Search for Cobalt Free $Ni(OH)_2$ Cathodes for NiMH Batteries

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$Ni(OH)_2$/NiOOH redox couple is used as the cathode in NiMH and many other battery systems. However, development of a high functioning cathode is a bottleneck for this technology. Because, the active material has a 3.0-3.5 eV of band gap [1]. Therefore, it is an insulating material and conductivity must be imparted with additives. Adding cobalt based compounds as conductive additive is the commercially used remedy to this problem [2]. Even though, Co based compounds works well due to formation of continuous and homogeneous network [3], their high cost raise interest toward cheaper options like carbon derivatives. Different carbon based materials are investigated to impart conductivity to the cathode active material [4]. Although, some success has been obtained with these materials, they are not commercialized yet. Being low density and hydrophobic, it is difficult to prepare a homogenous blend of carbon and $Ni(OH)_2$ which adversely effects the electrochemical properties [5].

This study investigates the electrochemical properties of cathodes prepared with two different carbon based materials i.e. carbon black and plasma black. During the blending of the materials two different techniques are used. The first technique is ball milling the powders together to form a homogenous mixture before slurry preparation. And, the second one is the so called dispersion method in which $Ni(OH)_2$ is dispersed in DI water and carbon derivatives are dispersed in ethanol-DI water mixture. Positive charge accumulates on the surface of the $Ni(OH)_2$ and negative charge accumulates on the surface of carbon particles. Combining the two dispersions together while stirring and evaporating the liquids, blending of the carbon and the active material is achieved with electrostatic attraction between the particles.

A reference battery is also prepared by ball milling $Co(OH)_2$ with $Ni(OH)_2$ and then preparing a slurry. The full theoretical capacity of 289 mAh/g is achieved with this battery. Best performing battery is obtained when carbon black and plasma black are used together and dispersion method is employed and 228 mAh/g capacity is attained. However, this capacity wasn't stable and a capacity decay is observed for the batteries prepared with carbon derivatives unlike the reference battery.

Observation of the XRD patterns of the cathodes at different cycles shows that the unwanted γ-NiOOH formation occurs for the batteries prepared with carbon derivatives. XRD pattern of the reference battery revealed no γ-NiOOH formation during cycling. Reaching lower capacity values and having a capacity decay with cycling is attributed to the formation of this phase.

Charge profiles are studied and it is seen that charging potentials were higher for the batteries produced with carbon. And, there was no apparent difference between the oxidation reaction of $Ni(OH)_2$ and oxygen evolution reaction. This difference was quite prominent for the reference battery. Cyclic voltammetry is used to investigate these reactions and same result was obtained. The oxidation reaction and oxygen evolution reaction was well separated for the reference battery and there was an overlap of these reactions for the batteries prepared with carbon derivatives.

The formation of the γ-NiOOH phase is attributed to overlap of competing oxidation and oxygen evolution reactions. Moreover, this overlap is thought to be due to the higher polarization of the batteries. This is under investigation with impedance measurements.

References

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