

### Inhibition Of Lithium Dendrites In Composite Polymer Electrolytes Based On Mixed-Molecular Weight Polyethylene Oxides And Fumed Silica

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Lithium metal is of interest as a negative battery electrode because of its high-negative potential and large theoretical specific capacity. However, dendrites formed on the lithium electrode surface during charge can lead to a gradual fade of anode capacity, or worse, the short-circuiting of cells. The suppression of dendrite formation is a significant challenge in the development of lithium batteries [1]. A possible approach to mitigate dendrite formation is to disperse nanometer-size fumed silica particles into mixed-molecular weight (MW) polyethylene oxide (PEO)-based polymer electrolytes to form a continuous network. Earlier research in our laboratory shows that the resulting composite electrolytes combine the high conductivities of gel-like systems with the mechanical stability of thermoplastic polymers, yet maintains electrochemical stability [2]. In this communication, we report *in-situ* microscopic observation of dendrite formation in fumed silica-based mixed-MW polymer composite electrolytes. The baseline polymer electrolyte was PEO (MW 600K, Dow) + polyethylene glycol dimethyl ether (PEGdm, MW 250, Aldrich) (weight ratio = 1:1) + lithium bis(trifluoromethylsulfonyl)imide ( $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ , LiTFSI, 3M), where the Li:O ratio is 1:20. Two types of fumed silicas (Degussa) with differing surface groups were used: A200 (hydrophilic, native silanol) and R805 (hydrophobic, octyl group at ~48% surface coverage).

Figure 1 shows dendrites formed at 65 °C in mixed-MW polymer and composite electrolytes at 0.2 and 1 mA  $\text{cm}^{-2}$  (3.6 C  $\text{cm}^{-2}$ ; nominal Li thickness of 5  $\mu\text{m}$ ). In the absence of fumed silica, the dendrites are bright and have particle-like morphology at 0.2 mA  $\text{cm}^{-2}$  (Figure 1a), but the dendrites become black and present tree-like morphology at 1 mA  $\text{cm}^{-2}$  (Figure 1d). Considering that the nominal thickness of lithium for 3.6 C  $\text{cm}^{-2}$  is 5  $\mu\text{m}$ , the dendrites formed in polymer electrolytes have a noncompact structure. Dendrite formation has been related to the current fluctuation on the non-uniform passivation layer at the electrode/electrolyte interface.<sup>3</sup> From Figure 1, it is seen that the addition of fumed silica greatly inhibits dendrite formation at both current densities. Dendrite inhibition can be attributed to the ability of fumed silica i) to form a continuous network with elastic-like properties and ii) to scavenge impurities from the electrolyte. It is also seen that hydrophilic A200 has a better effect in inhibiting dendrite formation than hydrophobic R805, especially at 1 mA  $\text{cm}^{-2}$ . The improvement is believed to be associated with the higher capacity of A200 to scavenge impurities, which results in an improved electrode/electrolyte interface and reduced current fluctuation.

One consequence of dendrite growth is the short-circuiting of cells if dendrites cross through the inter-electrode gap. Figure 2 shows the short-circuit times ( $t_{\text{sc}}$ ) for mixed-MW polymer and composite electrolytes at 0.2 mA  $\text{cm}^{-2}$ . For comparison, the  $t_{\text{sc}}$  values for low-MW

liquid and composite electrolytes are also shown in Figure 2 [4]. It is seen that the  $t_{\text{sc}}$  values of mixed-MW polymer and composite electrolytes at 65 °C are larger than those of their corresponding low-MW liquid and composite electrolytes at 25 °C, indicating that the former electrolytes have better dendrite inhibition ability than the later ones. However,  $t_{\text{sc}}$  of mixed-MW electrolytes decreases greatly at 80 °C. From Figure 2, it is also seen that addition of fumed silica increases  $t_{\text{sc}}$ , with A200 having a more pronounced effect than R805. These results agree with the dendrite observations.

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#### References

1. M. Dollé, L. Sannier, B. Beaudoin, M. Trentin, and J.-M. Tarascon, *Electrochem. Solid-State Lett.*, **5**, A286 (2002).
2. S.A. Khan, P.S. Fedkiw, and G.L. Baker, *Composite Polymer Electrolytes*, BATT Review Meeting, LBL, (2003).
3. P.C. Howlett, D.R. MacFarlane, and A.F. Hollenkamp, *J. Power Sources*, **114**, 277 (2003).
4. X.W. Zhang, Y.X. Li, S.A. Khan, and P.S. Fedkiw, *J. Electrochem. Soc.*, 2004, In press.

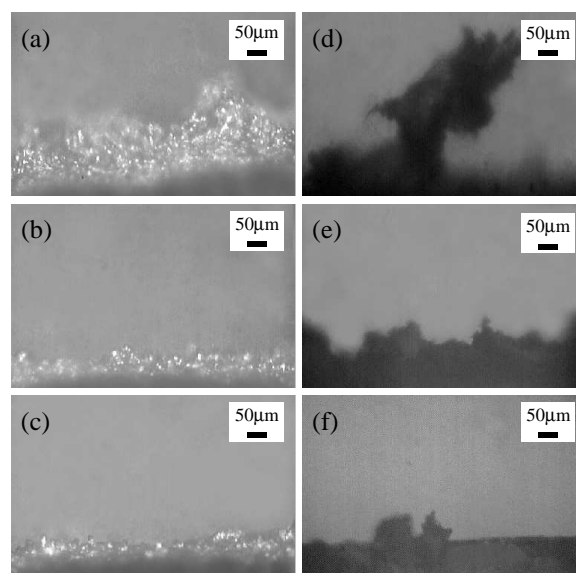


Figure 1. Micrographs of lithium dendrites (3.6 C  $\text{cm}^{-2}$ ) formed at 65 °C in mixed-MW polymer and composite electrolytes: (a, d) filler free; (b, e) 10 wt % R805; and (c, f) 10 wt % A200. Current density: 0.2 mA  $\text{cm}^{-2}$  (a,b,c) and 1 mA  $\text{cm}^{-2}$  (d,e,f).

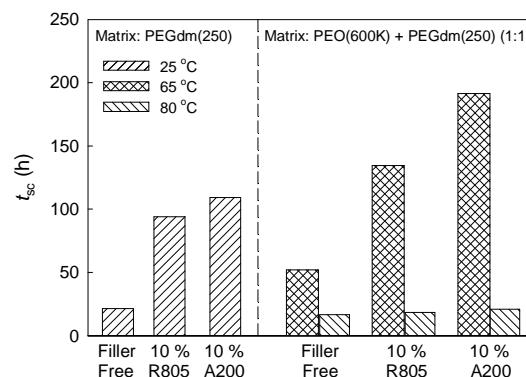


Figure 2. Short-circuit times  $t_{\text{sc}}$  for fumed silica-based low-MW and mixed-MW composite electrolytes and their corresponding liquid or polymer electrolytes. Current density: 0.2 mA  $\text{cm}^{-2}$ .

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