

Layered cobalt oxide as electronic conducting additive for the positive electrode of Ni-MH batteries

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The very low electronic conductivity of nickel hydroxide requires the presence of an electronic conducting additive in the pasted electrode technology. This additive must be stable in the overall electrochemical window used during the battery cycling. In this condition, carbon derivatives are oxidized while the classically used cobalt oxyhydroxides can be reduced at very low voltages. This reduction leads to the formation of partially soluble $\text{Co}(\text{OH})_2$, to a cobalt redistribution within the electrode and a significant loss of capacity.

In the scope of our general studies on the behaviour of cobalt layered oxides in electrochemical generators, the effect of the Na_xCoO_2 phase as conducting additive to $\text{Ni}(\text{OH})_2$ has been investigated.

The $\text{Na}_{0.60}\text{CoO}_2$ phase has been obtained by high temperature solid-state chemistry (Co_3O_4 , Na_2O at 550°C under oxygen). This material exhibits the P3 type structure with a very small monoclinic distortion. The CoO_6 octahedra share edges to form the CoO_2 slabs.

The electronic conductivity of the $\text{Na}_{0.60}\text{CoO}_2$ phase (four probe technique) is rather high (40 S.cm^{-1}), its decrease with increasing temperature shows a metallic behaviour. This character results from a delocalisation of electrons due to the presence of 30 % of “tetravalent cobalt” and to the very small Co-Co distance in comparison with the t_{2g} orbital extension.

Electrochemical behaviour

This material has been used as additive in nickel hydroxide electrode in comparison with CoO , the classical additive. (CoO is spontaneously transformed into $\text{Co}(\text{OH})_2$ in KOH medium and then in electronic conducting H_xCoO_2 during the battery cycling). Cadmium electrodes were used as negative electrodes; the

cells were cycled at the C/5 rate with a cut-off voltage of 0.9 V and 6 h charge.

The evolution of the Number of Exchanged Electrons (NEE) per nickel atom is reported in Fig. 1. For the electrode containing 33 % (in weight) of $\text{Na}_{0.60}\text{CoO}_2$ additive, 1.1 electrons can be exchanged upon cycling. When only 10 % of $\text{Na}_{0.60}\text{CoO}_2$ is used, the NEE is smaller (0.7-0.8) but increases regularly upon cycling and stabilizes to 0.90. Due to the large size of the $\text{Na}_{0.60}\text{CoO}_2$ particles, a significant amount of additive is required to have percolation within the electrode.

In order to test the electrode stability at very low voltage the following test was performed: after the 50th cycle the cells were shorted for 3 days across a 10 ohm resistor and then the cycling was continued for several cycles. In those conditions, the electrodes with $\text{Na}_{0.60}\text{CoO}_2$ do not show any capacity loss contrarily to those made with CoO .

In order to understand the intrinsic behavior of $\text{Na}_{0.60}\text{CoO}_2$ in the electrode of alkaline batteries, cells were made with this oxide as active material (without nickel hydroxide) and cycled. The number of exchanged electrons per cobalt atom is smaller than 0.05; the XRD diffraction study shows that the γ -type cobalt oxyhydroxide with general formula $(\text{Na}_x(\text{H}_2\text{O})_y\text{CoO}_2)$ is irreversibly formed without any trace of H_xCoO_2 . This behaviour has been confirmed by in situ X-ray diffraction.

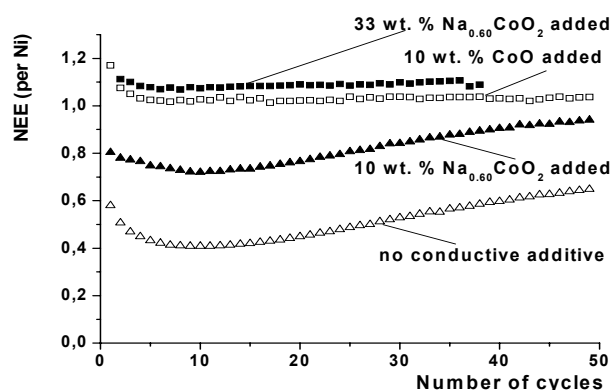


Fig. 1 : Evolution of the number of exchanged electron per nickel atom for nickel electrode containing 33 or 10wt % of $\text{Na}_{0.60}\text{CoO}_2$ as conductive additive.

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