

Anodic Polymerization of Vinyl Ethylene Carbonate in Li-Ion Battery Electrolyte

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Electrolyte additives are an important part of Li-ion battery technology yet their role in the battery chemistry is often not understood. Although there are numerous compounds in the patent literature that are claimed to have such properties, only a few have been studied and discussed in publications. The electrochemical reduction of additives such as VC and VEC has been studied in some detail¹⁻³. However, these studies have focused on the reduction chemistry of VC and VEC without discussing the anodic stability of the additive. In the present work, we report on a study of the anodic oxidation of vinyl ethylene carbonate (VEC) by electrochemistry and spectroscopy.⁴ We show the half-wave potential ($E_{1/2}$) for oxidation of VEC is ca. 3.6 V producing a resistive film on the electrode surface

Figure 1 (insert) shows the potential responses of an Au electrode, in 1.2 M LiPF₆/ethylene carbonate (EC) and ethyl methyl carbonate (EMC) (3:7 w/w) with 2 wt. % VEC and without VEC, after a current-step from open circuit to a constant anodic current of 10 μ A. When the electrode potential reached 4.1 V, it was held at this potential and the anodic current was measured until it dropped to a nominally low level (2 μ A). In the absence of VEC (solid line), the potential reached 4.1 V within 15 min, while with VEC added (dashed line) it required 35 min. On subsequent holding at 4.1 V, the current decayed to 2 μ A in 25 min. in the VEC-free electrolyte, with a total anodic charge of 3.1 μ Ah. On the other hand, in VEC containing electrolyte, the current decay required 200 min., and the total charge passed was 17.7 μ Ah, more than 5 times greater.

The chemical nature of the film on the Au electrode after anodization in electrolyte with VEC additive was investigated in more detail by ATR-FTIR and gel permeation chromatography (GPC). GPC analysis of the film on a gold electrode produced by anodization of a commercial Li-ion battery electrolyte containing 2 % VEC at 4.1 V showed the presence of polymers with a very wide molecular weight distribution. The FTIR spectra presented in Fig. 2a and 2b indicated these high molecular weight polymers are consisted of polycarbonate rings linked by aliphatic methylene and methyl branches.

We show that during the formation cycles VEC is anodically polymerized at the cathode, producing a resistive film on the active material. The cyclic voltammograms (CV) with and without 2% VEC reveals that the half-wave potential ($E_{1/2}$) for oxidation of VEC is ca. 3.6 V vs. Li/Li⁺.

References

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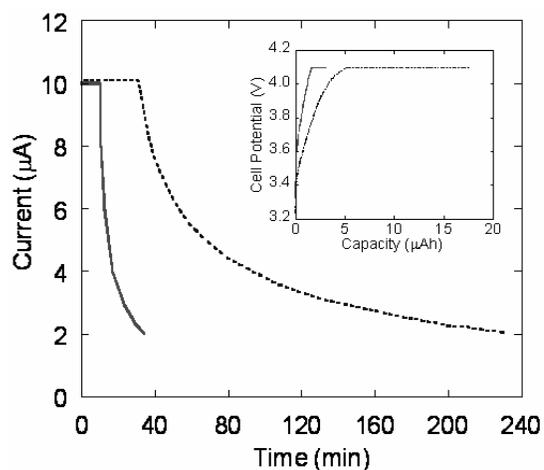


Figure 1. Time profiles of constant current followed by constant voltage anodization of the electrolyte using an Au foil electrode: solid line the Gen2 electrolyte and the dashed line representing with 2% VEC added. Insert: integrated charge.

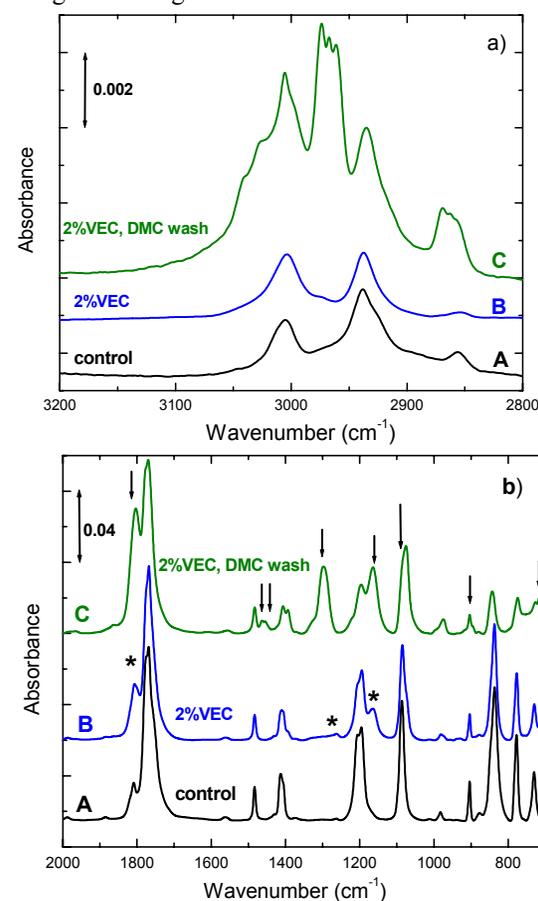


Figure 2. IR spectra obtained in the ATR mode from: A) electrode after anodization at 4.1 V in Gen2 electrolyte without VEC (control sample) without washing; B) after anodization in electrolyte with VEC additive without washing; C) after washing with DMC. All spectral regions were scaled with the intensity of carbonyl peak in the 1800 cm^{-1} region.