/5 with two initial formation cycles at C/10 between 4.9 V to 3.0 V and electrolytes are extracted after final discharge from the pouch bag using D₆-DMSO solvent.

Further, the salt depletion upon cycling is studied using nuclear magnetic resonance (NMR) at different cycling extents of cells using HVE552/HVE660 electrolytes (Figure 3h).¹⁰ Major observation is that LiDFOB is consumed much faster than LiTFSI, and LiPF₆, with these

remaining in the electrolyte in a significant concentration after cycling. Thus, in the case of LiPF₆ single-salt in FEC/EMC, the failure is not due to electrolyte/salt depletion, but it can be regarded as improper passivation of deposited lithium on copper, as evidenced in inhomogeneous-fibrous morphology and dead-lithium formation.³³ In HVE660, the consumption rate of LiDFOB salt surpasses that of LiTFSI salt, and after extensive cycling, only LiTFSI remains in the electrolyte and actively participates in the cycling process. Furthermore, using single-salt LiTFSI in carbonate solvent has previously been shown to result in inefficient lithium plating/stripping (Figure 1d). Therefore, after the consumption of LiDFOB salt in HVE660, LiTFSI salt remains but fails to provide stable cycling performance. Eventually, sulfurous species like LinS (likely Li2S) are detected, stemming from the decomposition of LiTFSI. It is well known that Li₂S is both ionically and electrically insulating, simultaneously hindering the realization of Li-S batteries.³⁴ Ultimately, both salts in HVE660 are completely utilized, leading to cell failure due to salt exhaustion. On the other hand, in HVE552, although LiDFOB is initially consumed, LiTFSI and LiPF₆ remain in the electrolyte, ensuring stable cycling over an extended period. This results in a lithium fluoride (LiF)-rich surface, unlike HVE660, which lacks LiPF₆. It is well understood that pure alkali halides, such as LiF, develop Schottky defects during their growth under ambient conditions, facilitating ionic transport while maintaining electrical insulation.^{30, 35} Interestingly, beginning with two salts LiTFSI and LiPF₆ (HVE606) without LiDFOB cannot sustain stable cycling, as LiPF₆ alone is unable to sufficiently passivate aluminum to protect it from the corrosive attack of LiTFSI (Fig S27). Therefore, starting with three salts (HVE552) has a significant impact on cycling stability. Lastly, the understanding of salt chemistry leads to improved stability with the presence of LiPF₆ salt in HVE552, where the rapid utilization of LiDFOB is complemented by both LiTFSI and LiPF₆ salts.

Finally, a cell with a nominal capacity of 2.5 mAh cm⁻² is fabricated and discharged up to 4.66 V to retain a 40% lithium source on the negative electrode, rather than completely stripping lithium by discharging up to 3 V. Figure 4a illustrates the charge-discharge characteristics of the cell. Ultimately, stability is successfully improved, achieving 65 cycles with 80% discharge capacity or 100 cycles with approximately 50% discharge at a current density of about 0.5 mA cm⁻² as depicted in Figure 4b and Fig. S28. This stability can be attributed to the in-situ formation of a lithium metal reservoir on the negative electrode as well as improved negative electrode oxidation stability as it is observed while discharging the cell to 4.4 V rather than 3 V. Furthermore, this electrolyte formulation can be applied and extended

as well for the higher active material mass loaded electrodes for large scale application (Fig. S29).



Figure 4. (a) The Charge-discharge profile with HVE552 electrolyte where the discharge is kept at 4.66 V and the charge is 4.9 V in the full cell. The nominal capacity of the cell is 2.5 mAh cm^{-2} and a symmetric current density of 0.5 mA cm^{-2} is applied. (b) The cycling stability of the cell at the symmetric current density of 0.5 mA cm^{-2} between 4.9 V and 4.66 V with HVE552 electrolyte at room temperature. The arrow indicates the number of 65 cycles at 80% discharge capacity retention.

In conclusion, high voltage anode-less battery architecture promises the possibility of achieving a high energy density system at a comparatively low cost but finding a suitable electrolyte remains an enduring challenge. A combination of three salts with LiTFSI, LiDFOB, and LiPF₆ (HVE552) in carbonate solvent (FEC/EMC) is prepared to obtain a high energy-density Li-metal battery, not been realized so far without using negative electrode material. Being LiTFSI a highly corrosive salt towards the aluminum surface, we passivated the Al current collector using LiDFOB salt. Despite improvement, the dual salt combination of LiTFSI and LiDFOB (HVE660) cannot deliver long-term cycling performance as found with and without the excess of Li-metal. The most possible reason can be proposed as, upon cycling,

LiDFOB is consumed significantly at a faster rate than LiTFSI and the remaining salt LiTFSI leads to the deposition of LinS (preferably Li2S) compound which is irreversible, insoluble, and insulating towards the electronic and ionic conduction for Li-ion transport and redox activity respectively. Therefore, it blocks further ionic motion, and both salts are drained out concurrently. All combined detrimental effects lead to the sudden death of the cell. Upon addition of a third salt LiPF₆, i.e. obtaining HVE552, ameliorates the cycling instability of HVE660 and provides long-term performance. Through ToF-SIMS analysis, it is observed that HVE552 creates a LiF-dense composition, unlike dual-salt HVE660. Such alkali halides (e.g. LiF) provide Schottky vacancies for ionic conduction rather than electron flow through a solid electrolyte interface. While increasing the LiPF₆ salt amount in the electrolyte formulation i.e. HVE444 shows a detrimental effect on cycling stability. Moreover, it is found that single salt LiPF₆ often leads to mostly irreversible or isolated lithium deposition. A low LiPF₆ concentration of 0.02 M in HVE_XYZ formulation impedes the prolonged performance as it cannot passivate enough. Hence, not only a multiple-salt combination but also an optimal concentration has paramount importance for Li-metal nucleation/crystallization while depositing on bare copper without its source. Such formulation can even be applied to beyond 5 V-battery chemistry and concomitantly enables lithium passivation. In the long run, we are re-inventing the wheel – a return to Li-metal battery. Let's perceive it in anode-less architecture, a step towards realizing high-energy-density devices for the future.

Supporting Information

Experimental details, cyclic and linear sweep voltammetry, galvanostatic charge-discharge, NMR, DOSY-NMR, FTIR, KF-Titration, SEM, XPS.

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Contributions

S.P. and A.V. have envisaged the concept, and experimental design principles. S.P. has executed the experiments and analyzed the data. Initially, the manuscript is written by S.P. and

further assisted by A.V. and N.C. S.P. and C.P. carried out ToF-SIMS and S.P. analyzed further. S.P. and G.B.C. performed the NMR-experiment and S.P. analyzed later. P.A., D.T., V.R.B., R.D., X.L., A.K., C.U., M.B., helped in the experiments. The project grants and fundings are acquired by A.V. and M.B.

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