Electroactive Poly-Dilithium Phthalocyanine Coatings for Lithium Battery Materials

Nathanael P. Fackler[a] and Christopher S. Johnson*[b]

[b]Electrochemical Technology and
Basic Sciences Program
Chemical Technology Division
Argonne National Laboratory
Argonne, Illinois 60439, USA

[a]Department of Chemistry
Nebraska Wesleyan University
Lincoln, Nebraska 68504, USA

The dilithium phthalocyanine (Li_2Pc) compound has been studied as a possible solid phase electrolyte for lithium batteries. In the solid-state, it is predicted to self-assemble into a unique helical structure that can create coordinative structural pathways or channels for lithium ions to migrate through the solid phase [1]. A number of experiments and calculations have been conducted on the material to determine whether or not it might effectively transport and deposit lithium at a substrate Cu electrode. Cyclic voltammetry (CV) of the solid-state Li_2Pc at a Cu working electrode have shown indications of stripping and plating of some redox species, possibly lithium metal at the Li_2Pc/Cu interface [1].

However, the Li_2Pc molecule is sensitive to oxidation in air which can lead to a free radical anion which is electronically conductive. EPR spectroscopy has confirmed the presence of the free radical and data shows that its concentration grows over time leading to a mixed conductor (electronic and ionic) for the Li_2Pc in the solid state [2]. Because of these reasons, we have pursued instead, using the Li_2Pc in a polymerized form (poly-Li_2Pc) as an electrode coating to improve the electrode kinetics of positive electrode (cathodes; lithium transition metal oxides, i.e. $LiCoO_2$, $LiCo_{1-x}Ni_xO_2$, or 4 V $LiMn_2O_4$ and 5 V $LiNi_{0.5}Mn_{1.5}O_4$ spinel) materials in an organic liquid electrolyte lithium battery environment.

The polymerization reaction chosen was similar to the synthesis of Li_2Pc, except that 1,2,4,5-tetracyanobenzene was substituted for dicyanobenzene [3]. The polymerization was carried out in the presence or absence of the solid oxide cathode powder in order to compare conditions. The tetracyanobenzene was added as a solid directly to a solution of lithium pentaoxide under argon. The solution immediately darkened and formed a solid mass which prevented mixing. A number of soxhlet extractions were done to separate by-products.

The poly-Li_2Pc and the poly-Li_2Pc/oxide nanocomposite were characterized by a number of methods such as powder XRD, IR, EPR, Raman and TG-DTA. The electrochemistry was carried out in lithium coin cells (Hohsen size 2032) with an electrolyte solution of 1 *M* $LiPF_6$ in 1:1 EC/DEC (w/w%; ethylene carbonate:diethylcarbonate). Conventional laminate electrode making was used. Constant current galvanostatic cycles were also used in order to compare the electrochemical performance with either physically blended poly-Li_2Pc and cathode oxide powder or the poly-Li_2Pc/oxide nanocomposite versus the baseline (uncoated or unblended) cathode oxide powders.

The XRD pattern of the poly Li2-Pc without the presence of the cathode oxide powder showed the material was amorphous and did not give a peak at $2\ \Theta = 30°$, indicating that cyclization was successful.

Acknowledgments

Argonne National Laboratory is supported by the U.S. Department of Energy under Contract No. W-31-109-ENG-38. Additional financial support for this work was provided by the U.S. Air Force Research Laboratory (AFRL/PRPS).

References

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