The effect of some electrolyte additives on $LiCoO_2$/graphite pouch cells

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Introduction

Electrolyte additives are commonly used to extend the lifetime of Li-ion batteries.

Several electrochemical methods have been developed recently to rapidly assess the effectiveness of an additive and determine at which electrode an additive acts. Amongst them are high precision coulometry [1, 2] and electrochemical impedance spectroscopy (EIS) on symmetric cells [3, 4]. The first method allows the effect of an additive on the cycling behavior of a Li-ion cell to be assessed in a matter of a few weeks through the measurement of coulombic inefficiency (CIE), charge endpoint slippage and capacity fade with a high precision [5]. A low coulombic inefficiency usually correlates with long cycle life. The second method can determine at which electrode an additive acts by following its effect on the charge transfer resistance (R_{ct}) by EIS. A change in the charge transfer resistance indicates a change in the nature of the solid electrolyte interphase (SEI). The results from these two techniques can be used to help understand how additives work.

Experimental

Machine-made wound $LiCoO_2$/graphite pouch cells (402030 size, 200 mAh) were filled with 1M $LiPF_6$ EC/EMC electrolyte containing various amounts of vinylene carbonate (VC) and vinyl ethylene carbonate (VEC). To measure the CIE, the pouch cells were cycled on an ultra high precision charger over a period of a few weeks. To measure R_{ct} of the positive electrode and negative electrode, the cells were opened (at 3.780 V) in an argon-filled glove box. From the long electrodes, 3 positive symmetric coin cells, 3 negative symmetric coin cells and 3 full coin cells were assembled. The electrochemical impedance spectra of the reassembled cells were measured at different temperatures. Rct of the positive and negative electrodes were calculated by fitting the spectra with an appropriate equivalent circuit model as described by Petibon et al. [4].

Results and discussion

Figure 1 shows the coulombic inefficiency (CIE = 1 - CE) and R_{ct} of the positive electrode and negative electrode of $LiCoO_2$/graphite pouch cells containing various amounts of VC and VEC.

Figure 1a shows that the CIE is reduced with incremental addition of VC up to a concentration of 2% VC. Figures 1c and 1d show that adding 0.5% VC and 1%VC has a great impact on the R_{ct} of the positive electrode and almost no effect on the R_{ct} of the negative electrode. Compared to 1% VC, adding 2% VC has a minimal impact on the R_{ct} of the positive electrode and a significant impact on the R_{ct} of the negative electrode. Adding more VC to the cell slightly affects the R_{ct} of the positive electrode and greatly affects the Rct of the negative electrode. Figures 1a, 1b, 1c show that the benefits that VC brings to the CIE come primarily from its effect on the positive electrode and possibly from its effect on the negative electrode.

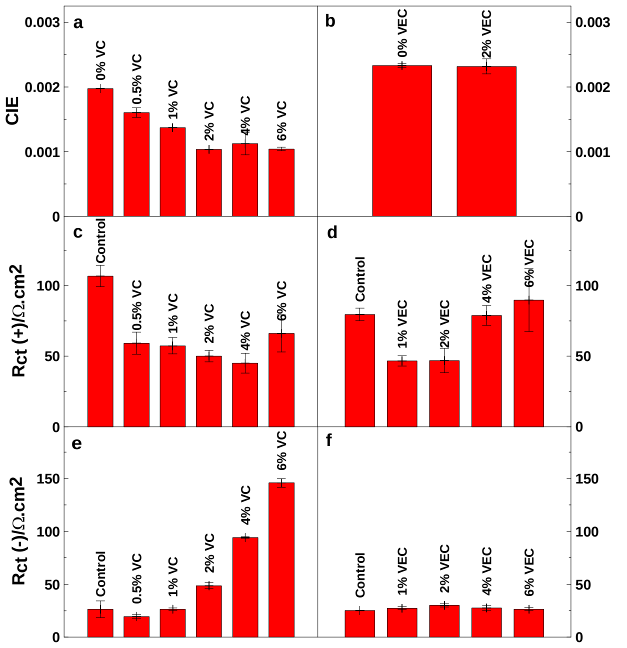

Figure 1. Coulombic inefficiency (a, b), Rct of the positive electrode (c, d) and Rct at 10°C of the negative electrode (e, f) of $LiCoO_2$/Graphite pouch cells containing VC and cycled at 40°C (a, c, e) and VEC cycled at 30°C (b, d, f)

Figure 1b shows that VEC has no effect on the CIE of the cells tested. Figures 1d shows that 1% VEC and 2% VEC reduce the R_{ct} of the positive electrode. However adding more than 2% VEC increases the Rct of the positive electrode. This might indicate that VEC undergoes a different reaction pathway depending on its concentration. Figure 1f shows that VEC has almost no effect on the negative electrode. This indicates that in this cell chemistry, VEC does not show any film forming property at the negative electrode. It is important to note that VEC cells produce significant amounts of gas during formation and this gas is removed during degassing of the pouch cells. Therefore the effects of VEC may be different in cylindrical cells.

Conclusion

High precision coulometry and EIS on symmetric cells allow one to assess the effect of an additive on the cycling behavior of a cell and on the surface of the positive electrode and negative electrode in a relatively quick fashion. Results for other additives will also be discussed.

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