Graphical Abstract

Stable lithium electrodeposition in salt-reinforced electrolytes

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Abstract

Development of high-energy lithium-based batteries with good safety remains a challenge due to the non-uniform lithium electrodeposition during repeated charge and discharge cycles. We report on the effectiveness of lithium bromide (LiBr) salt in common liquid electrolyte (i.e. propylene carbonate (PC)) on the stability of lithium electrodeposition. From galvanostatic cycling measurements, we find that the

presence of LiBr in PC provides more than 20-fold enhancement in cell lifetime over the control LiTFSI/PC electrolyte. Batteries containing 30 mol% LiBr additive in the electrolytes are able to cycle at least 1.8 months with no observations of cell failure. From galvanostatic polarization measurements, electrolyte with 30 mol% LiBr shows a maximum improvement of lifetime. The formation of uneven lithium electrodeposits is significantly suppressed by the Br-containing SEI layers, evidenced by impedance spectra, post-mortem SEM and XPS analyses. The study also concludes that good solubility of halogenated salts is not necessary for achieving the improvements of cell lifetime.

Keywords

Lithium-metal battery; lithium bromide; dendrite; liquid electrolyte; electrodeposition

1. Introduction

In recent years, the urgency for renewable energy sources has increased for ideally zero emission vehicles (i.e. electric vehicles) or controlled emission vehicles (i.e. hybrid electric vehicles (HEVs) and plug-in hybrid electric vehicles (PHEVs)). Secondary lithium-based batteries have received intensive attention because of their high specific storage capacity on both a mass and volume basis. [1-3] Today's state-of-art lithium-ion batteries (LIBs) are operating close to their theoretical storage limits due to the low specific capacity of both the graphite carbon anode and lithiated cathode materials in current widespread use. A rechargeable lithium metal battery (LMB) that uses metallic lithium as the anode is attractive because use

of Li metal in place of carbon at the anode increases the anode theoretical capacity by a factor of 10 (from 360 mAh g⁻¹ to 3800 mAh g⁻¹). LMBs are attractive also because the lithium metal anode provides considerable flexibility in choosing the cathode from among a spectrum of high-energy non-lithiated materials such as sulfur, oxygen and carbon dioxide. It is understood however that significant improvement in the stability of lithium metal electrodeposition is needed for stable and safe cell operation. Indeed, although LMBs were among the first rechargeable lithium batteries discovered, they are not as widely used as lower-energy LIBs because of non-uniform lithium electrodeposition on the negative electrode, which exposes the cells to premature – even catastrophic – failure by dendrite induced short circuits. LIBs are designed to eliminate this problem by hosting lithium in a graphite material, but in practice a LIB can be transformed to a LMB by charging too fast or too much because the potential difference between lithium ion insertion and deposition is relatively small (<100mV) [1]. Thus, solving the dendrite problem is critical for both LMBs and LIBs.

Recent discoveries and advances have focused on electrolyte configurations that facilitate suppression or even elimination of dendrite formation. These efforts have so far achieved only limited success because of the inherently difficult transport processes that lead to dendrite nucleation and growth at the anode. A particularly persistent challenge concerns the difficult of achieving electrolytes that simultaneously allow high ionic conductivity and stable lithium electrodeposition. This difficulty has for instance prevented widespread use of many high-modulus polymeric materials or single-ion conductors that showed early promise. [4-9] Of the various options, electrolytes based on the ionic liquid platform seems to be the most promising to achieve liquid-like transport properties at room temperature as well as the ability to create a desirable solid electrolyte interface (SEI) [10-14]. Howlett et al [15], for example, reported that pyrrolidinium-based ionic liquid would initiate the formation of an inorganic compact lithium-salt layer (i.e. Li₂O, Li₂CO₃, LiOH and LiF) that covers the anode surface by reacting with lithium metal during the first few cycles. Such lithium salts, with a great proportion of LiF appear to be the reduction products of the ionic liquid (i.e. (TF)₂N⁻ anion) and lithium. LiF was detected by the authors to exist in the inner layer

of such films, close to the lithium metal surface, but the importance of this layer was until very recently not understood. As pointed out by Winter [16] and Park et al. [17], however, the electrolyte will continuously decompose owing to contact with fresh lithium surface through cracks in the SEI layer. Thus, a good SEI layer should be stable during the decompose-rebuild process for smooth lithium deposition. It should be both chemically and physically stable with favorable composition as well as unchanged thickness. To study the effect of LiF on lithium electrodeposition, we previously reported [18] electrochemical cycling and polarization studies in symmetric lithium metal cells employing electrolytes with controlled levels of LiF salt. In particular, we found that by employing lithium fluoride-reinforced liquid electrolyte, the cycle life of a rechargeable lithium battery can be extended by a factor of 10 or more, which is even longer than the cells with any previously reported ionic liquid-based electrolyte[10,14]. Adding lithium fluoride salt to conventional liquid electrolytes (i.e. PC, ethylene carbonate: diethylene carbonate (EC:DEC)) was argued to spontaneously create favorable passivation layers on the lithium anode which facilitate stable lithium deposition, minimizes reaction with the electrolyte, and boost the cell safety over extended cycling. The study also suggested that the presence of other lithium halide salts in liquid electrolytes should also yield large improvements in smoothening lithium electrodeposition by similar mechanism.

Herein, we report on LiBr-containing liquid electrolytes using PC as the liquid host and study their effect on lithium metal electrodeposition and dendrite suppression in rechargeable LMBs. We show that both the stability of lithium electrodeposition and cell lifetime are significantly improved by addition of LiBr salt to a liquid electrolyte. We also find that LiBr in the electrolytes forms favorable SEI layers, which lead to smooth lithium electrodeposition. In addition to these benefits, our results suggest that good solubility of halogenated lithium salts in electrolyte solvents is not necessary for achieving stable lithium electrodeposition in LMBs.

2. Experimental

2.1 Preparation of electrolytes

Predetermined quantities of LiBr salts with and without Lithium bis(trifluoromethane sulfonyl) imide (LiTFSI) were dissolved in PC. If LiTFSI was added, the total lithium salt concentration in the electrolyte was kept at 1M (i.e. $(1-y)$ LiTFSI + y LiBr in PC); otherwise, the lithium salt concentration was determined by the amount of LiBr (i.e. y M LiBr in PC). All materials used for the study were dried rigorously by previous reported method [10].

2.2 Electrochemistry measurements

Lithium metal foil of a thickness of 0.75mm was used as received from Alfa Aesar (99.9%, metals basis). The symmetric lithium metal coin cell was assembled in an argon filled glovebox (MBraun. Labmaster). Symmetric lithium-metal coin cells (2032 type) were used for dielectric spectroscopy, impedance spectroscopy, and galvanostatic cycling and polarization measurements. Dielectric loss of all electrolytes were measured as a function of frequency (10^7 - 10^{-1} Hz) in a step heating procedure (-5, 10, 25, 40, 55, 70, 85, 100 °C, see supporting information Fig. S1) using a Novocontrol N40 broadband dielectric spectrometer equipped with a liquid cell containing copper electrodes. The galvanostatic cycling and polarization measurements were conducted using a Neware CT-3008 battery tester. Impedance spectra were measured as a function of frequency (3×10^6 - 10^{-1} Hz) using impedance spectrometer.

2.3 Electron microscopy measurements

For post-mortem studies, cells were disassembled in an argon-filled glovebox and the lithium metal electrodes were harvested and rinsed thoroughly with PC before the analyses. Lithium metal electrodes were analyzed using scanning electron microscopy (SEM, LEO1550-FESEM) and X-ray photoelectron spectroscopy (XPS). The composition profiles of Br, C, F, Li and O in the electrode were characterized using a Surface Science Instrument SSX-100 with operating pressure approximately 10^{-8} Torr.

Monochromatic Aluminum K-alpha X rays (1486.6eV) were used with a beam diameter of 1mm and photoelectrons were collected at a 55-degree emission angle. A hemispherical analyzer determined the

electron kinetic energy, using a pass energy of 150V for wide/survey scans, and 50V for high resolution scans. Samples were etched using 4kV Argon ions over a 2×4 mm area with 5 microamp beam current. A flood gun was used for charge neutralization of non-conductive samples. The PC wash step was not employed for electrodes analyzed using energy dispersive X-ray detector (EDX).

3. Results and Discussion

Electrolytes were prepared by blending predetermined amounts of LiBr salt, LiTFSI salt in PC liquid host. Electrolytes with equivalent concentrations of LiBr salt were studied in two different systems: with LiTFSI and without LiTFSI. LiTFSI salt, if doped, was kept the total Li cations in the electrolyte constant at 1M. For simplicity, the electrolytes appear in the form of y M LiBr/PC (without LiTFSI) and 1M (1- y) LiTFSI + y LiBr/PC (with LiTFSI), where y is the mole fraction of LiBr in the electrolyte. LiBr additive has greater solubility than the previous reported LiF salt dissolved PC at room temperature [18], and was used as conductive lithium salt in liquid electrolytes in early studies [19,20] (also see supporting information Fig. S2), which allows us to test the stabilization provided by halogenated lithium salts in a more typical case. Fig.1 reports the DC conductivities for y M LiBr/PC and 1M (1- y) LiTFSI + y LiBr/PC electrolytes as a function of mole amount y M of LiBr salt in the electrolytes. It indicates that by adding LiTFSI salt, the electrolyte conductivity is enhanced by an order of magnitude (i.e. from 10^{-3} to 10^{-2} S cm $^{-1}$). For 1M (1- y) LiTFSI + y LiBr/PC systems, the conductivities are almost identical when $y < 0.1$ and fall with increasing LiBr fraction, meaning that the addition of LiBr reduces the lithium salt dissociation and the mobile ion concentration, relative to LiTFSI. For y M LiBr/PC electrolytes, the conductivities are also similar when $y < 0.1$ and increase by doping LiBr salt. It exhibits an acceptable room-temperature conductivity of 4×10^{-4} S cm $^{-1}$ for moderate LiBr content (i.e. $y=0.3$), which is suitable as room-temperature electrolytes for lithium batteries and therefore was chosen for galvanostatic cycling measurement in this study.

Fig. 2 shows the lithium electrodeposition in both electrolytes using galvanostatic cycling of symmetric lithium metal cells. Three-hour interval of strip/plate was chosen to allow enough lithium to transport between electrodes, and therefore short-circuit could be observed from the voltage profile if dendritic bridges form. To eliminate other possible barrier, a separator is not included in the measurement so that the only resistance is from the liquid electrolyte. Fig. 2(a) displays the voltage profiles of electrolytes with and without LiBr at fixed current density of 0.4 mA cm^{-2} . The electrolyte without LiBr is less stable and shows irreversible voltage increase after 60h (10 cycles) while the one with 30 mol% LiBr can cycle stably for at least 1290h (215 cycles, 1.8 months) without cell failure. The battery operation time is enhanced at least 22 times by the addition of LiBr in liquid electrolyte. Fig. 2(b) and (c) show voltage profiles of electrolytes without LiTFSI at the same current density as Fig. 2(a). With lower ionic conductivities and less mobile lithium ions, the two voltage profiles show higher steady-state voltages. In both cases y M LiBr/PC with y=0.3 and 1), the cells show no evidence of failure during the measured 1290h. However, the stability of the cycling is essentially reduced by the absence of LiTFSI since the steady-state voltage plateau is less smooth and stable. Fig. 2(d)-(f) are the results of the same measurements of those in Fig. 2(a)-(c) but with a high current density of 0.6 mA cm^{-2} . Fig. 2(d) shows that the cell with the control LiTFSI/PC electrolyte fails quickly whereas the one containing LiBr in the electrolyte sustains at least 300h. Fig. 2 (e) and (f) show the instabilities of battery cycling with only LiBr in the electrolytes. Such instability might come from two possible factors: the low ionic conductivity of LiBr system without LiTFSI and the instability of LiBr at high voltages. Electrochemical stability of LiBr-containing electrolytes was characterized by cyclic voltammetry and the result was reported in Fig. S3. The LiBr system shows a low oxygenation voltage at around 2.5V. It indicates that additives with wide electrochemical stability window are necessary for cycling batteries with LiBr-containing electrolytes.

The morphologies of the lithium metal electrode surface harvested from galvanostatic cycling measurements are analyzed by scanning electron microscopy. Fig. 2(g)-(i) show the lithium surface

before cycling, after cycling for 100h in PC/LiTFSI electrolyte, and after cycling for 1200h in (1-y) LiTFSI + y LiBr/PC with y=0.3, respectively. The lithium electrode contact with the control PC/LiTFSI electrolyte forms needle-like nanostructures growing towards the other electrode while the lithium surface contact with LiBr-containing electrolyte forms mossy-structured lithium electrodeposits. The results demonstrate that the voltage instabilities observed in Fig. 2(a) is probably due to the dendrite-induced short-circuit and the improved stability is from the addition of LiBr.

Fig. 3 provides additional details about the effectiveness of LiBr-containing electrolytes for extending cell lifetime by galvanostatic polarization measurement, an aggressive and accelerated method. The lithium metal was continuously stripped from one side and plated on the other side at a fixed current density. A sudden drop-off in the voltage indicates the failure of the cell operation, and provides an estimate for the cell lifetime. Note that only systems with LiTFSI were studied to enable high-current density measurement due to the relatively low conductivity of pure LiBr electrolytes. Fig. 3(a) compares the cell lifetime of 1M (1-y) LiTFSI + y LiBr/PC electrolytes with y=0.3 at low (i.e. 0.03 mA cm^{-2}) and moderate (0.07 mA cm^{-2}) current densities. It is extended from 400h to 950h by reducing the operating current density. Fig. 3(b) shows the impedance spectra of the three stages (s1: before polarization, s2: during steady state, s3: after cell short-circuit) for electrolyte systems in Fig. 3(a). In both current densities, the bulk impedances during steady state are similar to the one at initial stage while the interfacial impedances increase before reaching steady state, suggesting the formation of SEI layers. After the cell short-circuit, both bulk and interfacial impedances reduce, indicating the appearance of lithium dendritic bridges between electrodes, also evidenced by the SEM observation (inset, Fig. 3(a)). Fig. 3(c) and (d) report the short-circuit time (T_{sc}) as a function of LiBr mole fraction and as a function of current density (J), respectively (also see Fig. S4). At both low current density and moderate current density, the effect of LiBr-containing electrolytes reaches a maximum lifetime extension at 30 mol% of LiBr dopant. At 30 mol% LiBr, the cell lifetime is 23 times longer than the control LiTFSI/PC system. For high LiBr mole fraction ($> 50\%$), the operation time is reduced, probably due to the low conductivity and the poor

dissociation of LiBr salt in PC. As shown in Fig. 3(d), LiBr-induced electrolytes show 10-fold or more improvements in cell lifetime over the control LiTFSI/PC electrolyte. Electrolytes with 30 mol% LiBr exhibit comparable lifetime enhancements with the previous reported 30 mol% LiF systems [18]. The results indicate that both LiBr and LiF have the ability of stabilizing lithium electrodeposition in good or poor electrolyte solvents and that solubility of halogenated lithium salt is not a requirement for achieving this effect.

Fig. 4 reports the post-mortem X-ray photoelectron spectra (XPS) of lithium metal electrodes harvested from the above galvanostatic polarization measurements for 1M (1-y) LiTFSI + y LiBr/PC electrolytes with y=0.3. The element signals were identified by the characteristic binding energy. Fig. 4(a)(b) and Fig. 4(c)(d) show the Br, C, F, Li, and O signals at different depth (deep to 195nm, approximately) starting from the anode surface before polarization and after short-circuit respectively. Bromide depth profile in Fig. 4(a) and (b) indicates that the LiBr salt distributes uniformly on the surface of the lithium electrode before polarization whereas the Br signals in Fig. 4(c) and (d) show the Br exists in the inner layer (at least up to 195nm) of the lithium electrode after the polarization measurement. The results indicate that the LiBr salt or other Br-containing SEI components are perhaps close to the lithium metal surface, relative to other SEI components.

4. Conclusions

We report on LiBr-containing liquid electrolytes for LMBs and their effect on lithium dendrite suppression. We show that batteries with LiBr-containing electrolytes are able to cycle at least 1.8 months with no observations of cell failure or dendrite-induced short-circuit. We also find that LiBr-containing electrolytes exhibit maximum improvements in dendrite suppression at 30 mole fractions of LiBr salt. Compared with the control LiTFSI/PC system, electrolytes with 30 mol% LiBr as the lithium salt provide more than 20-fold improvements in cell lifetime. The morphologies of lithium metal after cycling show that LiBr in the electrolytes facilitate smooth lithium electrodeposition, and thus retard the dendrite-

induced cell short-circuit. By analyzing SEI on the anode surface, we show that SEI components that contain Br exist in the inner layers of the SEI, close to the lithium metal surface. The results conclude that LiBr in liquid electrolytes can effectively suppress lithium dendrites and favor the stability of lithium electrodeposition.

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Fig. 1. Direct current conductivities as a function of temperature for y M LiBr/PC electrolytes (without LiTFSI, open symbols) and for 1M (1- y) LiTFSI + y LiBr/PC (with LiTFSI, filled symbols). The open symbol values are results for LiBr/PC electrolytes with an equivalent LiBr concentration as the LiBr+LiTFSI/PC systems.

Fig. 2. Voltage versus time for a symmetric lithium cell with each half-cycle lasts 3h. (a) Voltage profiles for 1M (1-y) LiTFSI + y LiBr/PC with y=0.3 (black) and y=0 (red) at a fixed current density of 0.4 mA cm⁻², (b) Voltage profile for y M LiBr/PC with y=0.3 at a fixed current density of 0.4 mA cm⁻², (c) Voltage profile for y M LiBr/PC with y=1 at a fixed current density of 0.4 mA cm⁻², (d) Voltage profiles for 1M (1-y) LiTFSI + y LiBr/PC with y=0.3 (black) and y=0 (red) at a fixed current density of 0.6 mA cm⁻², (e) Voltage profile for y M LiBr/PC with y=0.3 at a fixed current density of 0.6 mA cm⁻², (f) Voltage profile for y M LiBr/PC with y=1 at a fixed current density of 0.6 mA cm⁻², (g)-(i) SEM analyses: (g) Lithium anode before galvanostatic cycling, (h) Lithium anode in contact with 1M (1-y) LiTFSI + y LiBr/PC with y=0 after 100h at 0.4 mA cm⁻², (i) Lithium anode in contact with 1M (1-y) LiTFSI + y LiBr/PC with y=0.3 after 1200h at 0.4 mA cm⁻².

Fig. 3. Galvanostatic polarization measurements for symmetric lithium metal cells. (a) Voltage versus time profiles for 1M (1-y) LiTFSI + y LiBr/PC electrolytes with y=0.3 at fixed current densities of 0.03 and 0.07 mA cm⁻², and the inset SEM image shows the morphology of lithium anode after cell short-circuit at 0.07 mA cm⁻², (b) Impedance spectra of the three stages (s1: before polarization, s2: during steady state, s3: after cell short-circuit) for electrolyte systems in (a), (c) Short-circuit time (T_{sc}) as a function of LiBr mole percentage at 0.03 and 0.07 mA cm⁻², (d) T_{sc} as a function of current density (J) for 1M (1-y) LiTFSI + y LiBr/PC electrolytes with y=0, 0.1, 0.3.

Fig. 4. Post-mortem XPS analyses of lithium metal electrodes harvested from galvanostatic polarization measurements for 1M (1-y) LiTFSI + y LiBr/PC electrolytes with y=0.3. (a) Bromide signals at different layers of the lithium anode surface before polarization measurement. (b) Atom percent of Br, C, F, Li, and O at different layers before polarization measurement, (c) Bromide signals at different layers of the lithium anode surface after short-circuit, (d) Atom percent of Br, C, F, Li, and O at different layers after short-circuit.