

Mathematical Modeling of Lithium Ion Cells and Batteries

Ralph E. White

Department of Chemical Engineering

University of South Carolina

Columbia, SC 29208

white@cec.sc.edu

The development of macroscopic, physics-based models of lithium ion cells and batteries will be reviewed beginning with relatively simple models. In 1979, Atlung et al.¹ presented a relatively simple cell model for the Li/TiS₂ couple. Their model includes the diffusion on lithium ions in different shaped particles of TiS₂, which they called a solid solution. They used their model to predict several aspects of this cell including the specific energy. Their model was used later by Haran et al.² to model the impedance of a spherical metal hydride particle. After that, Subramanian et al.³ extended Atlung et al.'s model to include a variable diffusion coefficient. Also, Subramanian et al.⁴ developed an approximate solution for the concentration distribution in a spherical particle, which reduced the computation time needed to simulate cycling of a cell. Next, Ning and Popov⁵ used Atlung et al.'s model to simulate cycling of a graphite, MCMB (Meso Carbon Micro Beads)/ LiCoO₂ cell with formation of a film on the graphite electrode on charge. This simple model provided the capability to estimate the capacity fade for tens of thousands of low rate cycles in less than an hour of computation time. Santhanagopalan et al.⁶ presented a review of several lithium ion cell models including our extension of Atlung et al.'s model and named this model the single particle (SP) model. Zhang and White⁷ used the SP model to make capacity fade predictions for small cells cycled at very low rate. Safari et al.⁸ used the SP model to study capacity fade as did Deshpande et al.⁹ who extended the SP model to include crack growth in a graphite particle followed by film formation in the resulting cracks with loss of lithium ions. Rahimian et al.¹⁰ used the SP model to study several possible mechanisms that could cause capacity fade of lithium ion cells. Santhanagopalan et al.¹¹ used the two term polynomial SP model to establish an on-line parameter estimation procedure to estimate the state of charge of a cell as it is being used. Guo and White¹² presented an approximate solution to the spherical diffusion problem with a fixed flux which provides high accuracy with only a few terms in a series when compared to the analytic solution with at least 100 terms. This approximate solution provides significant savings in computation time. In order to predict the performance of lithium ion cells operating at higher rates, more complicated models were developed.

In 1982, West et al.¹³ presented a Nernst-Planck model for porous insertion electrodes for a Li/TiS₂ cell. They pointed out the importance of coupling the transport of lithium ions between the insertion electrode and the electrolyte. In 1993, Mao and White¹⁴ presented a Nernst-Planck model of the Li/TiS₂ cell which included transport of lithium ions through the separator and demonstrated quantitatively how the utilization of the TiS₂ electrode could be improved by decreasing the thickness of the separator. Also in 1993, Doyle et al.¹⁵ published a concentrated solution theory model for a lithium/polymer/TiS₂ cell. Shortly after that in 1994 Fuller et al.¹⁶ published a concentrated solution theory model for a dual lithium ion insertion cell, which is known as dual foil and is available on-line for use by interested parties.

In 1996, Doyle et al.¹⁷ published a comparison of their model predictions to experimental data from a Bellcore plastic lithium ion cell. Unfortunately, the computation burden associated with using the program dual foil is too great to use their program for extensive simulations needed for parameter estimation and cell life predictions. Consequently, several papers have been published to provide methodology to reduce this computation burden. One of those papers is by Cai and White¹⁸ in which they used the orthogonal collocation method to solve the model equations for lithium ion cells to reduce the computation needed for simulation. Thermal management of lithium ion cells is extremely important and several papers have been published that may be helpful for the design of heat removal systems needed for lithium ion batteries. In 2008, Kumaresan, et al.¹⁹ published a thermal model for a lithium ion cell, which illustrated the need to treat transport parameters as functions of temperature to predict accurately the performance of lithium ion cells. Recently, Guo et al.²⁰ published a three dimensional thermal model for three lithium ion cells in series. It should be possible to use this model to design active cooling for lithium ion battery packs.

References

1. S. Atlung, K. West, and T. Jacobsen, J. Electrochem. Soc., 126 (8) 1311-1321 (1979).
2. B. S. Haran, B. N. Popov, R. E. White, J. Power Sources 75 (1998) 56-63.
3. V. R. Subramanian, P. Yu, B. N. Popov, R. E. White, J. Power Sources 96 (2001) 396-405.
4. V. R. Subramanian, J. A. Ritter, and R. E. White, J. Electrochem. Soc., 148 (11) E444-E449 (2001).
5. G. Ning and B. N. Popov, J. Electrochem. Soc., 151 (10) A1584-A1591 (2004).
6. S. Santhanagopalan, Q. Guo, P. Ramadass, R. E. White, J. Power Sources 156 (2006) 620-628.
7. Q. Zhang, R. E. White, J. Power Sources 179 (2008) 793-798.
8. M. Safari, M. Morcrette, A. Teysot, and C. Delacourt, J. Electrochem. Soc., 156 (3) A145-A153 (2009).
9. R. Deshpande, M. Verbrugge, Y-T. Cheng, J. Wang, and P. Liu, J. Electrochem. Soc., 159 (10) A1730-A1738 (2012).
10. S. K. Rahimian, S. Rayman and R. E. White, J. Electrochem. Soc., 159 (6) A860-A872 (2012).
11. S. Santhanagopalan, R. E. White, J. Power Sources 161 (2006) 1346-1355.
12. M. Guo, R. E. White, J. Power Sources 198 (2012) 322-328.
13. K. West, T. Jacobsen, and S. Atlung, J. Electrochem. Soc., 129 (7) 1480-1485 (1982).
14. Z. Mao, R. E. White, J. Power Sources 198 (2012) 322-328.
15. M. Doyle, T. F. Fuller, and J. Newman, J. Electrochem. Soc., 140 (6) 1526-1533 (1993).
16. T. F. Fuller, M. Doyle, and J. Newman, J. Electrochem. Soc., 141 (1) 1-10 (1994).
17. M. Doyle, J. Newman, A. S. Gozdz, C. N. Schmutz, and J.-M. Tarascon, J. Electrochem. Soc., 143 (6) 1890-1903 (1982).
18. L. Cai, R. E. White, J. Power Sources 217 (2012) 248-255.
19. K. Kumaresan, G. Sikha, and R. E. White, J. Electrochem. Soc., 155 (2) A164-A171 (1982).
20. M. Guo, G.-H. Kim, R. E. White, J. Power Sources 240 (2013) 80-94.

