Engineering Solvation Complex–Membrane Interaction to Suppress Cation Crossover in 3 V Cu-Al Battery

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Metal–metal batteries such as the 3 V Cu-Al system are highly desirable for large-scale energy storage owing to their low cost and excellent scalability of Cu and Al foils. However, the dissolved Cu cations will crossover from the cathode to the anode leading to poor electrochemical performance. In this work, it is demonstrated that the reversibility of the Cu-Al battery depends strongly on the interaction of the Cu ions with the electrolyte solvent and subsequently the affinity of the solvated Cu ion with the membrane separator. Specifically, a series of common carbonate-based electrolyte solvents are investigated via molecular dynamics and contact angle measurements to understand the interaction between the solvents and a polypropylene (PP) membrane, as well as that between cations and solvent. Among different solvents, fluoroethylene carbonate (FEC) is shown to drastically enhance the coulombic efficiency to 97%, compared to that of 27% with dimethyl carbonate. Remarkable cyclability of a 3 V Cu-Al battery with 3 m LiTFSI FEC and PP membrane up to 1000 cycles is further demonstrated. This finding opens new opportunities for the development of low-cost, high performance Cu-Al systems for stationary applications.

1. Introduction

Integration of intermittent renewable energy into modern electrical grid requires low-cost, scalable and high-performance energy storage systems.[1–3] Albeit the great success of lithium-ion batteries (LIBs) in the field of portable electronic applications, they are still expensive to scale up for stationary application.[4–6] As an alternative solution, metal batteries that utilize Earth-abundant metal elements as battery anodes, such as Zn, Mg, Al, Fe, and Ca, are attracting much attention due to their advantages in cost and capacity.[7–11] However, these metal anode systems are typically coupled with cathode materials that requires special and expensive engineering to accommodate the metal cation,[12–16] raising the capital and energy cost of the battery. Along this line, metal batteries that utilize low-cost cathodes with eco-efficient fabrication process are appealing for stationary applications.

In our previous work, we proposed a novel 3 V metal-metal system that uses low-cost and Earth-abundant Cu and Al metal foils directly as the cathode and anode, respectively, without any additional active material coating and structural engineering.[17] During cycling, the stripping/plating of Cu at the cathode is accompanied with the alloying/de-alloying of AlLi at the anode in a Li⁺-containing carbonate electrolyte with electrochemical reactions at each electrode shown below

Cathode: \( \text{Cu (s)} \leftrightarrow \text{Cu}^{+} + \text{e}^- \)  
Anode: \( \text{Al (s)} + \text{e}^- + \text{Li}^+ \leftrightarrow \text{AlLi (s)} \)

The battery is highly scalable, making it promising for large-scale applications. One essential question that dictates the practicality of the Cu-Al battery is how to restrict the crossover of Cu cations from the cathode to the anode. We have shown previously that glass fiber separators cannot selectively block the transport of Cu cations, resulting in a large amount of self-discharge and low coulombic efficiency (CE) during cycling. Replacing the separator with an anion exchange membrane (AEM) is effective in improving CE and maintaining good cycle stability,[17,18] but comes with a prohibitively high costs penalty (about USD 500–700 per square meter[19]). Therefore, it is highly desirable to find methods to enable reversible Cu-Al battery in non-aqueous electrolyte with a cost-effective membrane such as polypropylene (PP).

In this study, we identify that the interfacial energy between the electrolyte and the membrane separator and as such, the electrolyte solvent selection plays a large role in regulating the transport of Cu-ions from the cathode and anode. Contact angle analysis was performed on a series of carbonate-based electrolyte...
solvents on a commercially-available polypropylene membrane, showing lower interfacial energy (good wettability) for linear carbonates such as dimethyl carbonate (DMC), ethyl methyl carbonate (EMC) and diethyl carbonate (DEC), and high interfacial energy for cyclic carbonates such as propylene carbonate (PC) and fluoroethylene carbonate (FEC). The corresponding Cu-Al batteries with PP in 3 m lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in the different solvents show the same trend in CE—CE increases dramatically from 27% (for DMC) to 97% (for FEC), pinpointing FEC as a favorable solvent. Raman spectroscopy, $^{17}$O nuclear magnetic resonance (NMR) and molecular dynamics (MD) simulations suggest that Cu cation forms into a solvation complex with FEC molecule and TFSI$^-$ anion which is blocked by PP membrane because of the high interfacial energy between FEC molecules and PP. Furthermore, X-ray photoelectron spectroscopy (XPS) verifies that 3 m LiTFSI FEC also forms a robust solid electrolyte interphase (SEI) on the Al anode which improves the stability of the battery further. We demonstrate a Cu-Al battery with PP membrane in 3 m LiTFSI FEC can sustain stable operation for over 1000 cycles under a moderate current of 0.1 mA ($\approx$ 0.014 mA cm$^{-2}$), corresponding to a working time of 1900 h. Even when the current is raised to 0.72 mA ($\approx$ 0.1 mA cm$^{-2}$), excellent cycle performance of over 700 cycles can still be maintained. Our work shows an alternative method to carry out ion-selectivity by taking advantage of solvation complexes and their interaction with membranes, which can potentially be applied to batteries and other fields in the future.

2. Results

2.1. Reversibility of Cu-Al Battery

The schematics of a Cu-Al battery is shown in Figure 1. Cu and Al foils, with a thickness of 26 and 15 µm, respectively, were first cut into rectangular electrodes (2.4 cm $\times$ 3 cm) and then assembled with a PP membrane (Celgard 2400) as separator into a pouch cell. Different cells were filled separately with varying electrolyte compositions of 3 m LiTFSI in DMC, EMC, DEC, PC, or FEC. The cells were initially tested at a constant current of 0.1 mA ($\approx$ 0.014 mA cm$^{-2}$) with a charge capacity limit of 1 mAh (10 h charging) and a discharge voltage cutoff of 2 V (vs Li/AlLi). The small current used here allows us to clearly see the reversibility of the Cu-Al battery and the effect of self-discharge with different electrolytes.

As shown in Figure 2a (charge–discharge curves of all the cells during the third to fourth cycles), a charging plateau of about 3 V is observed for all the cells. This corresponds to the dissolution of Cu from the cathode foil into the electrolyte yielding Cu$^+$ and the alloying of Li and Al on the anode foil. The discharge process entails a reversed process where the Li-Al alloy anode is delithiated and the Cu metal is plated onto the Cu cathode. Though, the discharge capacity and CE differ much with different electrolytes. Specifically, CE (fourth cycle) of the battery is 27%, 27%, 40%, 94%, and 97% for DMC, EMC, DEC, PC, and FEC electrolyte, respectively. The loss in capacity and the low CE are attributed to a self-discharge process involving the crossover of Cu species through the PP membrane, which are then chemically

Figure 1. Schematic diagram of Cu-Al battery with a PP membrane.

Figure 2. Reversibility of Cu-Al battery in different carbonates-based electrolytes. a) Charge–discharge curves of Cu-Al battery with PP membrane in 3 m LiTFSI in DMC, EMC, DEC, PC, and FEC at a constant current of 0.1 mA and a capacity limit of 1 mAh. b) Contact angles (CA) for 3 m LiTFSI DMC, EMC, DEC, PC, and FEC on PP membrane at room temperature.
reduced at the anode. Our result shows that there are different degrees of self-discharge for the different cells—linear carbonates (DMC, EMC, and DEC) allow easier transport of Cu while cyclic carbonates (PC and FEC) block most of the Cu ions.

The blocking effect with the cyclic carbonate is only observed in the presence of PP membrane. This is verified by a control experiment where we compared two Cu-Al batteries with 3 M LiTFSI in FEC, one with a glass fiber membrane and the other with a PP membrane, as shown in Figure 3a,b. Both cells were charged with a current of 0.1 mA to a capacity of 4 mAh and discharged to 2 V. CE (fourth cycle) is only 4% for the cell with glass fiber membrane, whereas it is as high as 95.8% with PP membrane. For the cell with glass fiber membrane, black substance can be observed on Al foil anode after cycling (Figure 3e), and XRD data confirms that it is metallic Cu deposited on Al anode (Figure 3g). In sharp contrast, the Cu-Al cell with PP membrane still shows a glossy Al surface after cycling (Figure 3f), and only Al peaks are observed in the XRD pattern (Figure 3h). The results confirm that Cu crossover can be suppressed with FEC solvent in the presence of PP membrane, suggesting some form of interactions among PP, FEC molecule and Cu ion.

2.2. Interaction between Solvents and PP Membrane

It is well-known that different solvents show different degree of wettability on PP membranes.[20,21] To study the interaction between electrolytes (3 M LiTFSI in different solvents) and PP membrane, contact angles measurements were conducted and the results are shown in Figure 2b. We observe small contact angles for linear carbonate-based electrolytes (18°, 22°, and 23° for DMC, EMC, and DEC electrolytes, respectively), demonstrating good wettability and small interfacial tension between these electrolytes with PP. On the other hand, cyclic carbonate-based electrolytes exhibit big contact angles (41° and 60° for PC and FEC electrolytes, respectively), indicating a large interfacial tension. Interestingly, the trend in contact angle (DMC < EMC < DEC < PC < FEC) is the same as that of the CE of the Cu-Al battery, suggesting correlations between the interfacial tension and ion blockade.

The results suggest that the increasing interfacial tension between the electrolyte and PP membrane can effectively block the crossover of Cu species in electrolyte, contributing to the high coulombic efficiency for the Cu-Al battery. To further verify our hypothesis, we prepared a 3 M LiTFSI FEC/HFE = 2:1 (by vol) electrolyte for comparison.
(HFE = 1,1,2,2-tetrafluoroethyl 2,2,2-trifluoroethyl ether). HFE is a well-known solvent with low surface tension and good wetability,\textsuperscript{[21–23]} so the incorporation of HFE will change the characteristics of the electrolyte. We observe that the contact angle between electrolyte and PP membrane drastically decreases from 60° to 13° with the addition of HFE (Figure S1, Supporting Information). In relationship, the corresponding Cu-Al battery with PP membrane also exhibits poor reversibility, with a CE (fourth cycle) of less than 5% (Figure S1, Supporting Information). These results are as expected, and again indicates that the high interfacial tension is critical in restraining the dissolved Cu species in the electrolyte.

2.3. Interaction between Solvent and Ions

Apart from the type of solvent, the concentration of the electrolyte also plays an important role in stopping the crossover of Cu through the PP membrane. Figure 3c,d shows the charge–discharge curves of Cu-Al battery with PP membrane tested with 1 and 2 m LiTFSI FEC, respectively. Compared with 3 m LiTFSI FEC (Figure 3b), CE increases with increasing salt concentration. The result indicates that Cu ions are trapped more effectively in FEC with higher salt concentration.

This is supported by first-principle MD calculations, where we analyzed the interaction between Cu\textsuperscript{+} and FEC solvent in LiTFSI FEC electrolytes with the assumption that all Li\textsuperscript{+} ions in the electrolyte are replaced with Cu\textsuperscript{+}. As shown in Figure 4a, the binding energy between CuTFSI and FEC with a concentration of 3 m is calculated to be approximately 4 eV, which is stronger than that with 1 m electrolyte (about 3 eV). The trend agrees well with results by Zeng et al., who observed higher binding energy between cations and solvents with increasing salt concentrations.\textsuperscript{[24]} This suggests that the Cu ions are tightly bound into a solvation structure in the 3 m electrolyte and are harder to be extracted out compared to the 1 m case. Figure 4b,c shows the snapshot and the representative solvation structures of Cu\textsuperscript{+} in 3 m electrolyte. Cu\textsuperscript{+} ions are likely to be coordinated with two or three FEC molecules, or one FEC molecule and a TFSI\textsuperscript{−} anion.

A similar trend in binding energy of Li\textsuperscript{+} is also observed for 1 and 3 m LiTFSI FEC electrolyte as shown in Figure S2 (Supporting Information).

Raman and NMR spectroscopies are used to further study the interaction between cations (Li\textsuperscript{+}, Cu\textsuperscript{+}) and FEC solvent.

![Figure 4](https://example.com/figure4.png)

**Figure 4.** Solvation structure study of FEC based electrolyte with MD, Raman, and NMR. a) Calculated binding energies of CuTFSI-FEC electrolyte at a concentration of 1 and 3 m, as a function of the simulation time. b) Snapshot of the MD simulation cell for 3 m CuTFSI at 300 K. c) Representative Cu solvation structures in the electrolyte at a concentration of 3 m. d) Raman spectra of fresh, 1, 2, and 3 m LiTFSI FEC electrolytes. e) Raman spectra of 3 m LiTFSI FEC electrolytes extracted from a Cu-Al battery after charging to 4 mAh and 8 mAh. f) Change in chemical shifts of O nuclei of FEC in fresh FEC solvent and LiTFSI FEC electrolytes with different salt concentration after charging to 4 mAh; the inset shows the molecular structure of FEC molecule, with carbonyl O (I) and ethereal O (II and III).
First, the change in Raman vibrational signals of fresh electrolytes is investigated (Figure S3, Supporting Information). Figure 4d focuses on the range between 700 and 780 cm⁻¹ and compares the variation of the most intense peak at 730 cm⁻¹. While pure FEC solvent only shows a single peak centered at 730 cm⁻¹, which is assigned to ring skeletal deformation of FEC molecule,[23] this peak height decreases with the emergence of a new peak centered at 745 cm⁻¹ when increasing salt concentrations from 1 to 3 m. The peak at 745 cm⁻¹ is attributed to a Li-FEC coordination structure,[26,27] which suggests an incremental interaction between Li' and FEC solvent in FEC electrolytes with increasing LiTFSI concentration; and the result is consistent with our MD results (Figure S2, Supporting Information).

Second, the interaction between Cu ion and the electrolyte was studied by charging Cu-Al batteries with 3 m LiTFSI FEC to 4 and 8 mAh (electrochemically adding Cu-ions into the electrolyte, with Cu⁺ concentration of 0.075 and 0.15 m, respectively) and measuring the Raman profile of the extracted electrolyte. The result is exhibited in Figure 4e, showing an emerging peak centered at 769 cm⁻¹ around the vicinity of FEC ring skeletal deformation peak. Since this peak intensifies with increasing Cu ions in the electrolyte, we speculate that it originates from the Cu-FEC coordination structure. The result suggests that both Li and Cu are forming solvation complexes with FEC solvent molecules.

The interaction between Cu and FEC is further studied with ¹⁷O NMR. FEC molecule contains three sets of oxygen nuclei, as shown in the inset of Figure 4f. The NMR spectrum of FEC with ¹⁷O shows three peaks located at 223, 160 and 104 ppm, which can be assigned to the carbonyl O (I) and ethereal O (II and III), respectively. Cu-Al batteries with different salt concentration in FEC were charged to 4 mAh and the corresponding NMR spectra of the extracted electrolytes are also shown in Figure 4f. We can see that the carbonyl ¹⁷O signal is rather sensitive to the presence of salt, with a downshift displacement of the chemical shift with increasing Li' and Cu⁺ concentration. This is because Li' and Cu⁺ can directly interact with the lone pair electrons of carbonyl oxygen in FEC, leading to de-shielding of the nucleus. On the other hand, the ethereal ¹⁷O (II and III) peak positions are not affected by salt concentration. This indicates that the ethereal oxygen atoms do not directly coordinate with Li' and Cu⁺.

Overall, our experiment results and theoretical simulation supports the idea that the dissolved Cu ions are bound by FEC molecules and TFSI⁻ anion into a solvation complex, and that the high interfacial tension between FEC and PP prevents the solvation complex from permeating through the membrane, thus leading to higher CE.

2.4. Charge Carriers for Cu-Al Batteries with LiTFSI FEC Electrolyte

In order to identify the charge carriers in LiTFSI FEC-based electrolytes, we calculated the transference number number of Li⁺ in 1, 2, and 3 m LiTFSI FEC electrolyte with PP membrane. When a small constant voltage of 10 mV was applied on the cell, the current will decrease from an initial value (I₀) to a steady-state value (Iₛ). The amount of current contributed from the cation (Li⁺) transfer will be equal to the measured steady state current assuming there is no redox reaction of the anions. In addition, impedance spectroscopy (frequency range from 6 MHz to 0.1 Hz) was used to determine the electrode resistances before (R₀) and after (Rₛ) the potentiostatic measurements. Based on the results (Figure S4, Supporting Information), the transference number of Li' in 1, 2, and 3 m can be easily determined with the following equation

\[ t_{Li} = \frac{I_s (\Delta V - R_0 I_0)}{I_0 (\Delta V - R_s I_0)} \]

where Iₐ is the steady-state current, I₀ is the initial current, ΔV is the applied voltage, and R₀ and Rₛ are the electrode resistances before and after the potentiostatic measurements.

The transference number of Li in 1, 2, and 3 m LiTFSI FEC are calculated to be 0.04, 0.07, and 0.38, accordingly, which indicates that anions TFSI⁻ is the main charge carrier in FEC-based electrolytes in the presence of a PP membrane. We note that the transference number increases with salt concentration. This is attributed to different transport mechanism of Li⁺ depending on solvation structure. In particular, with low salt concentration (e.g., 1 m LiTFSI FEC), Li⁺ is surrounded by solvent molecules (Figure S2, Supporting Information) and so, most of the cations are transported by a vehicular mechanism where the cations move along with its solvation shells between the two electrodes.[28] In contrast, at a higher salt concentration (e.g., 3 m LiTFSI FEC), Li⁺ forms aggregates (AGG) with the FEC and TFSI⁻, so the transport mechanism switches to a Li-ion hopping-based mechanism,[30,31] which increases the Li⁺ transference number t_{Li⁺}.

2.5. Robust SEI with 3 m LiTFSI FEC Electrolytes

Apart from the suppression of Cu crossover with FEC and PP membrane, FEC also forms a robust SEI on the surface of the Al anode with 3 m LiTFSI electrolyte. This is verified by XPS measurements of the surface components of Al electrodes in charged Cu-Al batteries in 1, 2, and 3 m LiTFSI FEC (Figure 5). With increasing LiTFSI concentration, we observed an increase in peak intensity corresponding to C–F bond (at about 688.7 and 292.8 eV).[32] At the same time, the peak intensity of O=Si=O on TFSI⁻ also increases with increasing salt concentration, along with incremental sulfate species (SO₄²⁻). These results indicate that the anions are deposited on the surface and decomposed partially to become part of the SEI layer.[32] Such anion-derived SEI[33,34] is known to effectively passivate the electrode surface during initial cycling, leading to excellent capacity retention.[32,37]

XPS results also show the presence of Cu on the surface of the Al anode (at 932.0 and 931.4 eV) tested in 1 and 2 m LiTFSI FEC after cycling. In contrast, the Al electrode cycled in 3 m LiTFSI FEC shows no Cu signal, verifying that the 3 m LiTFSI FEC electrolyte is able to suppress crossover of Cu⁺ to the negative electrode. Similar results are also observed on the
2.6. Long-Term Stability of Cu-Al Battery

The long-term stability of Cu-Al system in 1, 2, and 3 m LiTFSI FEC with various currents and capacity limitations are compared. Figure 6a shows the cycle performances of the batteries tested at a moderate current of 0.1 mA ($\approx$0.014 mA cm$^{-2}$) with a capacity limit of 0.1 mAh (1 h charging). We can see that the battery with 3 m LiTFSI FEC can sustain for 1000 cycles, corresponding to 1900 h of operation time (Figure 6e). Even increasing the current and utilization to 0.3 mA ($\approx$0.042 mA cm$^{-2}$) and 0.3 mAh, respectively, 700 cycles can be sustained (Figure 6b). PP membrane separated Cu-Al battery with 3 m LiTFSI FEC can also maintain for more than 1000 cycles when the current was raised to 0.72 mA ($\approx$0.1 mA cm$^{-2}$) (Figure 6c). Such excellent cycle stability of the Cu-Al battery can be attributed to the following: 1) a strong interaction with FEC and TFSI$^-$ confines the Cu species in a large solvation complex; 2) the interaction between the solvation complex and PP membrane suppresses the crossover of Cu ions; 3) a robust SEI on the Al anode which promotes cycle stability further.

3. Conclusions

In summary, we have shown that by tuning the interactions between ions, solvent molecules and surfaces we can selectively block Cu-ion transfer to the anode while allow TFSI$^-$ and Li-ions to be transported through. Specifically, increasing salt concentration leads to stronger binding of Cu ions with the electrolyte. It was found that this Cu solvation complex will not pass through a PP membrane due to the increasing interfacial energy between the solvent and PP. Together with a robust SEI as generated in 3 m electrolytes, a $\approx$3 V Cu-Al battery with stable capacity and high CE for up to 1000 cycles is demonstrated based on our findings. Currently, the rate

Al anode in a discharged Cu-Al battery (Figure S5, Supporting Information).
performance and utilization of the Cu cathode is limited. With further optimization of the electrolyte, metal-metal battery with cost-effective cathode and anode materials may become an attractive alternative for large-scale energy storage. In addition, this novel method of ion selectivity through interaction of the membrane and solvation complex can be applied to other fields that require strict control of ion transports.

4. Experimental Section

Electrochemical Testing of Cu-Al Batteries: Cu and Al foils were cut into rectangular shape with a dimension of 2.4 cm × 3 cm. Battery was constructed with the Cu foil as the positive electrode (cathode) and the Al foil as the negative electrode (anode) in an Al laminated pouch cell. A PP membrane (Celgard 2400) was sandwiched between two glass fiber separators and inserted between the two electrodes. Aluminum and nickel tabs were used to connect both positive and negative electrodes to the outside, respectively. 1, 2, and 3 M LiTFSI in FEC, DMC, EMC, DEC, and PC were prepared and evaluated as the electrolytes. The cells were tested with Neware battery testers and a biological potentiostat (VMP3), typically between 2.0 and 4.0 V.

Characterizations: For the solvation structure characterization, Raman vibrational spectroscopy of the electrolytes was recorded using a 785 nm laser Raman spectrometer (Renishaw InVia Micro-Raman Spectroscopy). The samples were sealed in a transparent polypropylene film to allow the 785 nm laser to pass through.

XPS was conducted with the PHI 5600 multitechnique system (Physical Electronic Company) to characterize the surface of Al electrodes.

Figure 6. Electrochemical performance of polypropylene separated Cu-Al battery. Cycle performance of Cu-Al batteries in 1, 2, and 3 M LiTFSI FEC respectively at a) 0.1 mA for 1 h, b) 0.3 mA for 1 h, and c) 0.72 mA for 25 min. d) Charge–discharge profiles of Celgard separated Cu-Al system at various currents and capacity limits. e) Voltage profiles of 1900 h cycling for Cu-Al system at 0.1 mA 1 h; insets are enlarged view of 70–75, 950–955, and 1860–1865 h.
in charged and discharged Cu-Al batteries. After stabilization at 0.1 mA and 4 mAh for 1 cycle, Al electrodes in Cu-Al cell were collected and washed with DMC in a glove box. After drying, the Al electrodes were attached to XPS sample holders in the glove box and rapidly transferred into the vacuum chamber of XPS under the protection of vacuum bags before tests.

For surface component identification, Al electrodes in a fully charged state (4 mAh) were extracted from a Cu-Al battery and washed with DMC before tests. For charged and discharged Cu-Al batteries, after stabilization at 0.1 mA and 4 mAh for 1 cycle, Cu electrodes in Cu-Al cell were collected and washed with DMC in a glove box. After drying, the Cu electrodes were attached to XPS sample holders in the glove box and rapidly transferred into the vacuum chamber of XPS under the protection of vacuum bags before tests.

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

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Conflict of Interest
The authors declare no conflict of interest.

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