Research Article

Solvent Effects on Kinetics and Electrochemical Performances of Rechargeable Aluminum Batteries

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The rechargeable aluminum batteries (RAB) have shown great potential for energy storage applications due to their low-cost and superior volumetric capacity. However, the battery performances are far from satisfactory owing to the poor kinetics of electrode reactions, including the solid-state ionic diffusion and interfacial charge transfer. The charge transfer reaction, typically the cation desolvation at the interface (Helmholtz plane), is crucial for determining the interfacial charge transfer, which induces the solvent effect in batteries but has not been explored in RABs. Herein, we provide a comprehensive understanding of solvent effects on interface kinetics and electrochemical performance of RAB by analyzing the desolvation process and charge transfer energy barrier. The pivotal role of solvent effects is confirmed by the successful application of Al(OTF)3-H2O electrolyte, which displays easy desolvation, low charge transfer resistance, and thus superior Al-ion storage performance over other electrolytes in our studies. In addition, based on the strong correlation between the calculated desolvation energy and charge transfer energy barrier, the calculation of dissociation energy of ion-solvent complex is demonstrated as an efficient index for designing electrolytes. The in-depth understanding of solvent effects provides rational guidance for new electrolyte and RAB design.

1. Introduction

Recent investigations into the application of multivalent rechargeable aluminum batteries (RAB) [1–7] have driven the development of energy storage systems forward. Among all the metal electrodes, the Al anode shows the highest specific volumetric capacity of 8040 mAh cm−3 [2, 8, 9], which is three times higher than lithium metal. Al anode also has a good gravimetric capacity of 2980 mAh g−1 [8, 9] and is low-cost guaranteed by the large abundance in the earth crust [3, 4, 8–12]. All the above intrinsic advantages make the RAB especially promising in large-scale energy storage systems.

For a long time, the ionic liquid electrolyte aluminum halide/halogenated imidazole [2, 13–20] is the only widely used electrolyte because of its ability to effectively stripe and plate aluminum, but the moisture sensitivity and high cost hindered its further application. Besides, the exclusive Al-halide bond splitting process before Al-ion intercalation from ionic liquids will limit the kinetics of the cathode. The Al(OTF)3 is a highly competitive aluminum salt of electrolyte for RABs due to the advantages of high oxidation limit and stable chemistry [21–24] that conventional ionic liquid electrolyte does not have [2, 13–16]. However, Al(OTF)3 electrolytes (Al(OTF)3−diglyme [25, 26] or Al(OTF)3−THF [13]) display unsatisfactory electrochemical performances (high overpotential [21] and low capacity [25, 26]) due to the inferior kinetics. In our previous work, the application of a new electrolyte Al(OTF)3-H2O, which enables aqueous RAB with superior electrochemical performance, is introduced [23, 27]. The cell with an aqueous electrolyte delivers a discharge capacity of 467 mAh g−1 (based on the mass of cathode materials Al3MnO2·nH2O) by the reversible intercalating of the Al3+3, while the counterpart cell with a conventional ionic liquid electrolyte only delivers a discharge capacity of 229 mAh g−1 and suffers from severe decay. This superior electrochemical performance of RAB in the aqueous electrolyte has been
confirmed in other materials like MnO₂ [28] and MnO [29]. The striking solvent effects point to interface reactions, in addition to bulk reactions inside cathode materials that can be overwhelming in the overall kinetics of RAB. Specifically, at the electrode/electrolyte interface, the desolvation accompanied by the charge transfer process (i.e., interfacial charge transfer, in contrast to bulk charge transfer in the intercalation process) will control the kinetics of cathode reactions but has remained unclear for RAB by now [30]. Thus, a comprehensive understanding of the solvent effects is urgently needed to clarify the origin of the improvement of aqueous electrolytes on interfacial charge transfer kinetics and electrochemical performances, so as to further develop active and effective electrolytes for RAB.

In this work, solvent effects on interfacial charge transfer kinetics, galvanostatic cycling, and cyclic voltammetry of RAB are investigated by coupling Al(OTF)₃ with H₂O [31, 32], DMSO [33], and diglyme [26]. The DMSO and the diglyme were chosen as the comparison due to the high dielectric permittivity (46.7 for DMSO and 7.2 for diglyme at 298 K) and fair good electrochemical stability. In addition, the diglyme shows a typical chelating effect due to the multicoordination sites [34] and thus the strong desolvation energy barrier, serving as the contrast counterpart to reveal the desolvation effects. The AlₓMnO₂·nH₂O is used as the cathode material due to the typical multielectron reaction and the stable electrochemical performance in aqueous electrolyte. Herein, the desolvation process [27, 33, 35–37] is firstly estimated by DFT calculations. Then, the kinetics of interfacial charge transfer reaction is evaluated at both the cathode and anode interface by using a three-electrode cell and a symmetric cell. The strong correlation between charge transfer energy barrier and desolvation energies reveals that the desolvation process determines the interfacial charge transfer kinetics, and DFT calculation of desolvation energy is proved to be a low-cost and effective strategy guiding for electrolyte design. The fast interfacial charge transfer kinetics and superior electrochemical performance of aqueous electrolyte coupling with cathode material of AlₓMnO₂·nH₂O further confirm the vital role of solvent effects on the electrochemical performance of RAB.

2. Materials and Methods

2.1. Electrolyte Preparation and Material Synthesis. Al(CF₃SO₃)₃ (Alfa Aesar), DMSO (Alfa Aesar), and diglyme (Alfa Aesar) were used as received. The concentration of three kinds of electrolytes was 1 mol L⁻¹ (abbreviated as M). Al(OTF)₃·H₂O (1 M), Al(OTF)₃·DMSO (1 M), and Al(OTF)₃·diglyme (1 M) were prepared by adding Al(OTF)₃ into deionized water, DMSO, and diglyme separately and stirring overnight at room temperature. The Al(OTF)₃·H₂O (1 M) and Al(OTF)₃·DMSO (1 M) and Al(OTF)₃·diglyme (1 M) were prepared in a glove box filled with dry argon.

2.2. Theoretical Calculations. All calculations were carried out using Gaussian 09 software with the density functional theory (DFT) method. The B3PW91 method with a 6-31G (d) basis set [25] was used for the solvent molecules and Al (solvent)₃⁺ complexes geometry optimization. The calculation of single-point energies used the optimized molecules and the LC-wPBE method with a 6-311G (d, p) basis set. All the calculations were evaluated by the self-consistent reaction field (SCRF) approach using the SMD model. The calculation of H₂O and DMSO desolvation energy used the default SMD method in Gaussian. Because diglyme is not parametrized for SMD, the tetrahydrofuran showing the similar physical properties with diglyme [25] was used for the calculation of diglyme. The desolvation energies for one-to-one complexes (E_{Dsol}) were evaluated as the energy differences as follows:

\[ E_{Dsol} = E[Al^{3+}] + E[\text{solvent}] - E[\text{complex}], \]

where \( E[Al^{3+}] \), \( E[\text{solvent}] \), and \( E[\text{complex}] \) are the zero-point energies of the free Al³⁺ ions, free solvent, and Al (solvent)₃⁺ complex, respectively. The correlation coefficient \( R^2 \) (cathode/anode) is obtained by the linear fitting and analyzing the correlation of the calculated desolvation energy and the charge transfer activation energy of the cathode/anode side.

2.3. Cathode Material Synthesis and Preparation of Electrode. The cathode material AlₓMnO₂·nH₂O was synthesized by in situ electrochemical transformation as reported in our previous work [27]: firstly, the Mn₃O₄ nanoparticle precursor was synthesized by the deposition method, the 8 mmol manganese acetate was dissolved into 120 mL deionized water, and 19 mmol hydrazine hydrate was dropped into the solution with constant stirring in room temperature. The precipitate was collected and calcined in argon at 473 K for 5 h. The as-prepared Mn₃O₄ nanoparticles were grounded together with super-P and polytetrafluoroethylene (PTFE) binder (mass ratio, Mn₃O₄: super-P: binder = 8 : 1 : 1) to form a slurry and be coated on carbon fiber paper (Toray, H90). The cathode electrodes, Al metal anode, and electrolyte Al(OTF)₃·H₂O (5 M) were assembled into a coin cell and charged to 1.8 V under the current density of 50 mA g⁻¹. After galvanostatic charging, the Mn₃O₄ was oxidized and transformed into AlₓMnO₂·nH₂O [12]. Then, the cell was disassembled, and the AlₓMnO₂·nH₂O electrode was further used as prepared.

2.4. Material Characterizations. The Mn₃O₄ nanoparticles were characterized by X-ray powder diffraction (XRD, Rigaku Ultima IVD/MAX-RB) with Cu Kα radiation (λ = 0.15406 nm) at
ambient temperature. The morphology and microstructure of cathode materials were explored by the field-emission scanning electron microscopy (SEM, HITAS-4800) and high-resolution transmission electron microscopy (TEM, Hitachi H-800).

2.5. Electrochemical Measurements. A DJS-1 type conductivity electrode was used to measure the ionic conductivity. Coin cell (2025) was assembled with AlₓMnO₂·nH₂O cathode, Whatman glass fiber paper separator, and Al foil anode to investigate the electrochemical performance of different electrolytes. Three-electrode cells (E200, ida Inc.) were assembled with the AlₓMnO₂·nH₂O cathode, Al foil anode, and Al ring reference to investigate the charge transfer resistance of the interface between the cathode materials and the electrolyte. Al-Al symmetry cells (2025 coin-type cells) were assembled with Al foil on both sides to investigate the charge transfer resistance at the interface between Al metal and electrolyte. All the cells used the Whatman glass fiber (GF/C) as separators. The cells using Al(OTF)₃·H₂O (1 M) were assembled in the air owing to the negligible influence of water and oxygen. Before assembling cells using Al(OTF)₃·DMSO (1 M) and Al(OTF)₃·diglyme (1 M), the Al metal anode was soaked in ionic liquid (AlCl₃/[BMIM]Cl (mole ratio = 1.11)) for 24 h to wipe off the passive Al₂O₃ layer [19, 21, 38]. Then, the cell was assembled with activated Al metal and electrolyte (Al(OTF)₃·DMSO, Al(OTF)₃·diglyme) in an argon glove box. Galvanostatic discharge/charge measurement was conducted on a LAND battery system (CT2001A, Wuhan, China) at 30°C under the current density of 100 mA g⁻¹. The galvanostatic capacity is calculated based on the weight of Mn₃O₄ (the precursor of the AlₓMnO₂·nH₂O) to keep consistent with the previous work [27]. The cyclic voltammetry (CV) and AC impedance spectroscopy were performed on CHI 606D electrochemical workstation. The CV scan rate was 0.1 mV s⁻¹.

3. Results and Discussion

3.1. DFT Calculation of Desolvation Energy of Al⁺⁺. In the desolvation process, metal ion dissociates from the covalently bounded solvent shells, which has been recognized as the rate-determining step in the interface reactions of batteries [30, 36]. Technically, desolvation is quite a complex process similar to the chemisorption at the electrolyte/electrode interface (i.e., inner Helmholtz plane) [39]. It can be indexed to the dissociation of ions and solvents in the first solvation shell, partial charge transfer, and addition the dipole interactions [40]. For a facile and effective evaluation, we follow the precedent model that only the overwhelming dissociation energy is concerned to demonstrate the feasibility, i.e., ion-solvent
dissociation energy as an approximation of desolvation energy. The density functional theory (DFT) calculation is used to determine the desolvation energies of the solvent H$_2$O, DMSO, and diglyme. The common solvent DMSO and diglyme are chosen as counterpart because of its activity and appropriate viscosity [25, 26, 37]. Typically, the diglyme is deliberately chosen to serve as the high desolvation barrier counterpart, because of the strong affinity towards the cations and a higher desolvation barrier than the monodentate ligands (the H$_2$O and DMSO) induced by the chelating effects with 3 coordination sites [41].

As shown in Figure 1, the structure of solvent and Al (solvent)$^{3+}$ complex is geometrically optimized by software Gaussian09. The calculated Al$^{3+}$-solvent dissociation energies of Al(H$_2$O)$^{3+}$ has a minimum value of 599.7 kJ mol$^{-1}$, much lower than Al(DMSO)$^{3+}$ (797.6 kJ mol$^{-1}$) and Al(diglyme)$^{3+}$.
Accordingly, the electrolyte Al(OTF)$_3$·H$_2$O with Al(H$_2$O)$_3^+$ is inferred to display the best kinetic performance among the three electrolytes.

### 3.2. Kinetics of Interfacial Charge Transfer Reaction

As is well recognized, multivalent-ion batteries are plagued by the poor kinetics of cathode reactions stemming from slow bulk diffusion [9]; particularly, the interfacial charge transfer to be discussed here. Such results have been well elucidated in Mg-ion [42, 43] and Zn-ion [44] batteries and suggested in Al-ion batteries as well.

Three-electrode cell is used to measure the charge transfer energy barrier at the cathode interface without the interference of the anode interface. The Al$_x$MnO$_2$·nH$_2$O is used as the cathode material in this three electrode cell. As shown in Figure 2, the precursor of Al$_x$MnO$_2$·nH$_2$O is a well-crystalized Mn$_3$O$_4$ nanoparticle (Figures 2(b) and 2(d)) and its XRD pattern matches well with the spinel Mn$_3$O$_4$ (Figure 2(a)). After the electrochemical transformation reaction, the Mn$_3$O$_4$ transforms into Al$_x$MnO$_2$·nH$_2$O, which are nanoparticles (Figures 2(c)) with the roughness edges, obvious amorphous, and layered structure (Figures 2(f) and 2(g)) [27]. This mixed structure of amorphous and layered material Al$_x$MnO$_2$·nH$_2$O delivers superior electrochemical performance with a discharge capacity of 467 mAh g$^{-1}$. To focus on the solvent effects on electrochemical performance, it is used as the typical cathode material.

The three electrode cells coupling with electrolytes of Al(OTF)$_3$·DMSO, Al(OTF)$_3$·diglyme were galvanostatically cycled 5 times and rested for 12 hours until stable, and then the charge transfer resistances were evaluated by AC impedance spectroscopy [36, 45]. As shown in Figure 3 (a), a semicircle and a Warburg impedance are observed, which is attributed to the charge transfer resistance and
semi-infinite diffusion of Al\(^{3+}\) in the cathode materials, respectively. The charge-transfer resistances were obtained by fitting the Nyquist plots with an equivalent circuit (Figure 3(a) inset), and the fitted charge transfer resistances are displayed in Table 1. The cell coupling with Al(OTF)\(_3\)-H\(_2\)O displays a much lower charge transfer resistance than Al(OTF)\(_3\)-DMSO and Al(OTF)\(_3\)-diglyme, indicating faster kinetics of the interface reactions in Al(OTF)\(_3\)-H\(_2\)O. To quantify the charge transfer energy barrier, the activation energy is calculated by the Arrhenius equation [36],\(1/Rct = A \exp \left(-E_a/RT\right)\), where \(Rct\), \(A\), \(E_a\), \(R\), and \(T\) denote the charge-transfer resistance, frequency factor, activation energy, gas constant, and absolute temperature, respectively. A typical Arrhenius behavior of interfacial charge transfer was obtained (Figures 3(c) and 3(d)). And the activation energy of 18.7 kJ mol\(^{-1}\) of Al(OTF)\(_3\)-H\(_2\)O was obtained (Figures 3(c) and 3(d)).

To obtain further insight into the desolvation process. The desolvation energy and charge transfer activation energies indicates the desolvation of Al(solvent)\(^{3+}\) is the rate-determining step in the bulk phase. The electrolyte Al(OTF)\(_3\)-DMSO and Al(OTF)\(_3\)-diglyme show much higher activation energies of 11.8 kJ mol\(^{-1}\) and 20.1 kJ mol\(^{-1}\), implying inferior kinetics of the cathode interface reactions in Al(OTF)\(_3\)-DMSO and Al(OTF)\(_3\)-diglyme.

As shown in Figure 3(e), the desolvation energy is positively correlated with the charge transfer activation energy; the Al(OTF)\(_3\)-H\(_2\)O shows the lowest desolvation energy and charge transfer resistance, while the value of Al(OTF)\(_3\)-DMSO and Al(OTF)\(_3\)-diglyme are in increasing order. Even though the value of calculated desolvation energies of Al(solvent)\(^{3+}\) complex is much higher than that of monovalent ions like Li\(^+\), Na\(^+\), mainly due to the high charge density of the trivalent Al\(^{3+}\), similar to the case of Mg\(^{2+}\) [37], the correlation coefficient of the desolvation energy and the charge transfer activation energies of the cathode and anode side is quite high, which are 0.7756 (\(R^2\) (cathode)) and 0.9957 (\(R^2\) (anode)), respectively. The high dependence between the desolvation energy and charge transfer activation energies indicates the desolvation of Al(solvent)\(^{3+}\) is the rate-determining step in interface reaction and determines the overall kinetics of RAB.

Furthermore, the conductivities of electrolytes were investigated. As displayed in Figure 5, the conductivity of the Al(OTF)\(_3\)-H\(_2\)O is 60.2 ms cm\(^{-1}\) (30°C), which is about 8 and 220 times higher than that of Al(OTF)\(_3\)-DMSO (7.1 ms cm\(^{-1}\) 30°C) and Al(OTF)\(_3\)-diglyme (0.27 ms cm\(^{-1}\) 30°C), respectively. This distinct difference can be understood on account.
of the high dielectric property of solvent H$_2$O, which ensures the high degree of dissociation of anion-cation of Al(OTF)$_3$ salt. The high conductivity of Al(OTF)$_3$-H$_2$O further underlies the fast ion transportation in RAB.

3.3. Electrochemical Performance Comparison of RAB with Different Electrolytes. To investigate the influence of interfacial charge transfer kinetics on electrochemical performances, the CV and galvanostatic tests of RAB with the cathode of Al$_x$MnO$_2$·nH$_2$O are carried out. The cell coupling with Al(OTF)$_3$-H$_2$O displays one pair of redox peaks located at 1.67 V and 0.76 V, which are assigned to the intercalation and deintercalation of Al$^{3+}$ in the cathode materials (Figure 6(a)). It delivers an initial discharge capacity of 312 mAh g$^{-1}$ with a discharge plateau at 0.92 V and a charge plateau at 1.62 V (Figure 6(d)). The capacity increased to 344 mAh g$^{-1}$ at the second cycle due to the continuous electrochemical activation reaction [27] in the charging processes. The voltage profile reveals the bulk reaction in cathode material instead of electrochemical double-layer adsorption. In addition, the voltage hysteresis between discharge and charge is 0.7 V under the current density of 100 mA g$^{-1}$. In sharp contrast, the cells coupling with Al(OTF)$_3$-DMSO only show a very weak cathodic peak at 0.34 V (Figure 6(b)), resulting from a larger charge transfer activation barrier. Higher voltage hysteresis (1.51 V) is observed as the cell displays a higher charging plateau at 1.71 V and a lower discharging plateau at 0.20 V under the same current density in galvanostatic profiles (Figure 6(e)). The Al-ion intercalation
capacity is only 78 mAh g\(^{-1}\) and less than 30 mAh g\(^{-1}\) in the subsequent cycles. The fast capacity indicates the passivation of the Al anode in the Al(OTF)_3-DMSO [26]. Furthermore, due to the ultrahigh charge transfer energy barrier, the cell with Al(OTF)_3-diglyme displays the worst performance without any apparent peak in the CV curve (Figure 6(c)) or galvanostatic capacity.

Accordingly, it can be concluded that large charge activation energy results from the high desolvation energy of Al(solvent)\(^{3+}\) and further leads to poor electrochemical performance. Due to the low desolvation energy barrier, the Al(OTF)_3-H\(_2\)O possesses fast kinetics at interface reaction and superior electrochemical performance. The strong correlation between the desolvation energy, charge transfer barrier, and electrochemical performance concretely implies that the DFT calculation of the desolvation energy is an efficient chemical index for designing practical and kinetically accelerated electrolytes for RABs. Due to the low desolvation energy barrier, the Al(OTF)_3-H\(_2\)O possesses fast kinetics at interface reaction and superior electrochemical performance. The strong correlation between the desolvation energy, charge transfer barrier, and electrochemical performance concretely implies that the DFT calculation of the desolvation energy is an efficient chemical index for designing practical and kinetically accelerated electrolytes for RABs.

Therefore, the rate-determining interface reaction of RAB is inferred and displayed in Figure 7, the Al(solvent)\(^{3+}\) complexes migrate to the electrolyte/electrode interface, and then the charge transfer reaction occurs after the desolvation of Al(solvent)\(^{3+}\). The desolvation process at the interface determines charge transfer reactions and is a rate-determining step in the electrochemical reactions. Lower charge transfer activation energy means lower charge transfer barriers on interface reaction, faster interfacial charge transfer kinetics, and thus superior electrochemical performances. Accordingly, the superior interfacial charge transfer kinetics and electrochemical performance of aqueous electrolyte result from the ease of desolvation process of Al(H\(_2\)O)\(^{3+}\) and low charge-transfer energy barrier of interface reaction.

4. Conclusion

In this work, we have unraveled the solvent effects on Al-ion storage behaviors by analyzing the electrolyte/electrode interface reaction through both experimental evaluation and computational calculation. It is found that the solvent influences the electrochemical performance of RAB by determining the desolvation energy of Al(solvent)\(^{3+}\) complex. Owing to the fast interface reaction enabled by H\(_2\)O, the Al(OTF)_3-H\(_2\)O is used in the Al-Al\(_{13}\)MnO\(_2\)-nH\(_2\)O cell which delivers a superior reversible capacity of 334 mAh g\(^{-1}\) under the current density of 100 mA g\(^{-1}\). The successful application of the aqueous electrolytes highlights the crucial role of the interface in the overall kinetics of RAB. In addition, the correlation of desolvation energy and charge transfer activation energy implies DFT calculation is a low-cost and effective strategy guiding electrolyte design. We believe this in-depth understanding of solvent effects can provide a rational guideline for developing more effective electrolytes and better RABs for the energy storage application.

Data Availability

All data needed to evaluate the conclusions in the paper are present in the paper. Additional data related to this paper may be requested from the corresponding authors.

Conflicts of Interest

The authors declare no conflict of interest.
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