LiBr-coated Air Electrodes for Li-air Batteries

Yoshiya HAYASHI,a DOI Reo HONDA, Itsuki MORO,b§ Mika FUKUNISHI,b§§ Hiromi OTSUKA,c

Yoshimi KUBO,dDOI Tatsuos HORIBA,b§§ and Morihiro SAITO,b*,§§

© The Author(s) 2021. Published by ECSJ. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium provided the original work is properly cited. [DOI: 10.5796/electrochemistry.21-00096]

ABSTRACT

Li-air batteries (LAB) have a theoretical energy density as high as 3500 Wh kg⁻¹; however, many problems remain to be addressed before their practical application. Introduction of a redox mediator (RM) is commonly applied to reduce the high overpotential of the air electrode (AE) during the charge process. We try to fix an RM on the AE by coating it with a slurry of carbon black and binder on a carbon paper substrate to enable us not only to suppress the shuttle effect but also to concentrate the RM on the surface of the AE where it works. We use LiBr as the RM in this study and compare two types of LAB cells: one with a LiBr-coated AE and the other with LiBr dissolved in the electrolyte solution. The cell with the LiBr-coated AE exhibits a better cell performance than that with the dissolved LiBr.

The lithium-air battery (LAB) is one of promising next-generation batteries because of its theoretical energy density as high as 3500 Wh kg⁻¹. However, the battery still has some difficulties to be overcome in all of the main cell components: the air electrode (AE), lithium electrode, and electrolyte solution. If we focus on the AE, a large overpotential during charging is one of the most important issues. Introduction of a redox mediator (RM) by dissolving it into the electrolyte solution as a soluble catalyst is a common strategy to lower the overpotential. The RM usually reacts uniformly on the surface of the AE through an electrochemical oxidation of RM into RM⁺ followed by the chemical oxidation of Li₂O₂ to produce Li⁺, O₂, and RM. However, RM⁺ can also react with lithium metal when it diffuses and reaches the lithium electrode, which is called the shuttle effect, a type of self-discharge reaction to lose the charged capacity in vain.

In this study, we used LiBr as the RM because it exhibited excellent RM performance without any side reactions to decompose itself. Three types of LAB cells were compared in this study. The first was “no LiBr” cell as a reference that consisted of an AE coated on carbon paper (TGP-H-060, Toray Industries, Inc.), an electrolyte solution of 0.2 M lithium bis(trifluoromethanesulfonyl)imide/diethyleneglycol dimethyl ether (0.2 M LiTFSI/G2), and a Li metal negative electrode. The coated layer of the AE was prepared with carbon black (Ketjen Black (KB), Lion, Corp.) and polyvinylidene fluoride (PVDF) binder dispersed in NMP (N-methylpyrrolidone). The loading amount of KB was adjusted to be 1 mg cm⁻² and the ratio of KB/PVDF = 9/1 (m/m). The other two cells were almost the same as the no LiBr cell, except that they contained LiBr as an RM in different ways. The second cell was the “LiBr in EL” (electrolyte) cell, which employed 50 mM of LiBr contained in the 0.2 M LiTFSI/G2 base electrolyte solution. The third cell was the “LiBr on AE” cell, which contained LiBr in the slurry of KB-PVDF coated on carbon paper with the same amount of LiBr as that contained in 80 μL of the electrolyte solution of the LiBr in EL cell. Specifically, we coated 100 μmole of LiBr along with 50 mg of KB and PVDF binder on a 50 cm² (5 cm × 10 cm) piece of carbon paper to make the LiBr content in 2 cm² to be 4 μmole (= 50 mM × 80 μL). All electrodes for the cells were punched into pieces of 16 mm in diameter to have an area of 2 cm² and assembled into test cells in an air-tight metal case inserted by a separator (Celgard™ #2400) between an AE and a Li electrode in an Ar-filled glove box.

Discharge/charge cycle tests were carried out at a constant current density of 0.2 A (g-KB)⁻¹ with a constant capacity of 0.5 Ah (g-KB)⁻¹ in the voltage range of 2.0–4.5 V. Cyclic voltammetry of the cells was performed between 2.0 and 4.5 V at a scanning rate of 0.1 mV s⁻¹. Electrochemical impedance spectra were measured between 100 mHz and 100 kHz with a voltage amplitude of 20 mV. All cells for the electrochemical measurements were set in an isothermal chamber kept at 30 °C, and O₂ gas was supplied to the cell by the purge method. After cycle tests, the electrodes were taken out from the cell case and rinsed with G2 solvent in an Ar-filled
Figure 1. Discharge/Charge curves of each LAB cell: (a) no LiBr, (b) LiBr added in electrolyte solution, (c) LiBr coated on AE, and (d) cycle-variation of cell voltages at the 0.25 Ah (g-KB)$^{-1}$ point.

glove box for the surface to be observed and analyzed by scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM–EDS) using a JSM-7800F microscope (JEOL, Ltd.).

Figure 1 shows the discharge/charge cycle performance of the three types of LAB cells, where a better cyclability of the LiBr on AE cell, shown in 1c, was observed compared with that of the other cells, while that for the LiBr in EL cell, shown in 1b, was almost the same as the no LiBr cell, shown in 1a. These differences arose from the suppressed charge overvoltages for the LiBr on AE cell during the initial five cycles, as revealed in Fig. 1c. Moreover, the cell voltages at the point of 0.25 Ah (g-KB)$^{-1}$ in the discharge and charge process are plotted as midpoint voltages in Fig. 1d. The figure shows clear differences among the three cells: longer cyclability with suppressed charge overvoltages for the LiBr on AE cell and lower cyclability for the other two cells. Additionally, the LiBr in EL cell showed lower discharge voltages probably due to the shuttle effect of LiBr, which was also suggested by the unstable discharge voltages presented in Fig. 1b. Thus, different discharge/charge performances between the LiBr in EL and LiBr on AE cells were observed in spite of our concern about no difference being evident. We tried to elucidate the reason for this difference in the following sections.

First, cyclic voltammetry was applied to the three cells to elucidate the cause of the difference in the cycle test results shown above. Figure 2 shows the voltammograms measured under Ar and O$_2$ atmosphere. The no LiBr cell, shown in Fig. 2a, under Ar atmosphere showed only slight currents due to the double layer capacity between 2.5 and 4.0 V, while the LiBr in EL and LiBr on AE cells revealed definite and similar anodic current peaks between 3.5 and 4.0 V, which were ascribed to the following two oxidation reactions:

\[ 3\text{Br}^- \rightarrow \text{Br}_3^- + 2\text{e}^- \quad 3.6 \text{ V vs. Li/Li}^+ \]  
\[ 2\text{Br}_3^- \rightarrow 3\text{Br}_2 + 2\text{e}^- \quad 4.0 \text{ V vs. Li/Li}^+ \]  

The voltammograms under O$_2$ atmosphere, shown in Fig. 2b, revealed clear cathodic current peaks at approximately 2.5 V and anodic current peaks over 3.0 V. As for cathodic currents, the no LiBr cell showed the smallest current peak at approximately 2.2 V and the LiBr in EL cell showed a similar but slightly larger current peak. These cathodic currents were assigned to the following reaction:

\[ 2\text{Li}^+ + \text{O}_2 + 2\text{e}^- \rightarrow \text{Li}_2\text{O}_2. \]  

This cathodic peak was thought to arise from the coated LiBr, which enhanced the activity of Li$^+$ on the surface of the AE. As for the anodic current peaks, the no LiBr cell showed a clear current peak at approximately 3.4 V, which was assigned to the reverse reaction of Eq. (3). The LiBr in EL cell showed a slightly broader current peak at approximately 3.6 V, which was assigned to Eq. (1). The LiBr on AE cell showed the largest anodic current of the three cells between 3.0 and 4.5 V with double peaks at 3.4 and 3.7 V. Therefore, the anodic reaction was thought to consist of those for the no LiBr cell, by the reverse reaction of Eq. (3), and the LiBr in EL cell, by the reaction of Eq. (1). In other words, the LiBr-coated AE exhibited two kinds of active sites from the KB and LiBr, which caused the excellent performance of the LiBr on AE cell shown in Fig. 1. Moreover, the largest anodic current for the LiBr on AE cell over 4.0 V was ascribed to the reactions relating to Eq. (2).
Figure 3 shows the results for the electrochemical impedance measured for the three cells. Figure 3a shows that the impedance of the LiBr on AE cell in the discharged state after the 5th discharge was larger than that in the pristine cell and remained the same up to the 10th discharge. Figure 3b shows that the impedance in the charged state after the 5th and 10th charge was almost the same as that in the pristine cell. These results suggest that the electrode surface state remained steady up to the 10th cycle for the LiBr on AE cell. Slightly different results were exhibited by the other two cells. All results were analyzed into impedance elements by using the equivalent circuit shown in 3c. Figure 3d shows one of the analyzed results for the air electrode resistance \( R_{AE} \), in which the LiBr on AE cell showed regular reversible ups and downs of \( R_{AE} \), suggesting stationary discharge/charge reactions. However, the other two cells demonstrated similar but with some irregularities, which suggested changeable discharge/charge reactions and electrode surface conditions. Thus, the good reversibility of the LiBr on AE cell and less reversibility for the other two cells were well consistent with their different cyclabilities.

Figure 4 shows the surface morphologies of the three AEs after 10 discharge/charge cycles, which showed no serious difference among them, although clear cracks for the AE of the no LiBr cell should arise from the electrode preparation with a fluid slurry.

Tables 1 and 2 summarize the EDS analysis results for the AE and Li electrode surfaces after 10 cycles. In Table 1, the LiBr on AE cell showed that Br element apparently remained on the surface of the AE even after 10 cycles, though it might have been covered with a residual deposit. The AE of the LiBr in EL cell showed that a certain amount of LiBr in the electrolyte solution was trapped on the surface from the electrolyte solution during the cycling. Table 2 indicates that Br was captured on the Li electrode of the LiBr in EL cell while no Br was trapped on that of the LiBr on AE cell.
We analyzed the Br⁻ concentration in the electrolyte solutions of the cells after tests for 10 cycles by high performance liquid chromatography (HPLC: ion chromatography, ICS-2100, Dionex) to understand the results presented in Tables 1 and 2. Figure 5 shows the HPLC results. The pristine electrolyte solution of the LiBr in EL cell contained 50 mM of bromide ions as prescribed. However, the LiBr on AE cell showed about 5 mM or less of bromide ions from the pristine to 10 cycles after, although the loading amount of LiBr in the AE corresponded to 50 mM if all the LiBr dissolved into
the electrolyte solution of the test cell. It is, therefore, clearly shown that LiBr coated on the AE scarcely dissolved into the electrolyte solution during 10 cycles, which corresponded to at least 55 h. The limited dissolution of LiBr was presumably due to the binding by the PVDF binder and/or trapping in the micropores of KB with a high local concentration of LiBr in them. However, the real mechanism for the poor dissolution of LiBr still remains to be elucidated and how long the restricted dissolution continues before reaching equilibrium dissolution is another question from a practical point of view.

In spite of our initial concern, the LiBr on AE cell demonstrated not only suppression of the shuttle effect but also a better performance than the LiBr in EL cell as shown in Fig. 1, which was suggested to arise from the effect of catalytic activity of KB and LiBr as the RM, as evidenced by cyclic voltammetry. Electrochemical impedance analysis also supported the regular cyclability of the LiBr on AE cell. EDS analysis of the cell suggested less dissolution of LiBr into the electrolyte solution and this was confirmed by HPLC, which was also consistent with the cycle stability of the cell. Thus, coating LiBr on AE proved to deliver better results than dissolving it into the electrolyte solution.

However, further analyses of LiBr or Br, in both the AE and electrolyte solution, are essential to elucidate the mass balance of Br in the LiBr on AE cell during cycling and to confirm the merit of an RM-coated AE. Moreover, the data on cycle number or time dependency of the Br concentration were not sufficient to discuss the effect of the LiBr-coating on AE. In short, there are many things left to be addressed regarding the idea of an RM-coated AE. And we may be still at the entrance to full understanding of LiBr RM and the further studies on the mass balance of RM including the electrolyte solution consumption by decomposition in the LAB cells are now in progress.

Acknowledgment

This work was partly supported by the Japan Science and Technology (JST) Project for the Next Generation Batteries Area in Advanced Low Carbon Technology Research and Development (ALCA-SPRING JPMJAL1301), Japan.

Funding

Advanced Low Carbon Technology Research and Development Program: ALCA-SPRING JPMJAL1301

References

1. P. G. Bruce, S. A. Freunberger, L. J. Hardwick, and J. M. Tarascon, Nat. Mater., 11, 19 (2012).
2. G. Girishkumar, B. McCloskey, A. C. Luntz, S. Swanson, and W. Willeke, J. Phys. Chem. Lett., 1, 2193 (2010).
3. Y. Chen, S. A. Freunberger, Z. Peng, O. Fontaine, and P. G. Bruce, Nat. Chem., 5, 489 (2013).
4. B. J. Bergner, A. Schürmann, K. Peppler, A. Garsuch, and J. Janek, J. Am. Chem. Soc., 136, 15054 (2014).
5. N. Feng, X. Mu, X. Zhang, P. He, and H. Zhou, ACS Appl. Mater. Interfaces, 9, 3733 (2017).
6. H.-D. Lim, H. Song, J. Kim, H. Gwon, Y. Bae, K.-Y. Park, J. Hong, H. Kim, T. Kim, Y. H. Kim, X. Lepr, R. O.-Robles, R. H. Baughman, and K. Kang, Angew. Chem., Int. Ed., 53, 3926 (2014).
7. W.-J. Kwak, D. Hirsberg, D. Sharan, M. Afri, A. A. Frimer, H.-G. Jung, D. Aurbach, and Y.-K. Sun, Energy Environ. Sci., 9, 2334 (2016).
8. Z. Liang and Y.-C. Lu, J. Am. Chem. Soc., 138, 7574 (2016).
9. X. Xin, K. Ito, and Y. Kubo, ACS Appl. Mater. Interfaces, 9, 25976 (2017).
10. C. O. Laoire, S. Mukerjee, and K. M. Abraham, J. Phys. Chem. C, 113, 20127 (2009).
11. Z. Peng, S. A. Freunberger, L. J. Hardwick, Y. Chen, V. Giordani, F. Bardé, P. Novák, D. Graham, J.-M. Tarascon, and P. G. Bruce, Angew. Chem., Int. Ed., 50, 6351 (2011).
12. M. Saito, S. Kosaka, T. Fujinami, Y. Tachikawa, H. Shiroishi, D. Streich, E. J. Borg, P. Novák, and S. Seki, Electrochim. Acta, 252, 192 (2017).
13. D. A. Dornbusch, R. P. Viggiano, and V. F. Lvovich, Electrochim. Acta, 349, 136169 (2020).