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Degradation behavior of foamed nickel positive electrodes of Ni–MH batteries

Z.Q. Zhou*, G.W. Lin, J.L. Zhang, J.S. Ge, J.R. Shen

Institute of Hydrogen Storage Materials, Shanghai University, Shanghai, 200072 PR China

Abstract

The extrusion mechanism has been demonstrated to be the major cause for the capacity decay of the positive electrodes during cycling. However, based on our SEM and EPMA observations on cycled electrodes we found that some active material on the foamed nickel electrodes came off into scales especially as the electrodes cycled at 1C rate of discharge. This phenomena is suggested as another important cause for the capacity decay of positive electrodes and may be explained by the internal stress induced by the different volume change at the outer layer and the core due to phase and structure transformation during cycling.

Keywords: Foamed nickel electrode; Degradation behavior; Phase transformation stress

1. Introduction

The nickel electrode is currently the specific energy-limiting component in nickel–metal hydride batteries. Rapid growth in electric vehicle and other applications has created a need for improved nickel–metal hydride battery technology. Increased performance, with electrode specific energy as the primary figure of merit, is the major goal of this effort. However, cost reduction and cycle life are also important parts of the overall program. For foamed nickel positive electrodes of EV Ni–MH batteries, the capacity decay of the positive electrode should be considered. The objective of the present study is an attempt to gain a better understanding of the mechanism of the deterioration behavior of the foamed nickel positive electrode.

2. Experimental

The foamed nickel positive electrodes were made of a mixture of powders (including nickel hydroxide powder and various additives including cobalt oxide powder, zinc hydroxide powder and graphite powder, etc.) with a small addition of adhesive agent (PTFE aqueous solution). The mixture was filled into a foamed nickel substrate and dried at 80°C, then pressed into a sheet of 0.8 mm in thickness. The experimental open Ni–MH cell was designed to be nickel positive electrode limited. To investigate the surface morphology and composition change of the degraded nickel electrodes after the charging–discharging cycles, the degraded electrodes were washed thoroughly using pure water and then dried at about 80°C, then were examined using scanning electron microscopy (SEM), energy disperse spectroscopy analysis and EPMA.

3. Results and discussion

The basis for understanding the mechanism of the deterioration behavior of the foamed nickel electrode is the accurate knowledge of the structure and composition of the electrode and their distribution before cycling. The SEM photograph for surface of the foamed nickel electrode before cycling comprised various powders (including active material and various additive powders) with PTFE only, without foamed nickel substrate (Fig. 1a). For the understanding of mechanism of capacity decay it should be noted that there were two different layers (a thin outer layer and core) with different structure and composition in the foamed nickel electrode. The outer layer comprised various powders only (including active material and various additive powders) with some PTFE, while the core comprised foamed nickel substrate and various powders with PTFE. This is verified from the EPMA image of

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*Corresponding author.

E-mail address: zqzhou@online.sh.cn (Z.Q. Zhou)

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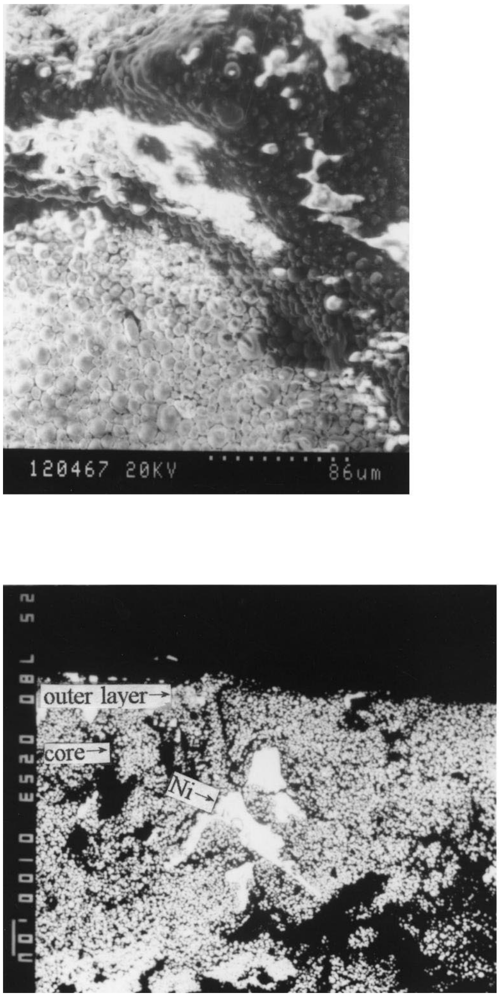


Fig. 1. Micrograph of the foamed nickel electrode before cycling (a) SEM photo of the surface; (b) EPMA image of nickel of the section perpendicular to the surface.

nickel for the section perpendicular to the surface (Fig. 1b).

Effect of charge–discharge cycling number on surface morphologies of the foamed nickel electrode is shown in Figs. 2–4. Fig. 2 shows the surface morphologies at the different places of the degraded nickel electrode, where discharge capacity has been decreased to 80% of the original capacity, in the meantime the thickness of the plate electrode increased from 0.80 to 1.08 mm. It can be seen from these photographs that:

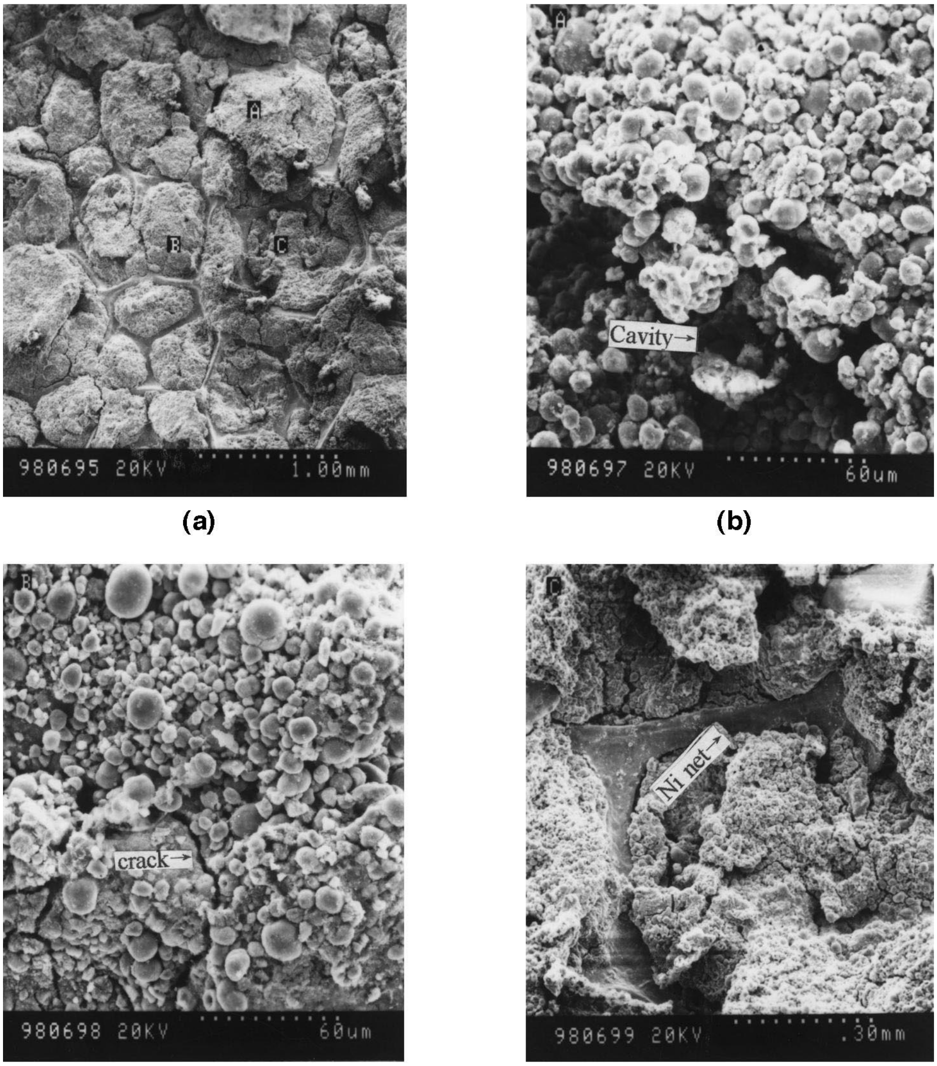
1. Small pieces of bond powders (including nickel hydroxide powder) in the outer scaled off from the electrode heterogeneously after cycling (Fig. 2a). The cavities due to the scaling off of some pieces of bonded powders in the outer layer are shown in Fig. 2b.
2. Cracks in some place of the outer layer before scaling off are shown in Fig. 2c.
3. The scaling off took place preferentially near the foamed nickel substrate at the interface between the outer layer and the core of the electrode (Fig. 2d). Energy disperse spectroscopy analysis of the morphology of unclosed net in Fig. 2d showed that the unclosed net was composed of nickel (Fig. 3).

Fig. 4 shows the SEM photographs for surface of the foamed nickel electrode after large number of cycling, when the capacity is decreased to 70% of the maximum capacity of the electrode. It has been shown from the charge–discharge cycling test that the greater the number of the cycle, and the greater the rate of discharge, the more seriously the electrode scales off (Fig. 4a). The SEM photo for the section perpendicular to the surface of the degraded electrode showed that there were cracks between the electrode and the active material powder block which will be scaled off from electrode very quickly (Fig. 4b).

In the conventional paste-type nickel electrode having a high energy density, a serious problem is usually caused by the swelling of electrode due to the decrease in density of the active material after repeated charging and discharging cycling [1]. It has been demonstrated that as the electrode is cycled the active material undergoes significant changes in phase, oxidation state, state of hydration, structure, crystallinity and density etc. which lead to the gradual extrusion of the active material out off the electrode substrate and into the electrolyte or separator in the cell. This causes the capacity decay of the electrode [2]. The above degradation behavior of positive electrode has been called the extrusion mechanism. However, some authors pointed out that peeling off or scaling off was another cause for the capacity decay of the positive electrodes during cycling. The extrusion mechanism does not explain why the heterogeneous scaling off takes place.

In the present study, the SEM observation of the foamed nickel positive electrode of the Ni–MH battery after degradation does reveal that the extrusion mechanism is not the only cause for the capacity decay of the electrode during cycling and in the meantime some active material on the positive electrode scales off preferentially near the foamed nickel net, namely at the interface between the outer layer and the core of the electrode especially as the electrode is cycled at 1C rate. This phenomena can be suggested as another important cause for the capacity decay of positive electrodes and may be explained by the internal stress induced by the different volume change at the outer layer and the core due to phase, oxidation state, state of hydration and structure transformation during cycling.

1. Before charge/discharge cycling the foamed nickel electrode is composed of two parts with different structures and compositions, the core and the outer layer. The core comprises nickel–hydroxide active material powder (including various additives), foamed nickel net and PTFE while the outer layer comprises



(a) (b)

(c) (d)

Fig. 2. Surface morphologies for different places (a,b,c,d) of the degradated foamed nickel electrode which capacity has been decreased to 80% of the original capacity.

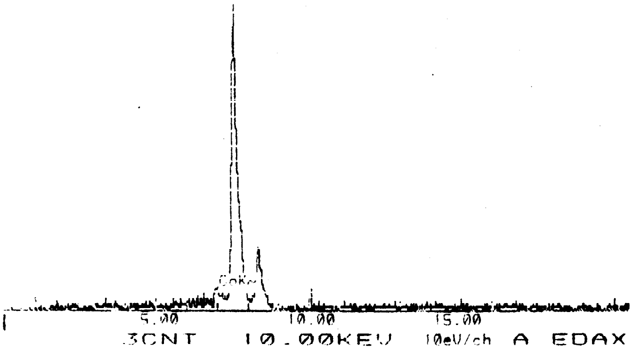


Fig. 3. EDS analysis of the unclosed netted morphology.

nickel–hydroxide active material, (including various additives) and PTFE only, without foamed nickel. The active material distribution in the foamed nickel substrate and its formation mechanism are somewhat similar to those of the MH electrode we described previously [3].

2. Different materials in the nickel electrode behave differently during cycling. As the electrode is cycled the active material undergoes significant changes in phase, oxidation state, state of hydration, structure, crystallinity and density etc., so it has a significant change in volume; but the foamed nickel substrate does not undergo the changes in phase and structure etc., so it does not have a volume change. Therefore, the change in volume in the outer layer with more active material will be greater than that in the core layer with less active material while cycling.

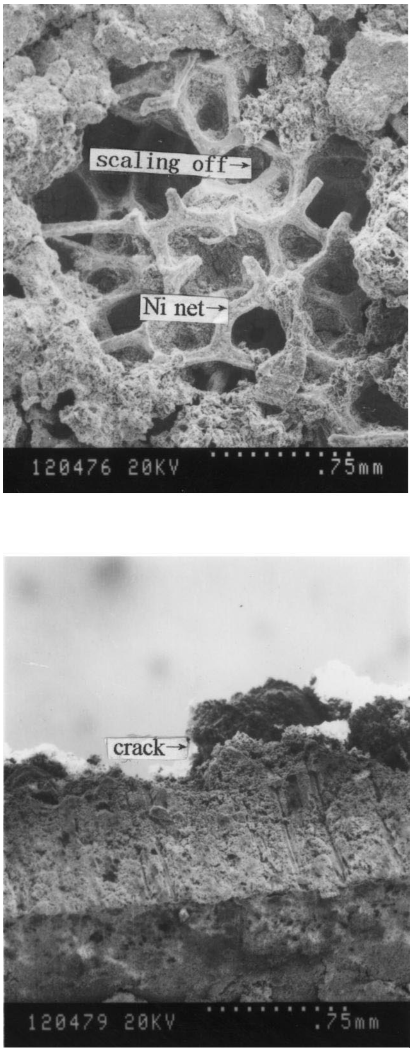


Fig. 4. SEM photo of the degraded foamed nickel electrode which capacity has been decreased to 70% of the original capacity (a) the surface (b) the section perpendicular to the surface.

3. The outer layer and the core are glued together by PTFE. During cycling the different volume change between the outer layer and the core causes an elastic interaction between these two parts. As the electrode is charged, the expansion caused by the phase and structure transformation in the outer is greater than that in the core. This will generate a stress state with a tensile stress at the core and a compressive stress at the outer. As the electrode is discharged, the contraction caused by the reverse transformation in the outer is greater than that in the core. This causes a stress state with a compressive stress at the core and a tensile stress at the outer, i.e. the stress state, will be reversed. When the tensile stress exceeds the strength of adhesion of PTFE or exceeds adhesive strength between the active material and the foamed nickel substrate, it may cause PTFE polymer chain cleavage or may result in the interface fissuring followed by the deep cracking. As the electrode cycles the cracks will continue to form and propagate preferentially along the interface where the adhesive strength between powders and foamed nickel net is the lowest, and causes the active material scaling off and the capacity decrease.
4. As the difference of the volume change between the outer layer and the core near the interface is the largest in the electrode, the elastic stress there must also be the largest. This explains why the scaling off take place preferentially near the foamed nickel substrate at the interface between the outer and the core of the electrode.

4. Conclusion

The extrusion mechanism is not the only cause for the capacity decay of the foamed nickel electrode during cycling. The scaling off of some active material on the foamed nickel electrode especially as the electrode cycled at 1C rate of discharge is another important cause, which may be explained by the internal stress induced by the different volume change at the outer layer and the core due to phase and structure transformation during cycling.

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