

Attenuation of Aluminum Corrosion in LiTFSI Electrolyte Using Silica Nanoparticles

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Introduction

Aluminum foil is widely used as a cathode current collector in commercial lithium-ion batteries since Al foil is mechanically strong, light, thin, and can form a protective passive oxide film.¹ Lithium hexafluorophosphate (LiPF₆) is commonly used as a lithium salt in lithium-ion batteries, but LiPF₆ reacts with H₂O to yield HF and thermally decomposes to LiF and PF₅.

Lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) is superior to LiPF₆ with respect to its thermal and hydrolytic stability.² However, use of LiTFSI in Li-ion batteries is problematical since the aluminum current collector undergoes corrosion in LiTFSI electrolytes.¹ We report here an attenuation effect of silica nanoparticles on aluminum corrosion in a LiTFSI electrolyte.

Experimental

The liquid electrolyte consists of poly(ethyleneglycol)dimethylether (PEG-dM, MW=250, Aldrich) + lithium bis(trifluoromethylsulfonyl)imide (LiTFSI, 3M) with a Li:O mole ratio of 1:20 to reach the highest conductivity.³ The composite gel electrolytes were prepared by dispersing 10 wt% fumed silica nanoparticles A200 or R805 (Degussa) into the liquid electrolyte. The primary particle size of silica is about 12 nm. The R805 fumed silica contains octyl surface group at ~48% coverage and silanol surface group at ~52% coverage, and the A200 fumed silica contains only native silanol on the surface. Al foil (Fisherbrand®, thickness 24 μ m) was punched into half-inch disk for use. Coin cells of Li/electrolyte/Al were assembled in an argon-filled glove box.

Results and Discussion

Linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) were used to study Al corrosion in LiTFSI electrolytes. The working electrode was Al foil and the counter and reference electrode was Li metal. The sweep rate for the LSV experiment was 5 mV/s, and the voltage range was from 2 to 5 V. The response current density of liquid electrolyte is higher than those of gel electrolytes for both 10% A200 and 10% R805 (Figure 1). The impedances of gel electrolytes change less than those of liquid electrolyte (Figure 2). The data indicate that the gel electrolyte may have the ability to attenuate aluminum corrosion in LiTFSI electrolytes. The enhanced stability of Al is suggested to be affected by the silica nanoparticles scavenging impurities such as water and oxygen, which is the same effect seen in the interfacial stability with lithium.⁴ Silica nanoparticles form three-dimensional continuous networks by self-assembly in liquid electrolyte. The composites exhibit desirable mechanical properties characteristic of solids (elastic

modulus $G' > 10^5$ Pa),⁵ which may also be helpful to attenuate Al corrosion.

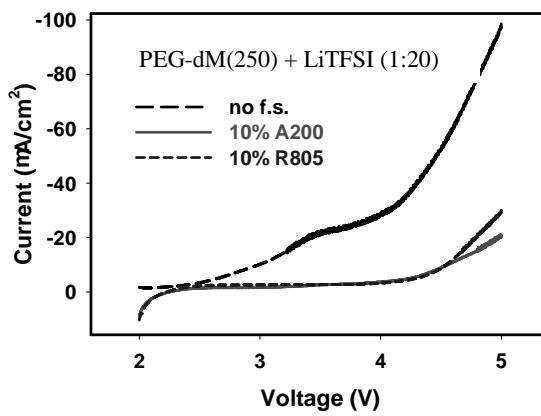


Fig 1. LSV response for Li/Electrolyte/Al cells at a sweep rate of 5 mV/s.

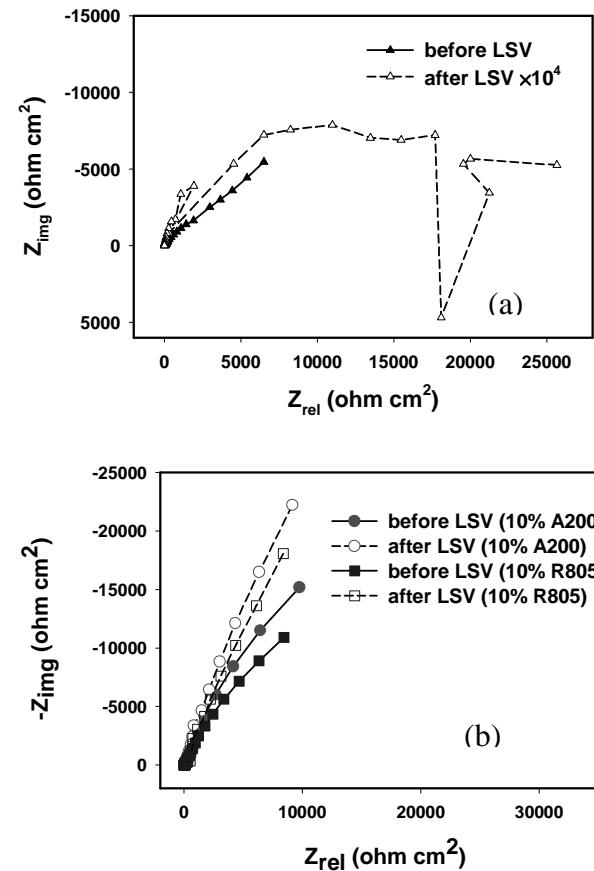


Fig 2. Impedance of Li/Electrolyte/Al cells before and after LSV: (a) liquid and (b) gel electrolytes.

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