

Quantification of Yttrium Effect on the Corrosion of AB₅ Type Alloys for Nickel-Metal Hydride Batteries

- L. LE GUENNE, O. ARNAUD, C. AUDRY, and P. BERNARD (SAFT)

As it exhibits higher energy storage capabilities than nickel-cadmium at reasonable cost and does not show any safety issue, nickel-metal hydride (Ni-MH) electrochemical system is predominant in a large range of portable appliances. One of the key point for the commercial success of Ni-MH batteries is life duration.

Previous results obtained at SAFT (i, ii) have shown that positive electrode endures no degradation during cycling and storage, and limitation of Ni-MH battery life duration is directly linked to negative electrode degradation : corrosion and decrepitation of alloy particles. The latter phenomenon is a consequence of volume changes occurring upon hydrogen solid solution/hydride phase transformation during cycling. During exposure of AB₅ alloy to a KOH aqueous electrolyte, a continuous nanocrystalline corrosion scale, composed of a metallic solid solution (Ni, Co), oxide solid solution (Ni, Co)O and mischmetal hydroxide, and well-defined needles of rare earth hydroxides are formed as corrosion products (iii). Temperature largely enhances this phenomenon.

It has been reported previously that adding Y₂O₃ (iv) (v) (vi) decreases storage corrosion rate. Yttrium is added as oxide either to the electrode or to the electrolyte(vii). It dissolves in the electrolyte and is then incorporated in the corrosion scale (continuous nanocrystalline corrosion scale) and mainly in the Mm(OH)₃ needles as hydroxide. The decrease in corrosion of the alloy is interpreted in terms of modification, due to yttrium, of the driving force for the diffusion of corrosion products (Mm³⁺) and corrosive species (OH⁻) across the corrosion scale.

Because of the high cost of Y₂O₃, it is necessary to optimise its effect on alloy corrosion as a function of utilisation conditions of batteries and Y₂O₃ content in the MH electrode.

In the present work, the influence of Y₂O₃ content in the MH electrode on the amount, the structure and morphology of corrosion products was investigated.

Yttrium effect on alloy corrosion has been observed for Y₂O₃ contents in the negative electrode varying between 0 and 2% (Figure 1 and Figure 2). Beyond 0.7% of Y₂O₃ in the MH electrode, there is no supplementary effect on cycling and storage corrosion rate as those observed with 0.7% of Y₂O₃. This limit corresponds to a morphological and structural change in the corrosion scale. For amount of Y₂O₃ less than or equal to 0.7%, corrosion products are formed with a Mm_{1-x}Y_x(OH)₃ type composition, a structure similar to Mm(OH)₃ and crystallising in hexagonal platelets. Below this limit, yttrium is thus incorporated in the corrosion scale as Mm_{1-x}Y_x(OH)₃ and allows the reduction of corrosion kinetics of the AB₅ alloy. On the contrary, beyond 0.7% of Y₂O₃, corrosion products have a Y_{1-x}Mm_x(OH)₃ type composition, a structure similar to Y(OH)₃ and crystallising in spherical grains. Beyond 0.7% Y₂O₃, yttrium precipitates and forms Y_{1-x}Mm_x(OH)₃ compounds between alloy particles and becomes less active as corrosion inhibitor.

Keywords: nickel metal hydride, cycle lifetime, corrosion, Yttrium

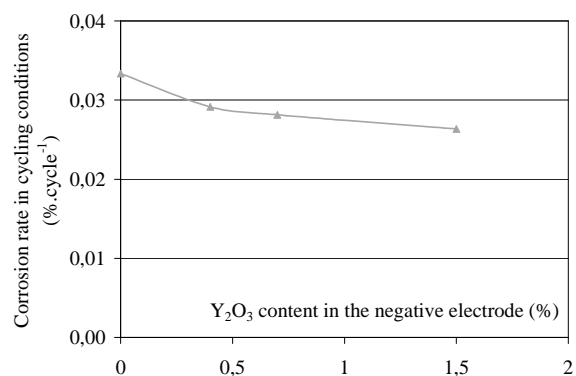


Figure 1 . Corrosion rate in cycling conditions as a function of Y₂O₃ content in the negative electrode

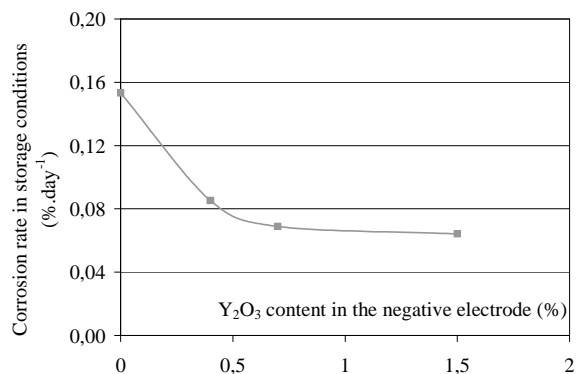


Figure 2 . Corrosion rate in storage conditions as a function of Y₂O₃ content in the negative electrode

- (i) . P. Leblanc, C. Jordy, B. Knosp, P. Blanchard *J. Electrochem. Soc.* (1998), **144**, 860
- (ii) . P. Bernard, *J. Electrochem. Soc.* (1998), **144**, 456
- (iii) . F. Maurel, B. Knosp, M. Backhaus-Ricoult, *J. Electrochem. Soc.* (2000), **147**, 78
- (iv) . F. Maurel, P. Leblanc, B. Knosp, M. Backhaus-Ricoult, *J. All. Comp.* (2000), **309**, 88
- (v) . H. Kaiya et Al., *J. Alloys Comp.* (1995), **231**, 598
- (vi) . K. Furukawa et Al., *Yuasa-Jiho*, (1997), **82**, 27
- (vii) . Matsushita, *Patent EP 0 607 806 A2* (1994)