

How Do Cyclic Carbonate Electrolyte Additives Improve Li-ion Battery Performance?

by Hadi Tavassol

Li ion batteries (LIB) are ubiquitous in portable electronics, and are increasingly used in automotive applications. Improvements in stability and long-term capacity of LIBs are essential to satisfy fast growing demands in both sectors. The electrolyte mixture in a LIB is often modified to boost the long term stability of the solid electrolyte interphase (SEI) which forms particularly at the surface of the battery anode. Small quantities of additives are known to increase the stability and long-term cyclability of LIBs.^{1,2} Some of the most widely used additives are cyclic carbonates such as vinylene carbonate (VC) and vinyl ethylene carbonate (VEC). This class of additives contain unsaturated C-C bonds, which are believed to facilitate the formation of a more stable SEI.

The exact mechanism of additive activity and their effect on the properties of the SEI remains unknown. The SEI is thought to consist of an inner inorganic part with an outer organic layer, likely formed via oligomerization of the solvent,^{3,4} the existence of which changes the mechanical properties of the electrode.⁵ The additives may change the SEI formation mechanism.⁶

Here we investigated the effect of added VC and VEC molecules on the SEI. We used an Au model anode system in a 1 M LiClO₄/propylene carbonate electrolyte solution, with and without added additive. Electrochemical analysis of the Au anode in the presence of low (0.2 %, v/v) and high (2.0 %) concentrations of the VC and VEC additives was performed in two different potential regions: between 3 V (vs. Li⁺⁰) and

0.25 V (Fig. 1a), and between 3.0 V and 0.15 V (Fig. 1b), where bulk lithiation occurred. In the absence of additives, early reductive features corresponding to the irreversible reduction of electrolyte components appeared at around 2.25 V. The presence of the additives caused only minor changes in the 1st cycle of the voltammogram. As bulk lithiation occurred, two major effects were evident: i) as the concentration of the additive increased, an overpotential in the onset of the bulk lithiation was observed, this effect was more pronounced with VEC; and, ii) addition of VEC and VC increased the maximum current observed during lithiation.

(continued on next page)

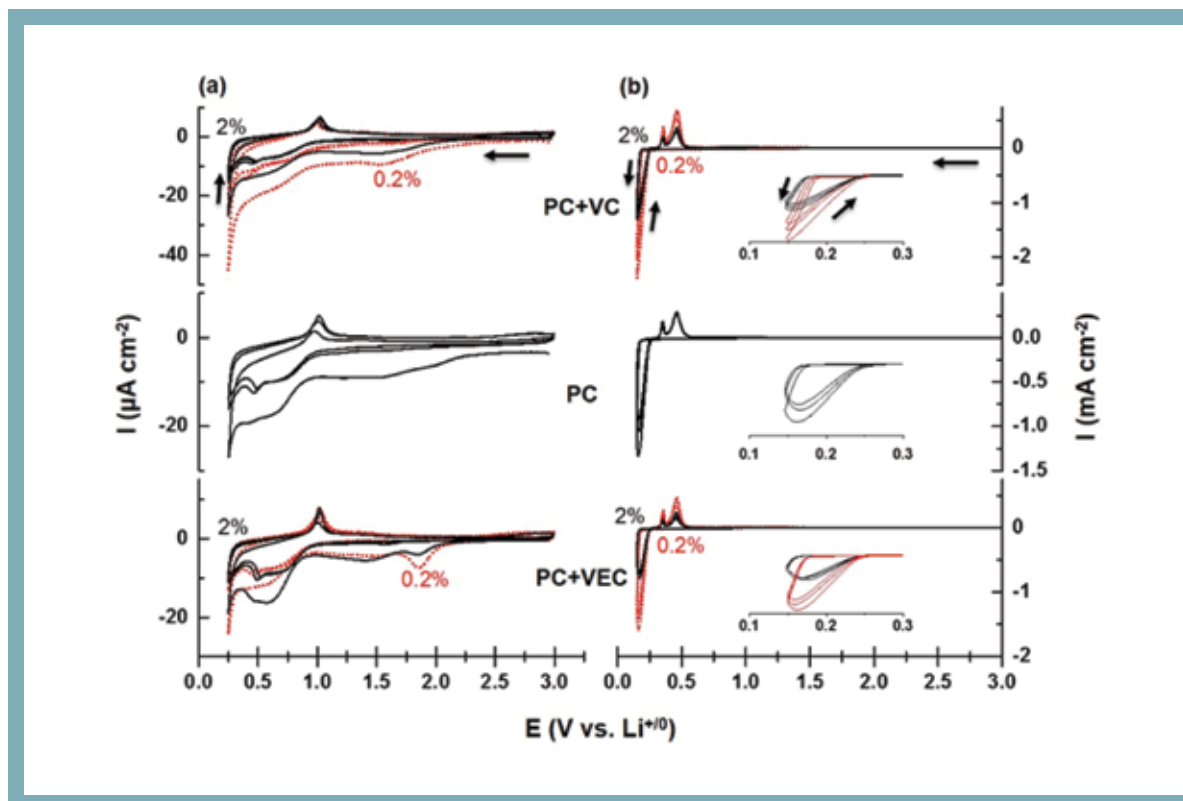


FIG. 1. Electrochemical analysis of additive containing electrolytes using cyclic voltammetry at 1 mV s^{-1} in 1M LiClO₄/PC with varying amount of VC and VEC additives. (a) Cyclic voltammetry of the 3 V (vs. Li⁺⁰) to 0.25 V region, and (b) 3.0 V to 0.15 V region, the insets show the onset of the bulk lithiation.

These observations led us to probe the physical properties of the SEI using an electrochemical quartz crystal microbalance (Fig. 2). Changes in the mass of the electrode during cycling are shown in Fig. 2a. The residual mass ($\delta \Delta m$) at the end of each cycle is a good estimate of the SEI mass. As expected, SEI mass increased with cycling in all electrolyte solutions. The major effect in the presence of the additives was the decrease in the magnitude of the SEI mass with extended cycling, relative to the additive-free case.

We also measured the motional resistance (R_m) of the QCM electrode. R_m is linearly related to $(\rho\eta)^{1/2}$, where ρ and η are respectively the density and viscosity of the film on the electrode surface. The residual motional resistance (δR_m) is the change in R_m from cycle to cycle. At the end of the 1st cycle, the δR_m from all additive containing electrolytes (Fig. 2b) pointed towards increased motional resistance, indicating that the presence of additive molecules increased the $(\rho\eta)^{1/2}$ which is proportional to film rigidity. The δR_m of the VC containing electrolytes reached steady state after only three cycles, while VEC-containing and additive-free electrolyte continue to evolve with cycling. After 7 cycles the electrolyte solution with VEC showed the highest δR_m , followed by additive-free electrolyte and VC-containing electrolyte. Addition of VC decreased film rigidity. Interestingly, VC-containing solutions exhibited the highest lithiation currents (Fig. 1b), possibly as a consequence of a more porous and Li-conductive SEI film. This study indicates that additives improve the performance of the LIB in part by modifying the physical state of the SEI.

Acknowledgments

The ECS is gratefully acknowledged for the H. H. Uhlig Summer Fellowship Award. I would also like to thank Professor Andrew A. Gewirth for his constant guidance and support. This work was supported in part by the Center for Electrical Energy Storage, an Energy Frontier Research Center funded by the U.S. Department of Energy. I also acknowledge Jennifer L. Esbenschade, my collaborator in this project. ■

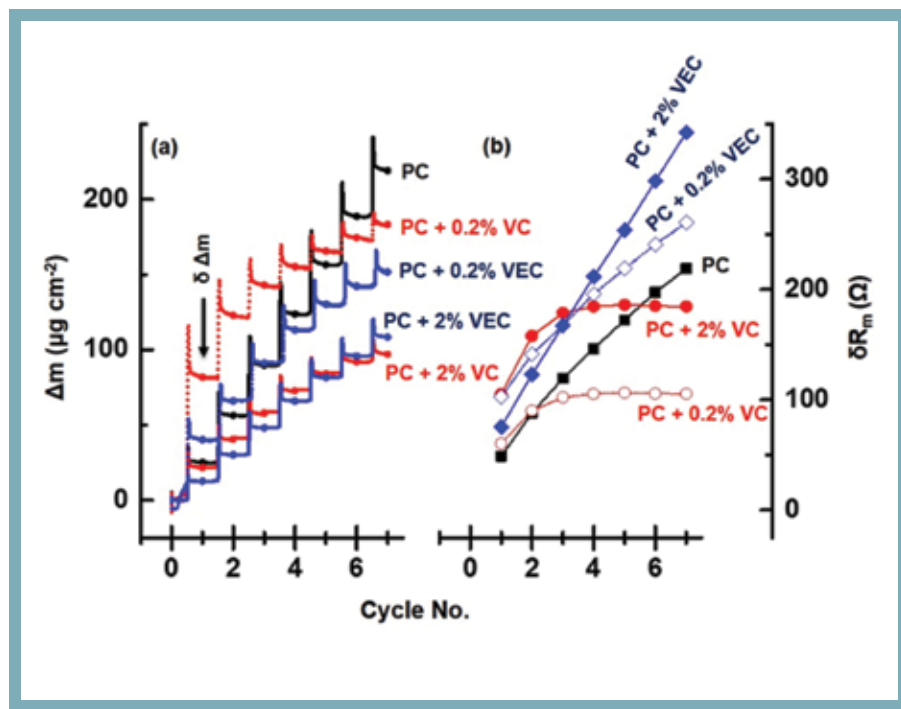


Fig 2.(a) Mass changes with cycling in different electrolyte mixtures, small solid circles indicate the residual mass at the end of each cycle ($\delta \Delta m$). (b) Changes in the motional resistance (δR_m) of the film with cycling.

About the Author

HADI TAVASSOL received his PhD in Analytical Chemistry from University of Illinois at Urbana-Champaign in August 2014. He completed his thesis under the supervision of Professor Andrew A. Gewirth studying Interfacial Process in Li-ion Batteries. He is currently a Postdoctoral Scholar at the California Institute of Technology working with Professor Sossina M. Haile. He may be reached at hadit@caltech.edu.

References

1. D. Aurbach, K. Gamolsky, B. Markovskiy, Y. Gofer, M. Schmidt, and U. Heider, *Electrochimica Acta*, **47**, 1423 (2002).
2. L. Chen, K. Wang, X. Xie, and J. Xie, *Journal of Power Sources*, **174**, 538 (2007).
3. H. Tavassol, J. W. Buthker, G. A. Ferguson, L. A. Curtiss, and A. A. Gewirth, *J. Electrochem. Soc.*, **159**, A730 (2012).
4. D. Bar-Tow, E. Peled, and L. Burstein, *J. Electrochem. Soc.*, **146**, 824 (1999).
5. H. Tavassol, M. K. Y. Chan, M. G. Catarello, J. Greeley, D. G. Cahill, and A. A. Gewirth, *J. Electrochem. Soc.*, **160**, A888 (2013).
6. K. Ushirogata, K. Sodeyama, Y. Okuno, and Y. Tateyama, *J. Am. Chem. Soc.*, **135**, 11967 (2013).
7. S. J. Martin, J. J. Spates, K. O. Wessendorf, T. W. Schneider, and R. J. Huber, *R. J. Anal. Chem.*, **69**, 2050 (1997).