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

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Abstract

A study of the anodic oxidation of vinyl ethylene carbonate (VEC) was conducted with post-mortem analysis of reaction products by ATR-FTIR and gel permeation chromatography (GPC). The half-wave potential ($E_{1/2}$) for oxidation of VEC is ca. 3.6 V producing a resistive film on the electrode surface. 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 a high molecular weight polymer. IR analysis indicated polycarbonate with alkyl carbonate rings linked by aliphatic methylene and methyl branches.

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Introduction

Electrolyte additives are an important part of Li-ion battery technology yet their role in the battery chemistry is often not understood. Prominent among these additives are those that appear to improve the selectivity of the electrolyte reduction chemistry on graphite electrodes, allowing the use of propylene carbonate (PC) based electrolytes versus the more established ethylene carbonate (EC) based electrolytes. PC based electrolytes are attractive for automotive applications in particular because of their superior low temperature conductivity [1-3]. 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. Examples are ethylene sulfite [4], and the unsaturated carbonates vinylene carbonate (VC) [5-10] and vinyl ethylene carbonate (VEC) [11-12]. The electrochemical reduction of both VC and VEC has been studied in some detail, including quantum chemical calculations of the energetics that identified the most probable reaction pathway [13-14]. Both VC and VEC appear to be reduced at potentials above 1.0 V (vs. Li/Li^+) and form a passivating film that prevents solvent co-intercalation and exfoliation of the graphite at lower potentials [6-7, 11]. However, these studies have focused on the reduction chemistry of VC and VEC without discussing the anodic stability of the additive. The chemical stability of VC is a concern [5], and the stabilizers typically added to VC have oxidation potentials in the 3.5 – 4.0 V region. Hu et al. [11] proposed that VEC was more stable than VC and demonstrated that it functioned successfully as a film forming additive in PC based electrolyte. Vollmer et al. [12] examined the reduction chemistry of EC, PC and VEC using quantum chemical Density Functional Theory and concluded that the reduction potential of VEC is ca. + 1 V

more positive than that of EC or PC, indicating that VEC would probably be preferentially reduced to form a passivating film. VEC was, therefore, studied as an additive to the GEN2 electrolyte in the U.S. Department of Energy Advanced Technology Development (ATD) program. Descriptions of the ATD program [15] and cell chemistry [16] have been reported previously, along with a number of post-mortem diagnostic studies [16-18].

In the present work, we report on a study of the anodic stability of VEC additive after finding some anomalous characteristics in the 18650 cell with the 2 wt% VEC additive. As with other cells in the ATD GEN2 program, the cell was assembled and pre-conditioned at Quallion and shipped to LBNL in the fully discharged state. Prior to shipping to LBNL, the cell was discharged to 2.7 V at the C/1 rate. The cell was opened as-received in a glovebox at LBNL and individual components removed for diagnostic analysis. During FTIR analysis of the graphite anode, we noticed that it was unusually (versus baseline Gen 2 anodes) reactive and possibly still contained active lithium, as confirmed by fast growth of significant thick Li_2CO_3 layer upon expose to air. This was in fact found to be the case, as we report here, on subsequent studies of the chemistry of VEC that caused this anode to contain residual lithium after a C/1 rate discharge to 2.7 V. We show that during the formation cycles VEC is anodically polymerized at the cathode, producing a resistive film on the active material. This may result in polarization and incomplete discharge at the relatively high C/1 rate. The anodic instability of VEC would appear to disqualify it as an effective electrolyte additive for high rate Li-ion battery applications.

Experimental

The anode, composed of 92 wt.% Mag-10 graphite (Mitsubishi) and 8 wt.% polyvinylidene difluoride (PVDF) binder, was harvested from an ATD 18650 Li-ion cell that was assembled and went through formation at Quallion. Prior to shipping to LBNL, it had been discharged at C/1 rate to 2.7 V. This particular cell had been assembled using electrolyte: 1.2 M LiPF₆ in ethylene carbonate (EC) and ethyl methyl carbonate (EMC) (3:7 w/w) (denoted as Gen2 electrolyte) with 2 wt. % vinyl ethylene carbonate (VEC). The residual discharge capacity, i.e. electrochemically active Li content, of the harvested anode (1.4 cm dia., 1.6 cm²) was measured in Gen2 electrolyte with Celgard 3401 (25 μm thick, Celgard Inc.) as the separator (1.9 cm dia., 2.8 cm²), Li metal as a counter and reference electrode, stainless steel current collectors (1.9 cm dia.) and a polypropylene union fittings (Cole-Parmer). A slight axial pressure was applied to the test electrode by an internal, stainless steel spring (0.95 cm dia.). The cell was assembled in a He-filled glove box with oxygen content < 1 ppm and water < 5 ppm. Residual lithium was extracted from the graphite anode at a constant current of 10 μA (C/40 rate) until its potential reached 1.0 V. The electrode was then recharged to 20 mV at a C/25 rate, and finally discharged again at 10 μA to determine its nominal (low rate) capacity.

A gold (Au) inert electrode (99.999%, 1 mil thick, 1.4 cm dia.) was used to study the electrochemical properties of the VEC additive. Two identical “Swagelok™”-type cells were assembled in the glovebox, with Celgard 3401 separators (1.9 cm dia.) and Li metal (1.9 cm dia.) as counter and reference electrodes. The cells were cycled in Gen2 electrolytes with or without 2 wt.% (0.2 M) VEC (Aldrich, >99 %), under otherwise identical conditions. A constant current of 10 μA was applied to each cell until the

potential of the Au electrode reached 4.1 V, and the potential was then held at 4.1 V until the current dropped below 2 μA . After one hour at open circuit potential, the cells were disassembled in the glovebox. The separators were peeled from the Au electrodes and the volatile EMC component was allowed to evaporate in the glove box prior to FTIR analysis. As a control, another Au electrode was simply stored in Gen2 electrolyte for several days in the glovebox, then dried and analyzed in the same manner as the electrode from the cells.

The Au electrodes were transferred from the glovebox to the helium-purged sample chamber of the FTIR spectrometer using a portable vacuum carrier. The measurements were performed on the sample surface, before and after rinsing with dimethyl carbonate (DMC), in attenuated total reflection (ATR) mode as described in Ref. 18. All spectra were acquired at a resolution of 4 cm^{-1} , and were summed over 512 scans.

Cyclic voltammetry (CV) was carried out using an EG&G 273A potentiostat, at 10 mV/s scan rate between 3.0 – 4.1 V, in a single-compartment three-electrode cell in the glovebox. The glass cell was sealed to prevent evaporation of the volatile electrolyte components. The working electrode was Au foil (1 cm x 1.5 cm), counter and reference electrodes were 1.5 mm thick Li foil.

For gel permeation chromatography (GPC), the film was solvent-stripped from the Au surface with DMC. After allowing the DMC evaporate in glove box, the gel like substance thus obtained was further diluted in tetrahydrofuran (THF) for GPC analysis. The molecular weights of polymers were determined by gel permeation chromatography (GPC) using a PLgel 20 μm Mixed B column and an Agilent 1100 Series differential

refractometer detector at 40° C. The lower mass detection limit for this detector is about 700 amu. THF was used as the eluting solvent at a flow rate of 0.33 mL/min, and monodisperse polystyrene standards were used to calibrate the molecular weight. The concentration of the polymer solutions used for GPC measurements depended on the amount generated during cell operation.

Results and Discussion

Residual capacity of the graphite anode

The low rate (C/40) discharge profile (Figure1) of the harvested anode from 18650 cell with 2% VEC additive exhibited two voltage plateaus (insert in Fig. 1), the first with a capacity of ca. 0.1 mAhcm⁻² at 150 – 235 mV, and the second (ca. 0.05 mAhcm⁻²) at 235 mV vs. Li⁺/Li. The discharge curve after subsequent recharging shows the features expected for a fully lithiated graphite electrode, e.g. voltage plateaus at 100 mV, 150 mV, 240 mV corresponding to different stages of intercalation [19,20]. Using a 1 V cut-off, the total residual capacity of the “discharged” anode as received (after formation in electrolyte with VEC additive) was 0.27 mAhcm⁻² versus a nominal capacity of 0.97 mAhcm⁻², or a residual capacity of 27 % of the nominal capacity. It is clear from comparison of the voltage plateaus that the anode in this cell, following the C/1 discharge at Quallion, was only partially discharged before the cell reached the 2.7 V cut-off. This would imply that this 18650 cell was anomalously polarized on the final C/1 rate discharge, leaving as much as 27 % of the intercalated Li in the graphite anode. Since other Gen2 cells from Quallion without VEC additive did not show such residual

capacity, the implication was that VEC had somehow caused this anomalous polarization to occur.

Cyclic voltammetry of the electrolyte at Au electrode

Figure 2a compares the cyclic voltammograms (CV) with and without 2% VEC when electrochemically scanned between 3 to 4.1 V at the relatively slow rate of 10 mV/s. At this slow sweep rate, the contribution to the current from the double-layer capacitance is quite small (ca. 1 μ A). The sloping curve in the VEC-free electrolyte is due to uncompensated resistance. The CV of the electrolyte with VEC has additional anodic current at all potentials on both forward and reverse scans, decreasing with time and/or successive sweeps, that we attribute to anodic oxidation of the VEC. The faradaic current for oxidation in the presence of VEC during the first two sweeps was obtained by subtraction of Gen2 electrolyte CV from that of the electrolyte with VEC, as shown in Figure 2b. The subtractively obtained CV indicates a half-wave potential for oxidation ($E_{1/2}$) of ca. 3.6 V. We postulate that oxidation of VEC in this potential region produced a passivating (resistive) film on the electrode surface, causing the subtractive CV to decrease on successive sweeps.

Spectroscopic investigation of anodic polymerization of VEC

Figure 3 (insert) shows the potential responses of an Au electrode 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 μAh . On the other hand, in VEC containing electrolyte, the current decay required 200 min., and the total charge passed was 17.7 μAh , more than 5 times greater. The Au electrodes were then removed from the cells, and the excess electrolyte on the surface was allowed to evaporate in the glovebox until the electrodes were “dry” in appearance. Any products of the electrochemical oxidation remaining on the surface of the electrode were examined by post mortem analysis.

As reported previously [21], the nearly invisible film, deposited on an inert electrode simply immersed in Gen2 electrolyte, consists of only of $\text{LiPF}_6\text{-EC}$ solvate precipitate. This is easily rinsed from the surface by DMC, leaving no IR active residue. This was also the case for electrode cycled in the electrolyte absent of VEC. On the other hand, a film was clearly visible on the electrode after anodization in electrolyte with VEC additive. The molecular weight distribution of this film analyzed by GPC is shown in Fig. 4. The film consists of species with molar masses ranging up to 10^8 , with the lower masses being more abundant. Such a broad range of molecular weight distribution is usually an indication of highly branched polymer, and is consistent with electrochemically-initiated polymerization, i.e. polymerization from electrochemically generated radical initiators [22].

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. The spectra obtained are shown in Fig. 5 divided into the two major spectral regions, 3200- 2800 cm^{-1} (panel a) and 2000-700 cm^{-1} (panel b). Even prior to DMC washing, the spectrum for the electrode anodized in electrolyte with VEC (curve B in Fig.5) appears to have new

spectral features (marked by asterisks) between 1600 cm^{-1} and 700 cm^{-1} not found on the electrode from electrolyte without VEC (curve A Fig.5), the latter closely resembling that from an electrode merely soaked in electrolyte at open circuit and attributed to solvate precipitate, i.e. EC-LiPF₆ (see discussion of solvate spectra in Song et al. [21]). As seen from spectrum C in Figure 5, the new spectral features from electrolyte with VEC were intensified by the DMC washing, during which the solvate precipitates are completely removed. It is known, both experimentally and theoretically [5 and references therein], that EC and EMC are oxidized on inert electrodes (like Au) at potentials higher than 4.2 V, a potential higher than used here. Therefore, it is reasonable to conclude that the features marked by arrows in spectrum C may be attributed to DMC insoluble products of VEC oxidation.

The marked features in spectrum C from the electrode were interpreted with the combined use of compilations of standard compounds [23], group frequency assignments [24], and quantum chemical calculations of group frequencies of candidate product molecules [23]. The detailed assignment is beyond the scope of this paper and will be presented in a more complete report on these calculations elsewhere [23]. Spectrum C has strong new features in the C-H stretching region, especially in the region near 2960 cm^{-1} and 2860 cm^{-1} with weaker but still significant new features near 3040 cm^{-1} . The vibrational modes near 3040 cm^{-1} are characteristic of vinylic CH in an unsaturated heteroatom cyclic ring, e.g. the ring in vinylic carbonate (VC) but with lower symmetry. The features at 3010 and 2930 cm^{-1} , common to all spectra in Fig. 5, are attributed to the methylene (-CH₂-) asymmetric and symmetric modes in a saturated heteroatom cyclic ring, e.g. in EC or PC. We note that the unique asymmetric stretch of

the vinylene group =CH₂ in VEC at 3094 cm⁻¹ is completely absent in all of the spectra in Fig.5a. Aliphatic methylene (-CH₂-) asymmetric and symmetric modes would be found at 2930±10 cm⁻¹ and 2850±10 cm⁻¹, respectively, and those of aliphatic methyl (-CH₃) would be found at 2960±10 cm⁻¹ and 2830±10 cm⁻¹. The multiplicity of peaks near the 2860 and 2960 regions indicates that there are mixture of aliphatic methylene (-CH₂-) and methyl (-CH₃) groups in the product film. Recall that EC solvate would have been washed from the electrode by DMC, and thus none of the features in spectrum C in Fig. 5a can be due to EC itself. Based on analysis of the carbonyl vibrational group frequency, the strong and broad carbonyl peak at about 1804 cm⁻¹ could not be attributed to a linear carbonate functional group (e.g. in DMC, DEC or EMC) including a linear polycarbonate [21, 24]. Interestingly, this carbonyl peak and the peaks at 1165, 1075 and 716 cm⁻¹, align well with those of vinylene carbonate (VC), except one medium intensity peak at 1292 cm⁻¹. Quantum chemical calculations of the vibrational frequencies of candidate molecules suggest the best assignment for 1292 cm⁻¹ feature is one CH bending mode coupled with the ring breathing mode of functionalized vinylene carbonate (VC). In other words, replacement of an H by aliphatic methyl or methylene group on VC to break its symmetry would give rise to this medium intensity 1292 cm⁻¹ feature as well as all the major vibrational frequencies observed in spectrum C. The two small peaks at 1464 cm⁻¹ and 1454 cm⁻¹ fall into group frequency region of aliphatic methyl asymmetric bending (-CH₃), -CH- bending and -CH₂- bending mode. The presence of these characteristic aliphatic bending modes correlates well with that of their stretching modes in 3000 –2800 cm⁻¹.

In combining the IR analysis and the GPC results, it appears that the DMC insoluble film formed on the Au electrode anodized at 4.1 V in electrolyte with VEC additive is polymeric, specifically a polycarbonate consisting of EC-like and VC-like carbonate rings linked by aliphatic methylene and methyl branches. All of the evidence points to anodic oxidation of VEC initiated at potentials above ca. 3.6 V to form the radical cation I (Fig.6), followed by loss of a proton to generate the delocalized allylic radical II, whose three resonance forms may each lead to polymers via attack on neutral carbonates. Radical II may also undergo a 1,4 H-shift rearrangement to give rise to radical III, with additional resonance forms IIIA and IIIB. Polymerization *via* these electrogenerated allylic radicals leads to a variety of highly branched polycarbonates. Note that delocalization of the double bond produces both EC-like and VC-like rings, consistent with all the vibrational group assignments.

Conclusions

Cyclic voltammetry at a Au electrode in a commercial Li-ion battery electrolyte with 2 % VEC has additional anodic current in the 3 – 4 V potential region on both forward and reverse scans, decreasing with time and/or successive sweeps, that we attribute to anodic oxidation of the VEC producing a passivating (resistive) film on the electrode surface. The half-wave potential ($E_{1/2}$) for oxidation is ca. 3.6 V. GPC analysis of the film produced by anodization of the electrolyte at 4.1 V indicated a polymer with a very wide molecular weight distribution. IR analysis confirmed the presence of polycarbonates consisting of EC-like and VC-like carbonate rings linked by aliphatic methylene and methyl branches. Their formation is believed to follow directly from anodic oxidation of VEC at potentials above ca. 3.6 V. The anomalous polarization (at

C/1 rate) of the prototype Li-ion cell with 2 % VEC additive in the electrolyte is attributed to the resistivity of this polymeric film formed on the cathode during the formation cycles.

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Figure captions

Figure 1. (insert) Residual capacity (at C/25) of the graphite anode harvested from an 18650 cell with a Gen2 electrolyte with 2 wt.% of VEC as an additive. Subsequent discharge curve is shown following re-charging (C/25) of the electrode to 0.1 V vs. Li/Li⁺.

Figure 2. a) Cyclic voltammograms of an Au foil electrode in the indicated electrolytes. Only the 1st cycles are shown. Scan rate: 10 mV/s; b) subtractive current-voltage curves (current with VEC minus current w/o VEC).

Figure 3. 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 4. Chromatogram traces of film, stripped from an Au electrode, after anodization at 4.1 V in Gen2 electrolyte with 2% VEC added.

Figure 5. 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.

Figure 6. Resonant structures of allylic radicals from VEC oxidation.













