Study on the Mixed Electrolyte of N,N-Dimethylacetamide/Sulfolane and Its Application in Aprotic Lithium–Air Batteries

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ABSTRACT: Aprotic lithium–air batteries have recently drawn considerable attention due to their ultrahigh specific energy. However, the chemical and electrochemical instability of the electrolyte is one of the most critical issues that need to be overcome. To increase the stability and maintain a relatively high conductivity of the lithium ion, a mixed electrolyte of sulfolane (TMS) and N,N-dimethylacetamide (DMA) was evaluated and tested in an aprotic lithium–air battery. The physical and chemical characterizations showed that the mixed electrolyte exhibited a relatively low viscosity, high ionic conductivity and oxygen solubility, and good stability. In addition, it was found that lithium–air batteries with an optimized electrolyte composition (DMA/TMS = 20:80, % v/v) showed a better cycle life and lower charge overpotential as compared to those with electrolytes with a single solvent, either DMA or TMS.

1. INTRODUCTION

The increase in the energy demand as a result of the rapid development of electronic devices and electric vehicles has motivated efforts to develop new energy-storage devices. Aprotic lithium–air batteries are gaining increasing attention due to their ultrahigh specific energies, which are almost 5–10 times those of advanced Li-ion batteries.1,2 However, electrolyte degradation during the lithium–air battery cycling process hampers its practical application and commercialization.3 Thus, developing a stable electrolyte is the key to improving current rechargeable aprotic lithium–air batteries.4–6

At present, a variety of aprotic electrolyte solvents, such as carbonates, ethers, ionic liquids, amides, and sulfones, have been proposed and evaluated for aprotic lithium–air batteries. Early research has shown that carbonate electrolytes were unstable toward O2•− and easily decomposed in the charge and discharge processes.7–9 Although ether electrolytes are relatively stable toward O2•−, they are easily autoxidized in an oxygen-enriched environment, accompanied by a series of byproducts.9,10 Ionic liquids are quite stable, but their oxygen solubility is lower than that of organic electrolytes.11–15 Although straight-chain alkyl amides, such as N,N-dimethylacetamide (DMA), showed superior stability in the O2-containing cathode as compared with organic carbonates and glymes and the ionic conductivity of DMA was higher than that of other common electrolytes because of its low viscosity, it was difficult for these solvents to form a stable solid–electrolyte interphase (SEI) on the lithium anode.11,16–18 To alleviate the reaction between DMA and the lithium anode, Walker et al.18 introduced lithium nitrate salt (LiNO3) to stabilize the SEI, and the Li–O2 battery utilizing a 1.0 M LiNO3/DMA electrolyte was able to run at 0.1 mA/cm2 for over 80 cycles, with a low overpotential (<10 mV) and a good capacity of retention. Sulfones, such as dimethyl sulfoxide (DMSO) and sulfolane (TMS), are another type of electrolyte previously investigated in Li–air batteries. TMS possesses a low toxicity, low vapor pressure (27 °C, 1.24 × 10−7 bar), and a wide electrochemical window. Its five-membered ring structure makes it superior to the other solvents in terms of chemical and thermal stabilities.19–21 Our group22 reported that the capacity retention of a Li–air battery containing a TMS-based electrolyte was better than that of a battery containing a DMSO-based electrolyte during discharge/charge cycling. Through optimizing the primary materials in Li–air batteries based on a TMS electrolyte, the Li–air battery was able to exhibit a cycle life as high as 800 cycles, with a specific capacity of 1000 mA h g−1, and an average energy efficiency of 74.72% was obtained.23 Unfortunately, TMS easily exists in the solid state at room temperature because its melting point is 28.4 °C, and its viscosity is substantially higher than that of other commonly used organic solvents, resulting in poor migration of lithium ions in the electrolyte.

To improve the ionic conductivity and stability of electrolytes for lithium–air batteries, researchers have tried to utilize the advantages of different solvents and have prepared electrolytes by mixing two or more kinds of solvents.24–27 Cecchetto et al.,25 who mixed an ionic liquid and organic electrolyte, reported that the addition of 1-butyl-1-methyl-
pyrrolidinium bis(trifluoromethanesulfonyl)imide (TFSI) could improve the conductivity of Li+ in tetraethylene glycol dimethyl ether (TEGDME), and their Li− air battery containing the mixed electrolyte showed a lower charge overpotential than that of the lithium−air cell with only the TEGDME solvent. Herranz et al.26 and Ferrari et al.27 also found that both the ionic conductivity and the electrochemical stability of the hybrid electrolyte were better than those of a single electrolyte. Combining TMS with other solvents to form a mixed electrolyte has already been studied in lithium-ion batteries. Li et al.28 showed that compared with a lithium-ion battery with a lithium bis(oxalate)borate (LiBOB)−ethylene carbonate/ diethyl carbonate (DEC) electrolyte, a battery with a LiBOB−TMS/DEC electrolyte exhibited a higher discharge plateau and a better cycle performance. In addition to experimental studies, simulation results from molecular dynamics simulations also have been used to demonstrate that TMS plays a major role in improving the stability of the mixed electrolyte.29

Inspired by previous works on mixed electrolytes, this work combined the high stability of TMS and high ionic conductivity of DMA to form a mixed electrolyte for a lithium−air battery. The physical and chemical properties, including the electrochemical window, viscosity, conductivity, and oxygen solubility, of the mixed electrolyte were tested and analyzed systematically. By optimizing the composition ratio of TMS and DMA, it was found that Li−air batteries with an optimized mixed electrolyte showed a better cycle life and lower charge overpotential as compared to those with a single solvent, that is, either DMA or TMS.

2. RESULTS AND DISCUSSION

2.1. Characterization of the DMA/TMS Mixed Electrolyte. As shown in Figure 1a, the LiTFSI−TMS electrolyte started to undergo oxidation at ~6 V and it started to undergo reduction at ~1 V, resulting in a stability window of ~5 V. After adding DMA, the electrochemical windows of the two DMA/TMS mixed electrolytes were both over 4 V versus those for Li/Li+. More importantly, it is found that the DMA/TMS mixed electrolytes are quite stable, not undergoing oxidation and reduction, in the potential range of 2−5 V versus Li/Li+, indicating their high stability in the operating potentials of the lithium−air battery.

As seen from Figure 1b, the viscosity of the electrolytes generally increases after the addition of the lithium salts, and the viscosity of the mixed electrolytes decreases with an increase in the DMA content. For example, the viscosity decreases from 10.27 to 3.98 mPa s at 28 °C when TMS is mixed with 20% DMA. In addition, it is seen that the viscosity of the mixed electrolyte is less influenced by temperature as compared to that of pure TMS or TMS containing lithium salts.
These results suggest that the addition of DMA, with a low viscosity, can effectively reduce the viscosity of TMS, which is beneficial for increasing the mobility of lithium ions.

Figure 1c shows the ionic conductivities of mixed electrolytes with various DMA contents. It can be found that the ionic conductivities of the mixed electrolytes with 20% DMA and 50% DMA are, respectively, 50 and 140% higher than those of TMS at 28 °C. These data indicate that the introduction of DMA into TMS indeed increases the lithium conductivity of the mixed electrolyte, which is in a good agreement with the results of viscosity measurements.

High oxygen solubility is another requirement for the electrolyte used in a lithium−air battery because most of its cathode is flooded with electrolyte and thus oxygen has to dissolve in the electrolyte to react with lithium ions. The oxygen solubilities of the mixed electrolytes at 28 °C are shown in Figure 1d. It can be found that the oxygen solubility increased with an increase in DMA; the oxygen solubility increases from 7.09 to 7.56 mg L⁻¹ with an increase in the DMA content from 0 to 50%. Hence, adding DMA into TMS slightly increases the oxygen solubility, although its improvement is less pronounced than that observed in the viscosity and ionic conductivity.

2.2. Study of the Stability of DMA and TMS toward Discharge Products. Figure 2 shows gas chromatography−mass spectrometry (GC−MS) graphs of solvents based on changes in the solvent chromatographic peaks in acetonitrile (AN) after reacting with KO₂ or Li₂O₂ for 1 week. As seen from Figure 2a,b, respectively, the characteristic peak of DMA or TMS dominates the whole screening process, which shows their high stability toward KO₂ or Li₂O₂. However, as a stable carrier solvent widely used in GC−MS, AN still encountered nucleophilic attack from adventitious moisture, as described. The acetamide chromatographic peak was detected after AN was treated with KO₂ or Li₂O₂, implying solvent degradation of AN. AN dimers, AN trimers, or other species from AN degradation may also exist, although GC−MS is unable to detect them in trace amounts. As a result, it can be seen from Figure 2c,d that the peak areas of DMA and TMS after reacting with KO₂ or Li₂O₂ are slightly larger than their pristine peak areas, which indicates a slight increase in the relative concentration of DMA or TMS in solvent AN. In summary, GC−MS analysis shows that acetamide is the only degradation product from AN, and no other product was detected when DMA and TMS were treated with KO₂ or Li₂O₂. This further confirms that no obvious reaction take place between the solvent and oxygen species. Both DMA and TMS are relatively...
stable solvents toward KO₂ or Li₂O₂ under normal circumstances.

However, this stability investigation toward KO₂ or Li₂O₂ is isolated from the battery. The oxidative decomposition of DMA following the discharging or charging process in a Li–air battery was proven by others to produce acetamide, Li₂CO₃, HCO₂Li, or other species. Besides, the corrosion reaction with the Li anode was also undoubtedly verified. These factors above would be the mortal obstacles for DMA to be a single stable solvent in a Li–air battery.

2.3. Electrochemical Test of the DMA/TMS Mixed Electrolyte. 2.3.1. Cyclic Voltammetry (CV) Characterization. Figure 3 shows the CV results attained with a scan rate of 100 mV s⁻¹ and a potential range of 1.82–4.40 V for various electrolytes, including DMA, TMS, and DMA/TMS, with mixing ratios of 20:80 and 50:50. It is seen that for all electrolytes there is one reduction peak at about 2.3 V and one oxidation peak between 3.2 and 3.5 V, which can be assigned to the oxygen-reduction reaction (ORR) and oxygen-evolution reaction (OER), respectively. More importantly, it is found that the addition of DMA to the TMS electrolyte results in improvements in the peak current densities and onset potentials of both ORR and OER, which might have arisen from increases in the conductivity of lithium ions and solubility of the reaction products (or intermediates). In addition, it is found that for the DMA electrolyte the peak area of ORR is much larger than that of OER. One possible reason for this might be that some soluble ORR products diffuse into the bulk DMA solution and hence would be absent from the OER during the forward scan, resulting in less charge transfer involved in the OER, consistent with the findings of the microelectrode study. On the basis of the CV results, it is inferred that compared with TMS, DMA has a better ability to dissolve the reduction products and that the addition of DMA could promote the ORR and OER.

2.3.2. Galvanostatic Charge/Discharge Test. Galvanostatic charge/discharge tests are used to evaluate the cycle performance of Li–air batteries containing four kinds of electrolytes. As shown in Figure 4a,b, no obvious difference in the discharge plateau is observed among the four kinds of electrolytes at the first and tenth cycles, whereas the battery containing the DMA electrolyte exhibits a much smaller charge plateau than that of the other three electrolytes. At the 50th cycle, however, the Li–air battery using DMA as the electrolyte shows serious polarization, with high discharge and charge overpotentials, likely due to the severe reaction between DMA and the lithium anode. Starting from the 50th cycle, the average charge potentials of the cells with mixed DMA/TMS electrolytes are much lower than those with the TMS electrolyte, as shown in Figure 4c,d. This may because the mixed electrolyte has a higher ionic conductivity and larger solubility of reaction products as compared with the TMS electrolyte.

To better compare the cyclic performances with various electrolytes, the terminal voltages, namely, the final voltages during charge or discharge, are presented in Figure 5. It can be seen that with cutoff voltages of 2.0 and 5.0 V the lithium–air batteries can undergo 50, 140, 200, and 200 cycles, respectively, on using DMA, DMA/TMS (50:50), DMA/TMS (20:80), and TMS as electrolytes. Although the cycle life of the cell with TMS is relatively high, its polarization, especially the charge voltage, is quite high and rises to 5.0 V only after 50 cycles, representing substantially low energy efficiency. As evident in Figure 5, the charge/discharge overvoltages can be lowered by adding 20% DMA to TMS, with the high cycle life still maintained, demonstrating the beneficial effect of DMA as an additive to TMS. However, it should be mentioned that the positive effect of adding DMA will be inevitably counteracted by its instability toward lithium metal when the content of DMA is too high. It can be also found that the overpotential of DMA/TMS (50:50) is higher than that of DMA/TMS (20:80) because adding too much DMA would cause more serious corrosion of the lithium anode. In particular, the discharge and charge voltages of the battery with only the DMA electrolyte reach 2.0 and 5.0 V, respectively, only after 50 cycles. However, it is undeniable that a high polarization (>2 V) of the battery is still observed after optimizing the electrolyte. This is because pure carbon cathodes were used in the batteries without any addition of catalyst, and carbon could be reacted with the discharge product of Li₂O₂, to generate the by-product Li₂CO₃, which caused great cathode passivation. Therefore, besides electrolyte optimization, the development of a carbon-free cathode also deserves significant attention to aid in overcoming the problem of serious polarization.

3. CONCLUSIONS

Instability of the electrolyte and the high overpotential during cycling are two challenging problems with regard to lithium–air batteries. Utilizing the synergistic effect of DMA and TMS, a binary mixed electrolyte with a high stability and low ionic resistivity was designed and tested in lithium–air batteries. GC–MS results confirmed that both DMA and TMS are relatively stable solvents toward oxygen species under normal circumstances. Physical and electrochemical characterizations demonstrated that the ionic conductivity of the mixed electrolyte was higher than that of TMS and the OER onset potential of the mixed electrolytes was lower than that of TMS. Moreover, galvanostatic charge/discharge tests showed that lithium–air cells with the mixed electrolyte (DMA/TMS = 20:80, % v/v) exhibited the best cycle life and lowest
overpotential, implying the effectiveness of the mixed electrolyte.

4. EXPERIMENTAL SECTION

4.1. Preparation of the Electrolyte and Cell Assembly.

DMA/TMS electrolytes were prepared inside an Ar-filled glovebox by dissolving 1 M dried LiTFSI (99% or higher; Aladdin) salt in 1 L of a mixture of TMS (99.00% or higher; Aladdin) and DMA (99.00% or higher; Aldrich) solvents in different volume ratios. The composition ratios of the DMA/TMS electrolytes are shown in Table 1; lithium salts were dissolved in the solvent completely on a magnetic stirrer.

In this work, a homemade 2032 coin-type cell with multiple Φ1 mm holes on the cathode cap was used for assembling the lithium−air batteries. For preparing the cathode slurry, a mixture of KB carbon (EC600JD; Shanghai Tengmin) and polyvinylidene fluoride (PVDF), as binder, in a weight ratio of 9:1, using N-methyl-2-pyrrolidone as the solvent, was stirred for 3 h before use. Then, the slurry was pasted on a carbon paper (HCP120; Shanghai Hesen Electric) and dried at 80 °C overnight. The mass loading (KB and PVDF) of the cathode (Φ1.5 mm) was about 0.3 mg (0.17 mg cm⁻²). The as-prepared
Table 1. Volume Ratios of DMA/TMS Electrolytes

| lithium salts | DMA (%) | TMS (%) | electrolyte              |
|---------------|---------|---------|--------------------------|
| 1 mol/L LiTFSI| 0       | 100     | TMS electrolyte          |
|               | 20      | 80      | mixed electrolyte (20:80 DMA–TMS) |
|               | 50      | 50      | mixed electrolyte (50:50 DMA–TMS) |
|               | 100     | 0       | DMA electrolyte          |

cathode, together with glass fiber (17 × 1 mm; Whatman GF/D) as a separator and a lithium disc (15 × 0.5 mm; China Energy Lithium) as the anode, was fabricated in the Ar-filled glovebox. Four different types of electrolytes, as listed in Table 1, with the same loading of 70 μL were used in the present work.

4.2. Electrolyte Characterization. The electrochemical window of the as-prepared electrolyte was analyzed in the absence of O₂ through linear scan voltammetry (LSV) in the three-electrode electrochemical cell tests, with a scan rate of 1 mV s⁻¹ and a potential range of −3 to 7 V. The electrochemical cell was constructed as reported by Ferrari et al., comprising a glassy carbon electrode as the WE, a Pt electrode as the CE, and an anhydrous Ag–Ag⁺ electrode as the RE. Four solvents, as listed in Table 1, were tested. All solvents were bubbled with high-purity dry Ar before and during the examinations to ensure saturation of Ar in the electrochemical cell. The viscosity of the electrolyte at a variety of temperatures was measured with a VT rotary viscometer (Brookfield). The oxygen solubility of the electrolyte was determined by a portable dissolved oxygen meter (Mettler Toledo, Switzerland), and the ionic conductivity of the electrolytes was attained by testing on Autolab (Metrohm, Switzerland). To evaluate the stability of the electrolyte in the presence of ORR products (or intermediates), lithium peroxide (Li₂O₂, 99% or higher; Aladdin) was used to simulate discharge product O₂⁻, and potassium superoxide (KO₂, 96.5% or higher, Aladdin) was used to simulate O₂⁻⁺. Qualitative and quantitative analyses of the electrolytes after reacting with KO₂ and Li₂O₂ were carried out by GC–MS (GC–MS-QP2010; Shimadzu). The decomposed electrolyte solution was diluted with AN (99.9% or higher, GC grade; Sigma Aldrich), with a volume ratio of 1:1000 before the GC–MS test.

4.3. Electrochemical Test. CV measurements of the three-electrode electrolyte cells used in the LSV test under an O₂ atmosphere, with a scan rate of 100 mV s⁻¹ and a potential range of 1.82–4.40 V, on an electrochemical workstation (CHI660D; CH Instruments). Galvanostatic charge and discharge tests of the cells containing various electrolytes were carried out using a battery-testing system (Land CT2001A), at a current density of 0.3 mA cm⁻² (1.77 A g⁻¹), with a fixed specific capacity of 1000 mA h g⁻¹.

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