Electrochemical Analysis of Lithiated Graphite Anodes

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Of the various forms of carbon being investigated for use in lithium-ion batteries, graphite appears to be the best choice when coulombic capacity per unit volume (and mass) and robust cycling performance of the active material are given primary consideration. The coulombic capacity corresponds directly to vehicle range in an electric vehicle, while the cycle life contributes to the battery pack life. We note that calendar life remains to be clarified for lithium ion systems operated in electric vehicle mode, as the deleterious effect of sustained high voltage (consistent with a vehicle tethered to a charger) must be addressed.

The utility of lithium-ion battery models for system design has been recognized.\(^1\) Individual electrode data (relative to a reference electrode) is required to determine the characteristics of the individual battery electrodes, and such data is often not provided.

In this work, the non-linear diffusion of lithium intercalate within the host carbon particles is treated without approximation,\(^6\) the concentration-dependent diffusion-coefficient data of Takami et al. are employed for the lithium intercalate species.\(^8\) Other important resistances result from ionic diffusion and migration within the solvent phase, interfacial reaction at the surface of the carbon particles, and electron transport within the solid phase. The unusual structure of the resulting matrix system of equations reflects the nodal and computational structure for the discretized problem shown in Figure 1.

The number of variables associated with the porous electrode is represented by \(N\); \(N=5\) for this study. Because the \(N\) finite-difference equations at each mesh point require three mesh points for each of the \(N\) variables to formulate derivatives, an \(N\times N\times 3\) computational stencil results for each meshpoint, which is coupled to the intra-particle problem that gives rise to a tridiagonal matrix associated with the variable for the intercalate lithium concentration. A solvent-casting procedure for constructing graphite anodes, employing a hydrocarbon [poly(ethylene-propylene-norbornene)] binder is implemented, and the resulting porous electrodes are characterized within an electrochemical cell utilizing a reference electrode and maintaining a substantially uniform current distribution (cf. Figure 2). The resulting calculations show good agreement with experimental results over a range of currents applicable to electric vehicle applications (cf. Figure 3).

Calculations are also used to indicate that the precise shape of the host particles does not play an important role in determining electrode performance. In addition, the nature of the carbon-electrode precursor (i.e., natural versus artificial graphite) is addressed. The overall analysis indicates that interfacial resistance plays a dominant role in limiting the available capacity at high rates of current passage, and it is unfortunate that the solid-liquid interface represents the least understood portion of the cell. This issue is discussed in closing and is an important area of research.

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