

Investigation of Aluminum Corrosion in Non-aqueous Solvent/Electrolyte Systems

Mateusz L. Hupert and Greg M. Swain

Department of Chemistry
Michigan State University
East Lansing, MI 48824

Aluminum is the most commonly used current collector material for the positive electrode in lithium-ion cells.¹ Aluminum is used mainly because of its low cost, low density, ductility and good resistance to oxidation due to the natural, protective oxide layer. It is still, however, susceptible to environmental degradation in the organic electrolytes typically used in lithium-ion cells.² The concern over corrosion stems from the fact that the current collectors are relatively thin (25-50 μm). Considering the high cell voltages and the long cycle life desired, corrosion and degradation of current collectors may likely become a dominant failure mechanism in future Li-ion batteries. Therefore, understanding the nature of aluminum corrosion in non-aqueous electrolytes is an important issue.

Our recent studies have been focused on investigating the susceptibility of aluminum to oxidation (formation of a passivation layer) and/or corrosion (pitting and metal loss) in three electrolyte/solvent mixtures: $\text{LiClO}_4/\text{EC-DMC}$, $\text{LiPF}_6/\text{EC-DMC}$ and $\text{LiBF}_4/\text{EC-DMC}$. Measurements were conducted on aluminum electrodes with an intact oxide layer on the surface or with a purposely damaged oxide layer. The influence of water contamination was also studied through the addition of controlled amounts of water to solvent/electrolyte mixture.

It was found that aluminum, with an undamaged oxide film, is resistant to corrosion in all three electrolytes. During anodic polarization (up to 5 V vs. Li/Li^+) only a small oxidation charge was observed during the first anodic scan in all three electrolytes. Thereafter, the surface was passivated and very little current flowed during subsequent cycles. Electrochemical quartz crystal nanobalance (EQCN) measurements were consistent with the oxidation charge being associated with the formation of a mixed aluminum oxide and hydroxide layer, as the apparent molecular weight to charge ratios (W/z) were in the range from 8–17. In LiPF_6 and LiBF_4 , XPS indicated elevated F levels consistent with the formation of an oxyfluoride layer. Both optical microscopy (OM) and AFM revealed no noticeable structural changes of the surface.

Water contamination had a significant effect on the corrosion of aluminum in $\text{LiClO}_4/\text{EC-DMC}$. At low water concentrations (< 200 ppm), a significantly increased oxidation charge was observed. This charge was accompanied by increase in electrode mass as indicated by EQCN. OM and AFM revealed the formation of mounds on the surface. The mounds were filled with corrosion products and entrapped solvent molecules, as revealed by Raman spectrometry and EDS.

In the case of the fluorinated electrolytes, both mechanical damage of the protective oxide layer and

water contamination did not cause significant corrosion. The increased oxidation charge was accompanied by an increased electrode mass and surface passivation. W/z ratios were in the range of 8-18.

In summary, obtained results indicate that:

1. None of the studied solvent/electrolyte systems is corrosive toward aluminum in a water-free environment, at least up to 5 V vs. Li/Li^+ .
2. Anodic polarization in $\text{LiClO}_4/\text{EC-DMC}$ in the presence of added water, causes pitting and progressive corrosion.
3. Anodic polarization in $\text{LiPF}_6/\text{EC-DMC}$ and $\text{LiBF}_4/\text{EC-DMC}$, in the presence of added water, does not cause pitting and corrosion. The surface remains effectively passivated by an apparent oxyfluoride layer.

References

1. J. R. Owen, *Chem. Soc. Rev.*, **26**, 259 (1997).
2. P. Arora, R. E. White, M. Doyle, *J. Electrochem. Soc.*, **145**, 3647 (1998).