

Short Communication

The Anodic Passivation of Lithium

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The present work shows that the phenomenon of anodic passivation, well-known with metals like Fe, Co, and Ni in neutral and acidic aqueous solution [1] with Zn in aqueous alkali [2] and with Pb in aqueous sulfuric acid [3] occurs also with Li in electrolytes appropriate to room temperature Li batteries. Above a certain critical, controlled current density, a Li anode suffers eventual passivation. This terminates the anode's useful life and forces its voltage to high positive values where anode substrate or anolyte species are oxidized. We present here preliminary data in two electrolytes and briefly discuss the implications of these findings for the safety and efficiency of Li batteries.

Test cells were made of Pyrex and contained about 100 cc of electrolyte under a positive pressure of dried argon. Lithium test electrodes were made by pressing Li onto Stainless Steel (304) substrates. They faced upwards towards counter electrodes of bare SS304. The reference electrode was made by plastering Li over the tip of a 1/8" SS 304 rod. The 1 M LiClO_4 in propylene carbonate (PC) was made up from its constituents whereas the 1.5 M $\text{LiAlCl}_4\text{-SOCl}_2$ solution was bought from Lithium Corpo-

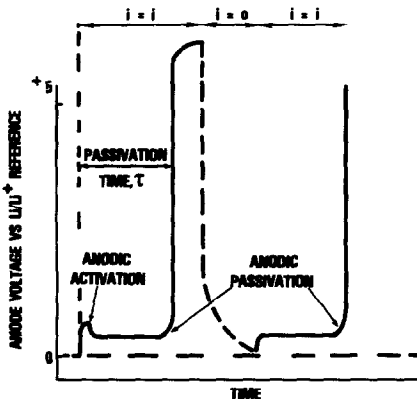


Fig. 1. The anodic passivation of lithium at constant current.

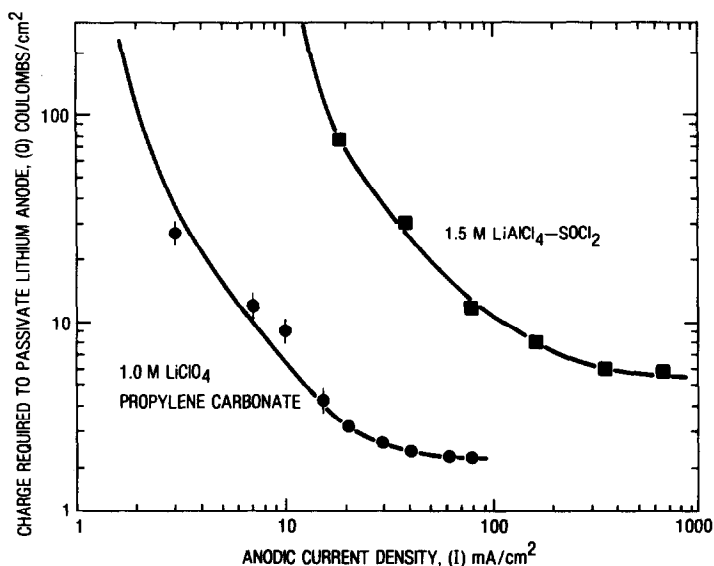


Fig. 2. Charge needed to anodically passivate Li in two unstirred electrolytes at 24 °C.

ration of America (contained 5 ppm Fe). Electrode preparation and cell assembly were carried out in a dryroom maintained at 0.4% relative humidity. Discharge curves were recorded at constant current, anodic to the test electrode. The behavior illustrated in Figs. 1 and 2 persisted, essentially unchanged, if Ni were substituted for SS304 in electrode hardware; for Li test electrodes from 0.1 to 10 cm² in area; at both recessed (shielded) and unrecessed Li; when catholyte was segregated from anolyte; irrespective of the presence of water and heavy metal ions.

Figure 1 shows typical results. The first curve in a series of runs sometimes contains the peak labeled 'anodic activation' where anodic current is disrupting a passivating film of Li salt responsible for the well-known 'voltage delay' effect. Then after a plateau at the Li voltage, anodic passivation occurs and anode voltage rises to a second plateau where the steel substrate and/or anolyte species are oxidized. It should be emphasized that anodic passivation is quite distinct from the well-known chemical passivation of Li. In Fig. 1, the same anodic current that eliminates chemical passivation during the 'anodic activation' peak subsequently engenders anodic passivation after the transition time. The voltage transition is not due to the complete consumption of Li because a few minutes wait at open-circuit suffices to depassivate the surface and the process can then be repeated as in Fig. 1 to give a fairly reproducible τ . Figure 2 shows passivation charge ($Q = i\tau$) vs. current density for Li in two electrolytes at room temperature in unstirred solution. Under these conditions, Li does not passivate below 1 and 10 mA cm⁻² in PC and SOCl₂, respectively. With rising current-density, Q falls, then levels off at 2 and 6 C cm⁻². So, in this region, τ varies inversely with current as though a discrete film were being formed on the Li surface. These limiting

charges are, however, very much larger than would correspond to monolayer coverage ($\sim 0.2 \text{ mC cm}^{-2}$). Preliminary data show passivation charge to be relatively insensitive to electrolyte impurity content but to have a pronounced dependence on the diffusion/convection conditions. This suggests that enrichment and eventual precipitation of the electrolyte salt may be passivating the anode. Work is underway to confirm this.

Anodic passivation has implications for the safety and efficiency of Li batteries. It represents a Li battery failure mode that has not previously been recognized; the Li anode has generally been assumed to be inherently efficient at high current-densities [4]. However, anodic passivation limits Li anode utilizability at high current densities. At 20, 100, and 625 mA cm^{-2} in neutral $\text{SOCl}_2\text{-LiAlCl}_4$, the Li passivates after 65 min, 100 s and 9 s corresponding to 78, 10, and 5.6 C cm^{-2} or a 0.11, 0.014 and 0.008 mm depth of Li respectively. As thinner, catalyzed carbons [5] provide higher cathode rates, this anode limitation will assume greater importance. The effect is, of course, much less restrictive if anode use is confined to a pulse mode where enough time is left between pulses to allow depassivation. Anodic passivation has relevance to Li battery safety because it has been reported that anode-limited Li-SO₂ [4] and Li-SOCl₂ [5] cells can vent or explode when driven into voltage reversal, especially if metallic Li remains at the failed anode. These conditions are obviously present in cases of anodic passivation.

Acknowledgement

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