CHAPTER 6:

CARBONS IN THE CATHODES
OF LITHIUM-ION BATTERIES;
ALTERNATIVE FORMS OF MnO$_2$,
CATHODE / CARBON MODELING
Chapter 6: Subject Overview

The seven papers in Chapter 6 are focused on cathode materials for lithium and lithium-ion batteries. Carbon is used as a conductive additive in composite electrodes for batteries. The type of carbon and the amount can have a large effect on the electrochemical performance of the electrode.

The first paper in this chapter is a contribution from R. Kostecki and F. McLarnon of Lawrence Berkeley National Laboratory and consists of a diagnostic study of the power fade issues related to high-power Li-ion batteries that contain a Li(Ni₀.₈Co₀.₁₅Al₀.₀₅)O₂ cathode. Li-ion batteries are prone to poor life and experience problems with impedance rise during elevated temperature aging. SEM, Raman and current-sensing AFM techniques were used to address the mechanism of power fade at the cathode with aged cells. From the results, the authors describe a process of carbon retreat/redistribution in the composite electrode upon accelerated aging. The carbon retreat/redistribution is said to have a major impact in the contribution to the cathode impedance rise and loss of power. They finish with a discussion on the loss of conductivity across the composite cathode as a result of carbon retreat/redistribution.

In the paper from V. Matveyev of the Ukrainian State University of Chemical Engineering, an examination of the role of conductive carbon additives in a composite porous electrode is conducted. A model for calculation of the local electrochemical characteristics of an electrode is presented. A comparison on the polarization of the electrode as a function of the redox state of the electroactive species is emphasized in the model. The electrochemical reaction of chloranil (tetrachlorobenzoquinone) was measured and results compare favorably to calculations derived from the model.

S. A. Kirillov et al. describe the design, synthesis and application of amorphous manganese dioxide in lithium batteries in the third paper of this chapter. A synthetic route of oxidation of Mn(II) aqueous solution with hydrogen peroxide was used to prepare the materials. The prepared MnO₂ material remains amorphous up until 600°C. The amorphous MnO₂ delivers higher capacity of 247 mAh/g versus 189 mAh/g for Russian commercial crystalline EMD when discharged to 2.0 V. Further testing has shown that the amorphous phase demonstrates reversible cycling with lithium. These results bode well for the development of a new class of amorphous manganese oxides for charge storage in lithium or perhaps lithium-ion batteries in the future.

The performance in Zn-MnO₂ alkaline cells of electrolytic manganese dioxide produced in the presence of fluoride ions is compared with commercial EMD materials by I. Makyeyeva et al. The material produced in the presence of fluoride ions was shown to have superior utilization to the commercial EMD. The authors state that the improved
performance of the manganese oxide synthesized in the presence of fluoride ions is due to an increased or larger number of defects in the crystalline structure. The defects are associated with a higher non-stoichiometry in the material due to the presence of more Mn(III). In addition, the authors explain that a higher percentage of hydroxide (OH⁻) moieties in their material are associated with an improved ionic conductivity.

In the fifth paper of this chapter on cathodes, an investigation of thin-film oxide-hydroxide electrodes containing Cr, Ni, and Co compounds was authored by N. Vlasenko et al. The thin-films were produced by electrochemical deposition from transition metal aqueous fluorine-containing electrolytes onto steel substrates. These thin-films were tested in Li coin cells. Electrochemical activity appears to scale with the amount of fluoride used in the deposition; the larger concentration of fluoride in the bath, the greater the capacity. One Ni oxide-hydroxide film electrode showed greater than 175 mAh/g reversible capacity on the 50th cycle with excellent coulombic efficiency.

In a second paper from Kirillov et al., synthetic aspects of liquid phase precipitation reactions are discussed in relation to the factors responsible for metal-oxide formation. In particular the Pechini reaction, a sol-gel process, was examined. A good reference section is provided to introduce the reader to previous literature. The authors stress that more work needs to be done to establish what factors are important for producing the highest quality metal-oxide powders from such reactions. The conclusion specifically lists the criteria needed in order to accomplish this task.

In the final paper of this chapter, authors S.-H. Kang and K. Amine from Argonne National Laboratory discuss high-power lithium ion batteries and present a new lithium nickelate material: Li(Ni₀.₄Co₀.₂Mn₀.₄)O₂ with a well-formed layered structure. The electrochemical performance in lithium cells is compared for materials that are uncoated versus coated with aluminum oxide. The capacity fade is less for coated material versus uncoated both at room-temperature up to 100 cycles and 50°C up to 70 cycles. The improvement was found to be linked to an interfacial impedance drop for electrodes of the coated material. The authors state that the surface coating suppresses the degradation of the cathode/electrolyte interface and that the mechanism may be involved with the scavenging of HF in the electrolyte by the coating. Thus the coating would protect the underlying layered oxide material to acid attack and possible dissolution/corrosion effects during cycling in the LiPF₆ organic electrolyte.

The editors hope that you enjoy reading the last chapter in this NATO series volume, and sincerely thank you for your interest in all of the papers from the NATO-Carbon Advanced Research Workshop and Conference (NATO-CARWC).