Design of Non-aqueous Liquid Electrolytes for Rechargeable Li-O₂ Batteries

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Liquid electrolytes for rechargeable Li-air batteries were chosen from viewpoints of the electrochemical stability against O_2 radical, O_2^- . Mulliken atomic charges of electrolyte solvents and their reversibility of O_2/O_2^- redox couple were first examined. In the carbonate-based electrolytes, the localization of positive charge in the molecules was confirmed, resulting in low reversibility of O_2 radical. The electrolytes must be decomposed by the nucleophilic O_2 radical. On the other hand, the nitrile-based and piperidinium-based electrolytes provided high O_2 radical reversibility because all of the atomic charges in molecules and cations were either negative or almost zero. It was found that the electronic distribution of electrolyte solvents affected their electrochemical stability against O_2 radical. Considering the electrolyte solvent in this study. The cell with piperidinium-based electrolyte achieved considerably low charging voltage of around 3.2 V and low voltage gap of about 0.75 V in the discharge-charge profiles, compared to conventional cells with carbonate-based electrolyte. It was, thus, concluded that the charging performances strongly influenced on the O_2 radical stability of electrolyte solvent.

Key Words : Li-O2 Battery, O2 Radical, Electrochemical Stability, Mulliken Charge

1 Introduction

Much attention has been devoted to develop rechargeable batteries with high energy density instead of graphite/LiCoO₂ based lithium ion batteries. Li-air battery is a promising candidate to realize such next generation batteries, because oxygen gas as a cathode active material can be continuously supplied from outside of battery, and furthermore, lithium metal anode with high theoretical capacity of 3860 mAh/g can be fully utilized. Since Abraham's group first demonstrated the rechargeability of Li-air battery in 1996,¹⁾ Read *et al.* and Kuboki *et al.* reported that the battery performances strongly depended on carbon materials and electrolyte solvents.²⁴⁾ In 2006, Bruce's group confirmed that the Li-O₂ cell with MnO₂ mixed cathode and carbonate-based electrolyte was discharged and recharged during 50 cycles.⁵⁾ They also found that the cell with no MnO2 catalyst was not repeatedly discharged and recharged.⁶⁾ Nowadays, many researchers have focused on carbon,⁷⁻¹⁰⁾ catalyst,¹¹⁻¹⁵⁾ electrolyte,¹⁶⁻²⁰⁾ Li anode^{21,22)} and O₂ gas²³⁻²⁵⁾ to enhance the discharge capacity, rechargeability and cyclability. Computational studies have been also carried out to estimate the theoretical potential of the battery²⁶⁾ and to understand the cathode reaction mechanism.²⁷⁻²⁹⁾ Moreover, using cyclic voltammetry and rotating disk electrode (RDE) technique, the oxygen reduction reaction (ORR) in non-aqueous systems has been intensively discussed.^{30,31)}

We have investigated the rechargeability and cyclability of Li-air batteries to be utilized as a secondary battery. In our previous report, the cell with carbonatebased electrolyte worked repeatedly for 100 cycles and maintained the capacity retention of over 60 $\%.^{\rm 32)}$ Considering the published data,^{5,6)} it was believed that the Li-O₂ batteries with non-aqueous electrolytes would behave as secondary ones. However, we found that unfavorable reaction products on a cathode were obtained during discharging and charging.³²⁾ According to our analyses of the reaction products, lithium peroxide (Li₂O₂) and lithium oxide (Li₂O) as expected compounds were not observed on a discharged cathode. Actually, lithium carbonate (Li₂CO₃) and lithium alkylcarbonate (R-O-(C=O)-OLi, R=alkyl group) were detected as discharged products. After charging, CO₂ gas was also generated by the decomposition of carbonate species. These products were formed by the decomposition of carbonate-based electrolyte solvents in discharging, because the discharged products were analogous in structure to the solvents. In general, O₂ gas dissolved in aprotic media is reduced via one-electron transfer process to form superoxide radical, which is abbreviated as O₂ radical and O_2^- . It was, thus, suggested that O_2 radical species such as O_2^- and LiO₂ were first formed in the carbonatebased electrolyte solvents and then decomposed the solvent themselves, forming carbonate species as discharged products. As a result, a large voltage gap of about 1.4 V in the discharge and charge profiles were necessary to decompose the carbonate species, which are also confirmed by many researchers.^{20,33,34)}

Recently, ether-based electrolytes such as dimethylether (DME) and tetraethyleneglycol dimethylether (TEG-DME) have been examined instead of carbonate-based electrolytes.^{19,34)} Although the electrochemical stability of those solvents against O₂ radical species and the existence of by-products such as carbonates are now open for discussion, it was observed that Li₂O₂ was formed as a main product after the initial discharging. This implies that the component of discharged products would strongly depend on the type of electrolyte solvents and their electrochemical stability. Katayama et al. have already reported that the electronic distribution of cations in ionic liquids influenced their electrochemical stability against O₂ radical.³⁵⁾ Takechi *et al.* also have investigated stable solvents against O₂ radical species by a novel nonelectrochemical screening technique using KO2 chemical.³⁶⁾ Design and selection of electrolyte solvents must be significant to control the cathode reaction in the Liair battery system and to enhance their battery performances.

In this paper, we focused on the electrochemical stability of electrolyte solvents under O_2 gas atmosphere. Various types of solvents were evaluated by combining molecular orbital calculation with cyclic voltammetry technique. In particular, the Mulliken atomic charge and reversibility of O_2/O_2^- redox couple were presented in the carbonate, nitrile and piperidinium based electrolytes. In addition, discharge-charge measurements were carried out to clarify the influence of electrolyte solvents on the voltage gap during discharging and charging. The relationship between the electrochemical stability of solvents and the discharge-charge performances will be also discussed.

2 Experimental

Among the battery grade organic solvents and ionic liquids, propylene carbonate (PC), acetonitrile (AcN), di-

methylether (DME), 1-ethyl-3-methylimidazolium bis(trifl uoromethansulfonyl)amide (EMITFSA) and N-methyl-Npropylpiperidinium bis(trifluoromethansulfonyl)amide (PP13TFSA) were selected as electrolyte solvents in this study. Tetraethylammonium bis(trifluoromethansulfonyl) amide (TEATFSA) as an electrolyte salt was used for cyclic voltammetry to evaluate the O_2 radical stability, while lithium bis(trifluoromethansulfonyl)amide (LiTF-SA) was used for discharge-charge measurements to check the cell performances. The concentration of electrolyte salt was arranged as described in the Figs. 2 and 3. Furthermore, the H₂O content in these electrolytes before and after O_2 gas bubbling was controlled to be less than 50 ppm by Karl-Fischer measurements.

Cyclic voltammetry was conducted with a potentio/ galvanostat (Solartron, 12608W) at room temperature. Glassy carbon rod and nickel ribbon were used as a working and counter electrode, respectively. The reference electrode consisted of a silver wire immersed in the acetonitrile solution with both 0.1 M tetrabutylammonium perchlorate and 0.01 M silver nitrate, which was separated from bulk solution with porous vycor glass. The potentials of this reference electrode in 0.1 M PC/ TEATFSA, 0.1 M AcN/TEATFSA, and pure PP13TFSA were respectively +0.187 V, +0.209 V and +0.07 V vs. ferrocene (Fc)/ferrocenium (Fc⁺). Oxygen gas with 99.99 % in purity was dissolved in the electrolyte by bubbling through a glass ball filter for 30 minutes under 1 atm at room temperature. The scan rate was 100 mV/sec.

Discharge-charge measurements were performed with a charge-discharge machine (Nagano, BTS2004H). Air cathode was composed of Ketjen Black, MnO_2 catalyst and PTFE binder with a weight ratio of 80 : 10 : 10. The



Fig. 1 Mulliken charges of carbon, nitrogen, oxygen, fluorine and sulfur atoms in the (a) PC, (b) AcN, (c) DME organic molecules, (d) EMI⁺, (e) PP13⁺ cations and (f) TFSA⁻ anion calculated by Gaussian 03 program with MP2/6-311G^{**} wave functions.

mixture was pressed by roll pressing to form a pellet, which was dried at 120° C overnight under vacuum. Lithium metal with 0.20 mm in thickness was used as an anode. Stainless steel disk and mesh were used as a current collector of anode and cathode, respectively. In a dry glove box filled with argon gas, these parts were set in our custom-made cell where the distance between anode and cathode is 5 mm. After the cell was put in a gas tight glass container, argon gas was completely replaced with pure oxygen gas at room temperature. The cell was discharged and recharged at the constant current density of 0.02 mA/cm² after holding for 3 h at a given temperature to dissolve oxygen gas into the liquid electrolyte.

Ab initio molecular orbital calculations were also carried out using Gaussian 03 program to estimate the electronic distribution of organic solvents and ionic liquids. The geometries of molecules were fully optimized at the HF/6-311G^{**} level. Then, the Mulliken atomic charges were accounted from the MP2/6-311G^{**} wave functions.



Potential [V vs. Ag/Ag⁺]

Fig. 2 Cyclic voltammograms of (a) PC/TEATFSA(0.1M), (b) AcN/TEATFSA(0.1M) and (c) pure PP13TFSA electrolytes saturated with pure O_2 gas. The voltammogram of AcN/TEATFSA(0.1M) saturated with pure Ar gas was also shown in the Fig. 2 (b).

3 Results and Discussion

First, the electronic distribution of electrolyte solvent molecules was examined to predict their electrochemical stability against O₂ radical. Figure 1 shows the calculated Mulliken charges at carbon, nitrogen, oxygen, fluorine and sulfur atoms for each electrolyte solvent as follows; (a) PC, (b) AcN, (c) DME molecules and (d) EMI^+ , (e) PP13⁺ cations and (f) TFSA⁻ anion. All the H atoms with positive charge are abbreviated. EMI⁺ cation had high positive charge at 2-position C atom, while PP13⁺ cation did not have at all atoms. TFSA⁻ anion also had high positive charge at all S atoms. Katayama et al. have suggested that high positive charge localized in the cations reduced the electrochemical stability against negatively charged O₂ radical anion in ionic liquids.³⁵⁾ EMITFSA ionic liquid was reported to be not stable against strong nucleophilic O₂ radical due to highly positive charge of EMI⁺ cation. It is, thus, speculated that the PP13TFSA ionic liquid would be stable against O2 radical. On the other hand, the carbon atom at 2-position in the PC molecule was charged to be highly positive, while all the atomic charges in the AcN and DME molecules were either negative or almost zero. Considering the speculation above, it is assumed that the PC molecule is not stable against O_2 radical, whereas the AcN and DME molecules are stable.

Next, in order to clarify the influence of the charge distribution for solvents on their O₂ radical stability, the reversibility of O_2/O_2^- redox couple was checked for three characteristic electrolyte solvents. Figure 2 shows the cyclic voltammograms of (a) PC, (b) AcN and (c) PP13TFSA based electrolyte solvents saturated with pure O_2 gas. The voltammogram of AcN saturated with pure Ar gas is also shown in the Fig. 2 (b). TEATFSA salt with a concentration of 0.1 M was dissolved in both PC and AcN solutions, while no salt was done in PP13TFSA. The potential was first swept from open circuit potential of around 0 V to -1.7 V vs. Ag reference electrode, and then it was reversed to anodic direction. In the voltammogram (b) of the AcN system, a pair of cathodic and anodic current peaks was observed at around -1.25 V under O₂ atmosphere, whereas no peak was obtained under Ar. As reported so far, 30,31,35) the cathodic and anodic peaks were respectively assigned to the one electron reduction of O₂ and oxidation of its reductant, O_2^- , which implies that the O_2/O_2^- redox reaction occurs in the AcN media with an ammonium salt. In addition, the ratio of the cathodic charge to the anodic one was approximately 1.0 as can be seen in the comparably symmetrical voltammogram, indicating that the strong nucleophilic O₂ radical is electrochemically stable in the AcN-based electrolyte. On the other hand, the different type of voltammogram was drawn in the Fig. 2 (a). In the PC-based electrolyte, the anodic peak due to the oxidation of O_2^- did not appear at around -1.1 V, although the cathodic peak at around -1.4 V was obtained. Instead of the oxidation peak, an irreversible anodic current of over 0.5 V was observed. Almost all O2 radical must be consumed on the ring opening reaction of PC solvent as described in the latest report.²⁰⁾ Carbon

atom at 5-position in the PC molecule is attacked by O₂ radical because the carbon atom at 2-position is surrounded by negatively charged triangular O atoms. As a result, alkylcarbonate species as by-products during O_2 reduction are formed, and then the carbonated species are easily oxidized and decomposed at higher anodic potential than 0.5 V. In other words, the PC solvent is instable against O₂ radical. Finally, the voltammogram in the pure PP13TFSA ionic liquid was described in the Fig. 2 (c). A redox couple with a comparably symmetrical curve was obtained, which is in good agreement with that of Fig. 2 (b). Compared with the voltamogram in the AcN-based media, the current density of O_2/O_2^- redox couple in the PP13TFSA media was guite small. This difference is considered to be caused by the viscosity of ionic liquid and its diffusion and solubility of O₂. The cells with PP13TFSA-based electrolytes will strongly affect the discharge capacity and rate capability. It is, however, found that the PP13TFSA ionic liquid is considerably stable against O₂ radical from viewpoints of the electronic distribution and O₂/O₂⁻ redox reversibility. Furthermore, the PP13TFSA ionic liquid is electrochemically and chemically stable against Li metal anode,³⁷⁾ although the AcN organic solvent is not. It is, therefore, summarized that the PP13TFSA ionic liquid as an electrolyte solvent is a promising candidate to create rechargeable Li-air batteries.

Here, the relationship between electronic distribution of electrolyte solvents and their reversibility of O₂/O₂redox couple is discussed. Based on the reported results of TFSA-based ionic liquids,³⁵⁾ some ionic liquids and organic solvents were examined in a similar way. It was confirmed that the reversibility of O₂ radical in the electrolyte solvents was closely related with their electronic distribution. In our consideration, it was also observed that the EMITFSA ionic liquid was not a comparably stable electrolyte solvent under O2 radical. However, according to another publication, the EMIBF₄ ionic liquid is reported to be stable against O₂ radical.³⁸⁾ The influence of water contamination on the ORR properties is also negligible in our study. It is suggested that the anion structure of ionic liquids might stabilize the electrolyte solvent molecules under the existence of O₂ radical. Further challenges to design the electrolyte solvents of Li-air batteries are now in progress.

Finally, using PC and PP13TFSA based electrolytes, the influences of electrolyte solvents on discharge-charge behaviors were examined. Figure 3 shows the first discharge-charge curves of Li-O₂ cells with 1 M LiTFSA/ PC and 0.32 mol/kg LiTFSA/PP13TFSA electrolytes. Thin and thick solid lines denote the cells with PC and PP13TFSA electrolytes, respectively. The applied temperatures were respectively set at 25 °C and 60 °C in the cells with PC and PP13TFSA electrolytes, because the LiTFSA/PP13TFSA electrolyte has much higher viscosity than LiTFSA/PC. The capacity was normalized by total weight of cathode. The cell with the PCbased electrolyte indicated a discharge plateau at around 2.7 V and a charge plateau of around 4.0 V, resulting in a large voltage gap of 1.3 V. On the other hand, in the cell with PP13TFSA-based electrolyte, a gradual voltage change from 2.8 V to 2.0 V was observed in discharging and a gradual change from 3.2 V to 3.8 V was also obtained in charging, which led to the voltage gap of about 0.75 V. Not only voltage gap but also charging voltage was decreased by choosing electrolyte solvents with high stability against O₂ radical. If the measured temperature in the cell with PP13TFSA-based electrolyte was set at room temperature, the discharge capacity was intensively decreased because of low O_2 solubility and diffusion in the electrolyte. However, almost the same trend, that is the lowering of charging voltage and voltage gap, was maintained. Figure 4 showed the capacity retention of the PP13TFSA-based Li-O₂ cell at 60° C. The discharge capacity was normalized by the 2nd discharge capacity. During cycling, the discharge and charge capacities were gradually decreased and the retention after 30 cycles was around 60 %. It was, also confirmed that the discharging and charging voltages did not change even if the cell was cycled. This means that almost the same cathode reaction would occur every cycle.

Here, the relationship between discharge-charge properties and electrolyte solvents is discussed. Laoire *et al.* have recently reported the ORR process in the aprotic media such as AcN and dimethyl sulfoxide (DMSO).³⁰⁾ O₂ dissolved in the electrolyte was first reduced to O₂ radical (O₂⁻) via one electron reduction, and then O₂⁻ chemically reacted with Li⁺ to form LiO₂ radical. After that, LiO₂ radical would change into Li₂O₂ via the disproportionation process. In the PC-based system, a discharge potential is derived from the formation of O₂ radical itself because the chemical decomposition of propylene carbonate due to radical species such as O₂⁻ and LiO₂ was dominant. However, in the PP13TFSA-based system,



Fig. 3 First discharge-charge curves of Li-O_2 cells with (a) PC/LiTFSA(1.0M) and (b) PP13TFSA/LiTFSA (0.32 mol/kg) electrolytes. The applied temperatures were respectively set at 25 °C and 60 °C in the cells with (a) PC and (b) PP13TFSA based electrolytes.

the above-referenced multiple cathode reactions occur because of no chemical decomposition of PP13TFSA solvent. Therefore, the gradual voltage change in discharging must be caused by a kinetically slow reaction process on a cathode. Furthermore, as can be seen in Fig. 2, the low diffusion and solubility of O₂ in the PP13TFSA ionic liquid would lead to high reaction resistance on a cathode, resulting in the ohmic discharge behavior. LiO₂ radical is also proposed to be highly reactive because LiO_2 is similar in structure to HO_2 radical as an intermediate during O_2 reduction in aqueous media. Not only $O_2^$ but also LiO₂ will have to be carefully checked in the future. On the contrary, the charging voltage in the PP13TFSA-based system was quite low and close to the theoretical potential, 2.96 V of Li₂O₂. The key point of improving the charging property is suggested to be the proper selection of electrolyte solvent and subsequent component of discharge products. PC solvent was considerably weak for radical species, resulting in the formation of carbonate species. Since the carbonate species needed comparably high voltage to be decomposed, high charging voltage and large voltage gap were required. Meanwhile, the PP13TFSA solvent stabilized radical species, and then Li_2O_x as discharged compounds would be formed. Thus, the charging voltage and voltage gap in the PP13TFSA-based cells must be lowered, compared to the PC-based cells. The gradual voltage change in charging will be related with the size and distribution of discharged products, because Li₂O_x as expected products is insulator. It is, thus, summarized that the electrolyte solvents intensively influence the discharge-charge characteristics of the Li-air batteries. Very recently, Shao-Horn's group have also succeeded in lowering initial charging voltage down to about 3.7 V by using Pt-Au alloy as a cathode catalyst, although the PC-based electrolyte was adopted.¹²⁾ Catalyst as well as electrolyte are thought to play an important role in decreasing the voltage gap and charging voltage. In the near future, the reaction scheme on a cathode will be clarified with the



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identification of discharged products, and furthermore, the requirements for catalysts will be discussed.

4 Conclusions

Li-air batteries with conventional carbonate-based electrolytes were repeatedly discharged and recharged, but a charging voltage was observed at around 4 V, resulting in a large voltage gap of 1.3 V in the dischargecharge profiles. The main reason for high charging voltage was suggested to be caused by the decomposition of carbonate solvents with O₂ radical species. In this study, in order to decrease both charging voltage and voltage gap, the electrolyte solvents with high electrochemical stability against O₂ radical were investigated. Molecular orbital calculation and cyclic voltammetry were performed as a screening method to select some candidates among all electrolyte solvents. In the carbonate-based system such as PC, a cathodic current due to O2 reduction was just obtained and the O_2/O_2^- redox reaction was not clearly observed. On the other hand, in the nitrilebased system such as AcN and piperidinium-based system such as PP13TFSA, the nice reversibility was observed with symmetrical voltammograms. These differences were explained using the electronic distribution of solvent molecules. In the PC molecule, a positive charge was localized at C atom, which led to the decomposition of the PC molecule due to strong nucleophilic O₂ radical. In the AcN molecule and PP13⁺ cation, all the atoms except for H atom were charged to either zero or negative, resulting in the stabilization of O₂ radical in the solvents. It was, thus, found that high electrochemical stability against O₂ radical was achieved in the electrolyte solvents where the positive charges were delocalized. In fact, the electrochemical and chemical stabilities against Li metal have to be considered to select the electrolyte solvents for Li-air batteries. In this study, the PP13TFSA ionic liquid was proposed as a candidate to examine the charging performances of the batteries. The cell with PP13TFSA-based electrolyte exhibited low charging voltage at around 3.2 V and furthermore low voltage gap of 0.75 V. The enhancement of charging properties was attributed to the O₂ radical stability of electrolyte solvents. It was, therefore, found that the design and selection of electrolyte solvents was an important key to improve Li-air rechargeable battery performances.

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Fig. 4 Cycle performance of the PP13TFSA-based Li- O_2 cell at 60 °C.

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