

Influence of surface film on the lithium-ion intercalation sites at highly oriented pyrolytic graphite

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To elucidate the influence of surface film on the lithium-ion intercalation sites at highly oriented pyrolytic graphite (HOPG), we investigated the relationship between electric double layer capacitances (C), which correlate closely with fraction of edge orientations^[1], and charge-transfer resistances for lithium-ion intercalation (R_{ct}) after formation of solid electrolyte interphase (SEI) films.

Using HOPG as a working electrode, we calculated C from cyclic voltammograms in $1.0 \text{ mol dm}^{-3} \text{ KCl}(aq)$, and derived R_{ct} from the electrochemical impedance spectra in a solution of ethylene carbonate (EC) and diethyl carbonate (DEC) (1 : 1 volume ratio) containing $1.0 \text{ mol dm}^{-3} \text{ LiClO}_4$ with or without the addition of 3 wt% VC.

Figure 1 shows the linear relationship between $1/R_{ct}$ and C . In addition, the slope of the straight line of with VC was smaller than that without VC. Based on the Arrhenius equation, R_{ct} mainly depends on the activation energy (E_a) and the frequency factor (A). Since E_a was unchanged by VC-derived SEI^[2], the decrease in A corresponds to the decrease in the number of insertion sites. This indicates the influence of the SEI component on the number of lithium-ion insertion sites.

References:

- [1] M. T. McDermott et al., *J. Phys. Chem.*, **96** (1992) 3124.
- [2] Y. Yamada et al., *Langmuir*, **25** (2009) 12766.

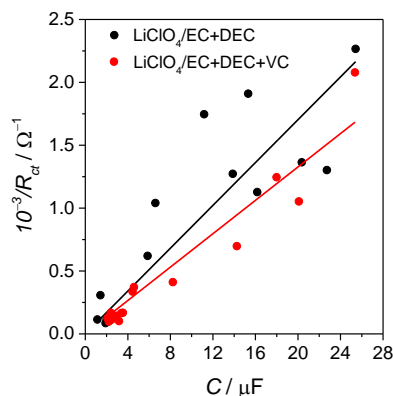


Fig. 1. Correlation between C and R_{ct} at HOPG.