

AC Impedance Electrochemical Modeling of Lithium-Ion Positive Electrodes

Evren Gunen^{a1}, Dennis Dees^b, Daniel Abraham^b,
and Jai Prakash^a

^a Department of Chemical and Environmental
Engineering
Illinois Institute of Technology
Chicago, IL 60616

^b Electrochemical Technology Program
Chemical Engineering Division
Argonne National Laboratory
Argonne, IL 60439-4837

Under Department of Energy's Advanced Technology Development Program, various analytical diagnostic studies are being carried out to examine the lithium-ion battery technology for hybrid electric vehicle applications, and a series of electrochemical studies are being conducted to examine the performance of these batteries. An electrochemical model was developed to associate changes that were observed in the post-test analytical diagnostic studies with the electrochemical performance loss during testing of lithium ion batteries. While both electrodes in the lithium-ion cell have been studied using a similar electrochemical model, the discussion here is limited to modeling of the positive electrode.

The positive electrode under study has a composite structure made of a layered nickel oxide ($\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$) active material, a carbon black and graphite additive for distributing current, and a PVDF binder all on an aluminum current collector. The electrolyte is 1.2M LiPF_6 dissolved in a mixture of EC and EMC and a Celgard micro-porous membrane is used as the separator. Planar test cells (positive/separator/negative) were constructed with a special fixture and two separator membranes that allowed the placement of a micro-reference electrode between the separator membranes [1]. Electrochemical studies including AC impedance spectroscopy were then conducted on the individual electrodes to examine the performance and ageing effects in the cell.

The model was developed by following the work of Professor Newman at Berkeley [2]. The solid electrolyte interface (SEI) region, based on post-test analytical results, was assumed to be a film on the oxide and an oxide layer at the surface of the oxide. A double layer capacity was added in parallel with the Butler-Volmer kinetic expression.

The pertinent reaction, thermodynamic, and transport equations were linearized for a small sinusoidal perturbation [3]. The resulting system of differential equations was solved numerically using a partial differential equation solver (FlexPDE) over the frequency range of interest.

The electrochemical AC impedance model was used as a diagnostic tool to examine ageing effects associated with the positive electrode, and to investigate ways to reduce the impact of these effects on the overall

cell performance.

Acknowledgment

The authors acknowledge the Department of Energy's Office of Advanced Automotive Technologies for its financial support under contract No. W-31-109-ENG-38 and Illinois Institute of Technology.

References

- [1] K. Amine, C. Chen, J. Liu, M. Hammond, A. Jansen, D. Dees, I. Bloom, D. Vissers, and G. Henriksen, *J. Power Sources* 97-98 (2001) 684.
- [2] J. S. Newman, *Electrochemical Systems*, Prentice-Hall, Ontario, Canada, (1991).
- [3] J. Meyers, M. Doyle, R. Darling, J. Newman, *J. Electrochem. Soc.* 147 (2000) 2930.

¹ Author's current address is
Hawaii Natural Energy Institute
University of Hawaii at Manoa
Honolulu, HI 96822