

Mixed LiTFSI and LiBOB salts for high-temperature LiFePO₄-based lithium-ion battery

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The salt LiPF₆ in commercial lithium ion batteries (LIBs) suffers from hydrolysis and thermal instability. The hydrogen fluoride (HF) and POF₃ (a strong Lewis acid) formed from the hydrolysis reaction of LiPF₆ as well as the PF₅ (another strong Lewis acid) generated from the thermal decomposition of the salt can lead to undesired side reactions such as corrosions to the solid electrolyte interface, cathode active materials (leading to elemental dissolution in cathode) or hardware of the cell. Thus a lithium salt, which is highly stable against water and temperature, is very important to lengthen the lifetime of LIBs. The extended lifetime of LIBs will result in lower cost in practical applications.

LiTFSI [lithium bis(trifluoromethanesulfonyl)imide, Li(CF₃SO₂)₂] is a promising electrolyte salt for LIBs to replace the current LiPF₆ salt because of its high thermal stability and good tolerance to water. However, the positive electrode current collector (Al foil) corrodes about 3.7 V vs. Li/Li⁺ when the LiTFSI is used as electrolyte salt¹⁻³. Many attempts have been made to suppress the corrosion of Al foil in LiTFSI-containing electrolytes. Matsumoto et al. found a passivation film composed of LiF was formed on aluminum to prevent aluminum corrosion after potential was applied at higher LiTFSI concentrations³. The addition of LiPF₆ or HF could also lead to the formation of LiF passivation layer. A very effective passivation film can also form on aluminum foil by adding LiBOB [lithium bis(oxalate) borate, LiB(C₂O₄)₂] into electrolytes⁴⁻⁸ though the mechanism remains unclear. However, few efforts have been made to study the passivation effect of LiBOB on the suppression of the corrosion of cathode current collector in a real cell with active materials coated on aluminum foil, especially at elevated temperatures (i.e. 60°C).

In this work, mixed salts of LiTFSI and LiBOB were investigated. The high temperature performance of LiFePO₄ cathode is significantly improved at 60°C after introducing LiBOB into LiTFSI electrolyte.

Figure 1 shows the optical images of Al foils from Li|Al cells polarized at 3.9 V for 5 hrs. When using the control LiTFSI-based electrolyte containing no LiBOB, the Al foil (Figure 1c) corroded and broke into pieces. In the LiTFSI-LiBOB co-salt-based electrolyte, the Al foil (Figure 1d) kept intact without any observable sign of corrosion comparing to the fresh Al foil (Figure 1a). In comparison, the Al foil in the LiPF₆-based control electrolyte shows a little bit corrosion (Figure 1b). This result does prove that the addition of LiBOB as a co-salt can stabilize Al foil in LiTFSI-based electrolytes by forming an effective passivation layer.

Further study shows the Li|LiFePO₄ cells using

1M LiTFSI-LiBOB based electrolyte can be cycled in the

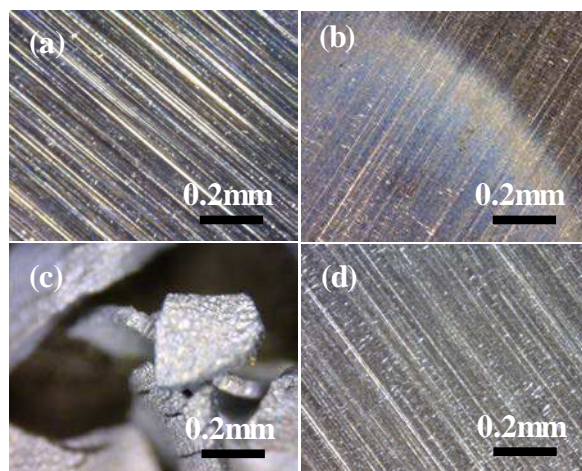


Figure 1. Image of (a) fresh aluminum foil and aluminum foils treated at 3.9 V for 5 days in (b) pure LiPF₆ based electrolyte, (c) pure 1M LiTFSI based electrolyte and (d) 1M LiTFSI-LiBOB based electrolyte

voltage range of 2.8 V to 3.9 V more than 100 cycles with a capacity fade about only 1.5% at 60°C, while the control LiTFSI electrolyte even cannot be cycled at room temperature. In contrast, the Li|LiFePO₄ cell with 1M LiPF₆-based electrolyte is not cycle-able at 60°C.

1. H. Yang, K. Kwon, T. M. Devine, and J. W. Evans, *Journal of The Electrochemical Society*, **147** (12), 4399-4407 (2000).
2. M. Morita, T. Shibata, N. Yoshimoto, and M. Ishikawa, *Journal of Power Sources*, **119-121** (0), 784-788 (2003).
3. K. Matsumoto, K. Inoue, K. Nakahara, R. Yuge, T. Noguchi, and K. Utsugi, *Journal of Power Sources*, **231** (0), 234-238 (2013).
4. S.-T. Myung, H. Natsui, Y.-K. Sun, and H. Yashiro, *Journal of Power Sources*, **195** (24), 8297-8301 (2010).
5. D.-T. Shieh, P.-H. Hsieh, and M.-H. Yang, *Journal of Power Sources*, **174** (2), 663-667 (2007).
6. K. Xu, S. Zhang, T. R. Jow, W. Xu, and C. A. Angell, *Electrochemical and Solid-State Letters*, **5** (1), A26-A29 (2002).
7. S. S. Zhang, *Journal of Power Sources*, **162** (2), 1379-1394 (2006).
8. X. Zhang and T. M. Devine, *Journal of The Electrochemical Society*, **153** (9), B365-B369 (2006).