Modeling Binder-free and Carbon-free High Energy Density $LiCoO_2$ Electrodes for Rechargeable Lithium Batteries

Corie L.Cobb and Chang-Jun Bae
Palo Alto Research Center (PARC)
Hardware Systems Laboratory
3333 Coyote Hill Road, Palo Alto, CA 94304

INTRODUCTION

Conventional thin electrodes, by volume, contain a large amount of electrochemically inactive material, which lowers the overall energy capacity of a cell, making it difficult to realize high volumetric energy with thin electrode architectures. Researchers have been actively pursuing methods which will enable the fabrication and full utilization of ultra-thick electrodes (< 200µm) to mitigate the amount of inactive material required in a cell. One approach which has emerged is to fabricate low tortuosity sintered electrode structures [1, 2].

This paper aims to correlate John Newman's macrohomogeneous porous electrode model [3, 4] to thick high energy density carbon-free and binder-free sintered electrode samples fabricated at Palo Alto Research Center (PARC) and prior art studies on tortuosity in $LiCoO_2$ [5]. Zhang *et al.* [6] have shown that it is difficult to correlate a macrohomogeneous electrode model across all rates. New model extensions often are created to capture better correlation at slow and fast C-rates. This is more difficult when dealing with a new materials set. We examine how assumptions about tortuosity and diffusion [7] effect model predictions of capacity. Our efforts focus on understanding the model parameters which can be used in Newman's existing model without modification to the underlying equations.

SINTERED ELECTRODES

Lai *et al.* demonstrated that densely sintered electrodes fabricated from brittle Lithium oxides can be cycled multiple times while still realizing full capacity utilization [1]. The discovery enabled the development of ultra-thick sintered electrodes on the order of hundreds of microns with enhanced areal capacity. Using thick binder-free and carbon-free sintered $LiCoO_2$, Bae *et al.* demonstrated the importance of tortuosity and proposed a novel design of battery electrodes with dual-scale porosity to minimize tortuosity and maximize performance [2]. Leveraging knowledge from prior art [1, 2], eight 300µm thick monolithic sintered $LiCoO_2$ electrodes have been fabricated with extrusion technology developed at PARC [8] and tested in a half cell format. The electrode samples were prepared using a mixed Umicore powder (raw as-received powder and milled powder) yielding a highly dense structure. A variety of sintering conditions were applied, resulting in a range of densities and tortuosity to enable correlation to modeling data.

Comparison of Modeling and Experimental Data

We utilize an existing macrohomogeneous porous electrode model in COMSOL [9] to compare modeling expectations of $LiCoO_2$ with experimental data for sintered electrodes. The model assumes a nominal particle diameter of 9.0µm based on the d_{50} of the mixed powder. Tortuosity is defined by equation [1] where ϵ is the electrode porosity and β is the Bruggeman coefficient, typically set at a value of 1.5.

$$\tau = \epsilon^{1-\beta} \qquad [1]$$

Figure 1 shows how model predictions of specific capacity match up to two of our electrode samples. When conventional assumptions of tortuosity are used based on the behavior of thin film $LiCoO_2$, the model significantly over predicts the rate capability of high energy sintered electrodes for rates faster than C/10. For the conventional model cases, a typical Bruggeman coefficient of 1.5 and a constant solid phase diffusion coefficient of 2.8e-10 cm^2/s [6] are employed. We found that by utilizing β values between 2.0-3.3, along with a solid phase diffusion coefficient which varies as a function of state of charge [7], better correlation can be obtained across a larger range of discharge rates for ultra-thick electrodes (see plots marked 'New' in Figure 1). Additional samples with a range of porosities have been correlated to the model. For researchers pursing the development of high energy density electrodes free of carbon and binder, we make model parameter tortuosity recommendations as a function of sintering condition, porosity, and particle size and highlight where limiting cases exist.

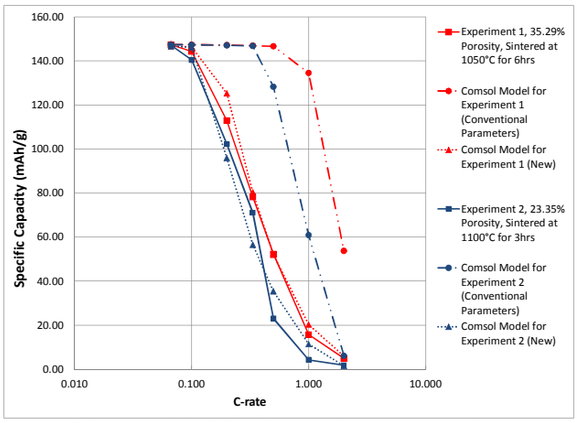

Figure 1: Model and experiment comparison

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