

STRUCTURAL COMPARISON OF NICKEL ELECTRODES AND PRECURSOR PHASES

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The solid state structure of the nickel electrode controls the electrochemical properties. Proton diffusion and electron conduction are examples of properties which critically depend upon the structure. Undesirable phases can cause battery failure. If we can define the critical structural components (including nonstoichiometry and disorder in fine particle size materials), it is possible to control the empirical variables to optimize the electrochemical properties. To do this we must know both how the structure controls properties and how the structure can be controlled during electrode preparation, including deposition and formation. Definition of structure allows one to sort out the complex property-preparation relationship. This third side of the triangle, which provides control of electrochemical properties, is defined if we know the other two sides, structure-property and structure-preparation.

In this paper we shall summarize our previous Raman spectroscopic results and discuss important structural differences in the various phases of active mass and active mass precursors. Raman spectra provide unique signatures for these phases, and allow one to distinguish each phase, even when the compound is amorphous to x-rays (i.e. does not scatter x-rays because of a lack of order and/or small particle size). The structural changes incurred during formation, charge and discharge, cobalt addition, and aging will be discussed and related to electrode properties.

Important structural differences include NiO₂ layer stacking, nonstoichiometry (especially cation-deficit nonstoichiometry), disorder, dopant content, and water content. Our results indicate that optimal nickel active mass is non-close packed and nonstoichiometric. The formation process transforms precursor phases into this structure. Therefore, the precursor disorder, or lack thereof, influences this final active mass structure and the rate of formation. Aging processes induce structural change which is believed to be detrimental. The role of cobalt addition can be appreciated in terms of structures favored or stabilized by the dopant.

In recent work, we have developed the *in situ* Raman technique to characterize the critical structural parameters. An *in situ* method is necessary if one wishes to relate structure, electrochemistry, and preparation. We collect *in situ* Raman spectra of cells during charge and discharge, either during cyclic voltammetry or under constant current conditions.

With the structure-preparation knowledge now on-hand, and the new *in situ* Raman tool, it will be possible to define the structure-property-preparation relations in more detail. This instrumentation has application to a variety of electrode systems.