Improved Water-stable Protected Anodes with Low Resistance for Aqueous Energy Storage Devices

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ABSTRACT

Multi-component anodes, fabricated by assembling lithium metal or pre-lithiated graphite negative electrode, a lithium-ion conducting solid electrolyte with water stability and a polymer or gel electrolyte in between the negative electrode and solid electrolyte, are promising as water-stable protected anodes for next-generation batteries and hybrid capacitors. By applying the protected anode to hybrid capacitors, operating voltage of 4 V can be achieved in aqueous electrolytes. However, the protected anode suffers from large resistance due to its multi-component structure, leading to insufficient power density and energy conversion efficiency. Here we analyze various protected anodes by using electrochemical impedance spectroscopy (EIS) to evaluate the bottleneck components in order to reduce the overall resistance. Protected anodes with different polymers or gel membranes, lithium salts and ionic liquid additives, negative electrode materials, binders, and solid electrolytes, were fabricated and the impedance components were analyzed. The resistance of the protected anode was successfully reduced by selecting proper materials.

1. Introduction

Lithium metal is one of the most promising negative electrode materials for rechargeable batteries since it has high theoretical capacity (3860 mAh g⁻¹) and a low electrode potential of −3.045 V versus standard hydrogen electrode. Due to its hygroscopic nature and instability in ambient atmosphere, protection of lithium metal from water is indispensable both for aqueous and non-aqueous lithium rechargeable batteries.1–4 Lithium metal can be protected from water by applying water stable solid electrolytes with Li⁺ conductivity and has been applied to aqueous Li-O₂ batteries.2–4 Such protected electrodes are often called water-stable protected lithium anodes or simply protected lithium anode.

The application of water-stable protected anodes has been recently expanded to aqueous hybrid capacitors which exhibit charge/discharge behavior typical of electrochemical capacitors.5,6 The adoption of aqueous electrolyte allows the use of pseudocapacitive positive electrodes (e.g. RuO₂ and MnO₂) with high specific capacitance,7–9 with the advantage of increasing the maximum operating cell voltage to 4 V instead of 1 V for pure aqueous electrolytes. However, owing to the multi-component structure, the total resistance of the protected anode is high and is not suitable for high power applications. In order to reduce the overall cell resistance of the 4 V aqueous hybrid capacitor, it is essential that the resistance of each component as well as interfacial resistance of the protected anode is reduced.

In this study, various protected anodes with different negative electrode materials, binders, polymer/gel electrolytes, as well as solid electrolytes, were prepared (Fig. 1). The resistance of the protected anodes was evaluated using electrochemical impedance spectroscopy (EIS). EIS provides valuable information regarding the resistive components and has been successfully used for analysis of Li ion batteries and electrochemical capacitors.10–12 The resistive components of the protected anodes were decomposed into multiple parts, bulk resistance from the electrolyte and inner-grain (R_bat), grain boundary resistance from both polymer/gel and solid electrolytes (R_gb), interfacial resistance between the negative electrode material, polymer/gel electrolyte and solid electrolyte (R_interface), and charge transfer resistance related to redox processes (R_o). Each component was analyzed to determine the performance dominating factors of the protected anode.

2. Experimental Methods

2.1 Materials

The Li⁺ conducting oxide-based solid electrolytes, LiₓTi2–x−yAlₓSiP3−x–yO12 (x ~ 0.25, y ~ 0.3), (LTAP, Ohara Glass Co., Inc.), with thickness of 50, 150 and 180 µm, were used as-received. Ionic liquids, 1-methyl-1-propyliperidinium bis(trifluoromethylsulfonyl)imide (PP13TFSI) and 1-methyl-1-propylpyrroldinidium bis(fluoro-rosulfonyl)imide (P13F3Si), and the supporting electrolytes, lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and lithium bis(fluoro-rosulfonyl)imide (LiFSI), were obtained from Kishida Chemical Co., Inc. Polyethylenoxide (PEO, average molecular weight: 6 × 10⁶) (Aldrich) or sodium alginate (Kimica Co., Inc.) were used to prepare polymer or gel membrane. Polyvinylidene fluoride (PVDF) (Alfa Aesar Co., Inc.) or alginate-based binder (iElectrolyte Co., Ltd.) were used as binder. Graphite powder (99.8%), 1-methyl-2-pyrrolidinide, and lithium sulfate were obtained from Wako pure chemical Co., Inc. All aqueous solutions were prepared by using ultrapure water (>18.4 MΩ cm).
2.2 Preparation of protected anode

The graphite electrode was prepared as follows. Graphite powder, acetylene black as a conductive additive, and PVDF or alginate-based binder were mixed with a mass ratio of 90:5:5 in 1-methyl-2-pyrrolidone. The obtained slurry was coated onto a copper foil by doctor blade method and dried for 1 h at 60°C and 16 h at 150°C under vacuum, and subsequently impregnated with lithium salt and ionic liquid under vacuum. The PEO polymer or alginate gel membrane and PEO-LiTFSI-BaTiO3 were prepared according to previously reported procedures.2,8,13,14 Ionic liquids with lithium based salts, LiTFSI/PP13TFSI or LiFSI/P13FSI, were impregnated under vacuum into the polymer or gel. The protected anode was obtained by laminating the three components, graphite or Li metal negative electrode, polymer or gel membrane doped with lithium salt and ionic liquid, and the LTAP solid electrolyte (Fig. 1). A 0.5 × 0.5 cm2 window was cut out from the aluminum film at the LTAP side to allow contact with the aqueous electrolyte.

2.3 Electrochemical impedance spectroscopy

EIS was conducted using a Solartron 1255B Frequency Response Analyser with a Solartron 1287 Potentiostat/Galvanostat. Measurements were conducted in a beaker-type cell with the protected anode as a working electrode and Pt electrode as a counter electrode in 1.0 M Li2SO4. The measurements were conducted by sweeping frequency from 1 MHz to 0.1 Hz at open circuit potential with an amplitude of 5 mV. The impedance data was normalized to the geometric area of LTAP exposed to the electrolyte (0.5 × 0.5 cm²). All experiments were conducted at 25°C.

3. Results and Discussion

3.1 Effect of lithium salts and ionic liquid additives to polymer or gel membranes

The interfacial resistance of the protected anode with different polymer or gel membranes, lithium salts and ionic liquid was studied. Ionic liquids, PP13TFSI and P13FSI, which were applied to aqueous hybrid capacitor in our previous report, were selected.5,9 EIS data of membranes were obtained by using a symmetric cell with Li as electrodes (Li | polymer or gel electrolyte | Li) (Fig. 2). First, BaTiO3-doped LiTFSI-impregnated PEO (PEO-LiTFSI-BaTiO3)2,15 is compared with LiTFSI/PP13TFSI-impregnated PEO (PEO-LiTFSI/PP13TFSI). The grain boundary resistance (Rgrain), which was estimated from the high frequency semicircle, decreased from 1.9 × 103 to 1.1 × 102 Ω cm², while the sum of the interfacial and charge transfer resistance (Rinterface + Rc-t) decreased from 7.6 × 103 to 3.1 × 102 Ω cm² by changing PEO-LiTFSI-BaTiO3 to PEO-LiTFSI/PP13TFSI, resulting in a 40% reduction of total resistance. Next, an alginate gel was selected to replace PEO polymer membrane. The total resistance of the LiTFSI/PP13TFSI-impregnated alginate gel (H+-Alg-LiTFSI/PP13TFSI) was smaller than that of PEO-LiTFSI/PP13TFSI, suggesting that Li ions can be transported into the structure of alginate gel more efficiently than that of PEO. The lower resistance for alginate gel than PEO may be attributed to more Li ion transportation paths in the alginate structure, which is a co-polymerized structure of δ-D-mannuronic acid and α-L-guluronic acid, than that in the PEO structure.16 In addition, lower viscosity and higher conductivity of alginate gel17 should also contribute to the reduction in resistance. The use of LiFSI/P13FSI further reduced the resistance, showing the lowest total resistance of the four polymer/gel membranes prepared in this work. Additionally, the higher ionic conductivities of the LiFSI-based electrolyte contributed to the resistance reduction compared with the LiTFSI-based electrolyte.18-20 It should be noted that the difference in the cations used in the formation of alginate gel, H+ and Ca2+, might influence the transportation efficiency of Li ions because the size of the vacancy for ion transportation paths depends on cross-linked alginate chain based on used cations.21,22 Thus Ca2+-Alg-LiFSI/P13TFSI was selected as a gel electrolyte in the following sections.
3.2 Lithium versus lithium pre-doped graphite negative electrode for protected anode

Next, Li metal or lithium pre-doped graphite (Li\textsubscript{x}C\textsubscript{6}) were examined as a negative electrode material. The electrochemical impedance spectra were obtained to analyze the resistance of the protected anode prepared with Li metal or Li\textsubscript{x}C\textsubscript{6} as a negative electrode in a beaker-type cell consisting of Li metal or Li\textsubscript{x}C\textsubscript{6} | Alg-LiFSI/P13FSI | Li\textsubscript{2}SO\textsubscript{4} | Pt (Fig. 3a). Based on the

![Figure 2](image1.png)

**Figure 2.** (a) Impedance spectra of various kinds of polymer or gel electrolyte membrane, (□) PEO-LiTFSI-BaTiO\textsubscript{3}, (△) PEO-LiTFSI/PP13TFSI, (○) H\textsuperscript{+}-Alg-LiTFSI/PP13TFSI and (◇) Ca\textsuperscript{2+}-Alg-LiFSI/P13FSI. The measurements were conducted at 25°C by using symmetric cell with Li electrodes (Li | polymer or gel electrolyte | Li). The equivalent circuit used to fit the experimental data is given in the inset. (b) Magnified view of the high-frequency region.

![Figure 3](image2.png)

**Figure 3.** Impedance spectra at 25°C of (a) (○) Li metal and (□) Li\textsubscript{x}C\textsubscript{6} | Alg-LiFSI/P13FSI | LTAP\textsubscript{150} | 1.0 M Li\textsubscript{2}SO\textsubscript{4} | Pt cell, (b) Li\textsubscript{x}C\textsubscript{6} combined with (△) PVDF and (◇) alginate-based binder | Alg-LiFSI/P13FSI | LTAP\textsubscript{150} | 1.0 M Li\textsubscript{2}SO\textsubscript{4} | Pt cell, and (c) Li\textsubscript{x}C\textsubscript{6} | Alg-LiFSI/P13FSI | (◇) LTAP\textsubscript{180}, (□) LTAP\textsubscript{150} and (△) LTAP\textsubscript{50} | 1.0 M Li\textsubscript{2}SO\textsubscript{4} | Pt cell. (d) Comparison of resistance of protected anode with different thickness of LTAP.
previously-reported literatures for the protected anode, the spectra were divided into four parts; high frequency resistance, two semicircles in the middle frequency region, and Warburg impedance at low frequency region. The spectra were analyzed and fitted with a nonlinear least-squares fit program based on an equivalent circuit previously reported for the protected anode.

The intercept of the high frequency semicircle with the real axis indicates the bulk resistance, \( R_{\text{bulk}} \). Which is a combination of the resistance of the aqueous electrolyte (negligible), inner-grain resistance of LTAP, and bulk resistance of the Alg-LiFSI/P13FSI membrane. The high frequency semicircles indicate the grain boundary resistance, \( R_{\text{grain}} \) of LTAP. The medium frequency semicircle is attributed to the sum of the interfacial resistance and charge-transfer resistance (\( R_{\text{interface}} + R_{\text{ct}} \)). \( R_{\text{interface}} \) is the interfacial resistance between the two phases, Li metal or Li\(_2\)C\(_6\) and Alg-LiFSI/P13FSI, as well as the interfacial resistance between Alg-LiFSI/P13FSI and LTAP. \( R_{\text{ct}} \) is the resistance associated with the reaction of Li dissolution/deposition or lithiation/de-lithiation of graphite.

The total resistance, \( R_{\text{total}} \), of the protected anodes using the Li metal negative electrode and Li\(_2\)C\(_6\) negative electrode were 347 \( \Omega \) cm\(^2\) and 148 \( \Omega \) cm\(^2\), respectively. The values of \( R_{\text{interface}} + R_{\text{ct}} \) were 249 \( \Omega \) cm\(^2\) for the Li metal negative electrode and 42 \( \Omega \) cm\(^2\) for the Li\(_2\)C\(_6\) negative electrode. The decrease in \( R_{\text{total}} \) matches the decrease in \( R_{\text{interface}} + R_{\text{ct}} \sim 200 \Omega \) cm\(^2\). This suggests that the interfacial contact between Li\(_2\)C\(_6\) and the gel membrane is much better than Li metal, which can be assumed to be a result of the higher contact area with particulate Li\(_2\)C\(_6\) compared with the flat surface of the Li foil.

As for binders, an alginate-based binder was employed assuming that the affinity with the alginate gel membrane would be better than PVDF. Figure 3b shows the impedance spectra of the protected Li\(_2\)C\(_6\) anode prepared with PVDF or alginate-based binder. The application of the alginate-based binder resulted in the significant reduction in the \( R_{\text{interface}} + R_{\text{ct}} \) by 73\%, owing to the structure of alginate being more interwoven with the alginate gel membrane. The decrease in resistance is attributed to the high affinity of alginate gel with Li\(_2\)C\(_6\) negative electrode.

3.3 Application of thinner solid electrolytes

The solid electrolytes protect the negative electrode from aqueous electrolytes, and should have high Li\(^+\) conductivity, low water permeability, and sufficient chemical stability. Naturally, thinner solid electrolytes should favor lower total resistance. The impedance spectra obtained by using three kinds of LTAP with thickness of 180 \( \mu \)m (LTAP180), 150 \( \mu \)m (LTAP150) and 50 \( \mu \)m (LTAP50) are shown in Fig. 3c. The grain-boundary resistance \( R_{\text{grain}} \) decreased from 114.4, 97.3 to 35.1 \( \Omega \) cm\(^2\) with the thinning of the solid electrolyte (Fig. 3d). The value of \( R_{\text{grain}} \) scales with the thickness of LTAP. The sum of interfacial resistance and charge transfer resistance \( R_{\text{interface}} + R_{\text{ct}} \) was almost constant regardless of the thickness since the value depended not on the thickness but the ionic conductivity of LTAP.

4. Conclusion

The resistive components of protected anodes for aqueous hybrid capacitors were analyzed by using electrochemical impedance spectroscopy. The total resistance of the protected anode was successfully decreased by changing the negative electrode materials, binders, the polymer/gel membranes, lithium salts and ionic liquids, and solid electrolytes. The selection and assembling of suitable components of the protected anode is very important to reduce the resistance. The best performing protected anode in this study (Li\(_2\)C\(_6\) | Ca\(^{2+}\)-Alg-LiFSI/P13FSI | LTAP30) had a total resistance of 92 \( \Omega \) cm\(^2\), 1/20 compared to 1220 \( \Omega \) cm\(^2\) for our initial protected anode (Li | PEO-LiTFSI-BaTiO\(_3\) | LTAP30).

Acknowledgments

This work was partially supported by an Advanced Low Carbon Technology Research Development Program of the Japan Science and Technology Agency (JST-ALCA, JPMJAL1008).

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