



Electrochemical impedance spectroscopy study of Ni/MH batteries

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Abstract

An electrochemical impedance spectroscopy study of Ni/MH batteries is reported. The surface structure change of MH electrodes during activation and charge/discharge cyclings of a Ni/MH battery is discussed by fitting EIS data to an equivalent circuit. The effect of surface treatment of hydrogen storage alloys on the electrochemical parameters of the electrodes is also reported. © 1999 Published by Elsevier Science S.A. All rights reserved.

Keywords: Nickel/metal hydride battery; Electrochemical impedance spectroscopy; Interface structure; Surface treatment

1. Introduction

Electrochemical impedance spectroscopy (EIS) is an important electrochemical method for investigating the electrode kinetics and its surface reactions, and has been successfully used in the study of Ni–Cd batteries, Pb-acid batteries and metal hydride electrodes [1–3]. Only a few EIS studies on Ni/MH batteries have been reported. Reid [4] measured the impedance of a spirally wound nickel/metal hydride battery cycled in a simulated low earth orbit. He found that the impedance of the spirally wound metal hydride battery changed only slightly over the course of 2000 LEO (low earth orbit regime) at 50% depth-of-discharge (DOD) with approximately 5% overcharge. Both the nickel electrode and the metal hydride electrode contributed to the impedance of the battery, with the larger portion from the nickel electrode. We employed EIS to study the early cycling deterioration of Ni/MH batteries and found that the deterioration first appeared as a voltage drop, which was then followed by a sharp decrease of the discharge capacity and voltage. The deterioration of voltage performance was due to the drying out of the separator which leads to an increase in R_s of the battery, while the decrease of the discharge capacity was due to the deactivation of the surface which leads to an increase of the charge transfer resistance of the battery [5]. It is useful and informative to determine the key factors affecting the performance of Ni/MH batteries by means of an EIS study.

An EIS study of a Ni/MH battery during activation and cycling as well as with different surface treatments is reported in this paper. A correlation between EIS and battery performance is found.

2. Experimental

Ni/MH batteries (4/5A size) with spirally wound electrodes were made and sealed immediately without any previous treatment. The positive electrode was fabricated by mixing spherical nickel hydroxide powder coprecipitated 4% Zn (Canada) with a certain proportion of additive (Co, Co(OH)₂, C) and binder to form a slurry which was then applied onto a foam-nickel substrate. The negative electrode was made by mixing AB₅-type hydrogen storage alloys (Eastern Metal Hydride Corp., China) and acetylene black with a binding medium to form a paste. Both pasted electrodes were dried at 60°C and press-shaped. The separator was non-woven polypropylene imported from Germany. The electrolyte was 7 mol l⁻¹ KOH+1 mol l⁻¹ LiOH. The nominal capacity of each battery was around 1500 mAh, with around 7 g positive paste, 10 g negative paste and 3.0 g electrolyte.

The powder of the hydrogen storage alloy treated with 6 M KOH alkaline solution or 6 M KOH alkaline solution containing 0.1 M KBH₄ reducing agent for 5 h was compared with untreated powder for investigation of the effect of surface modification of the negative electrode on EIS and battery performance.

Battery activation and cycling tests were performed on a

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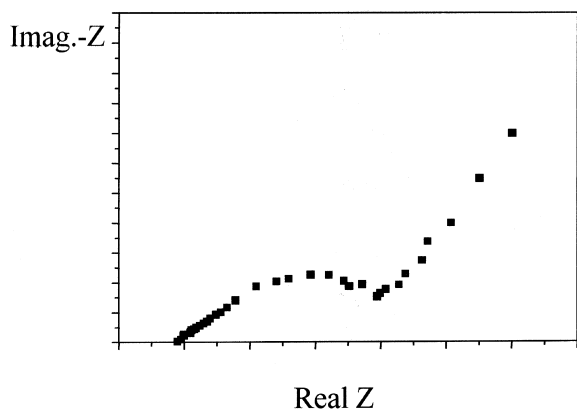


Fig. 1. Typical Nyquist plot of a battery.

DC-5 battery tester. The activation process was carried out by charging at a rate of 0.1C for 15 h and discharging at 0.2 C to 1.0 V (C is the nominal capacity of the battery). The process was repeated five times. The cycling test was

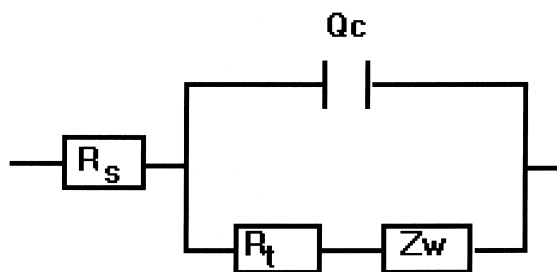


Fig. 2. Equivalent circuit for the Ni/MH battery in the EIS study, where R_s is the total ohmic resistance of solution and separator and electrodes, R_t is the charge-transfer resistance of the electrodes, Z_w is the Warburg impedance and Q_c is the constant-phase element related to the surface area of the battery electrodes in order to consider semicircles with a depressed shape.

conducted by charging at 850 mA for 2.2 h and discharging at 500 mA to 0.9 V. EIS was measured after every activation and every 10 working charge/discharge cycles. The EIS measurement was made at 20% charging state (SOC) of the battery using a Solartron 1250 Frequency Response Analyzer in conjunction with a Solartron 1287 Electrochemical Interface. The positive end of the battery was used as the study electrode. The negative end of the battery was used as the counter electrode and the reference electrode. The voltage perturbation used in the present work was 10 mV. Impedance was measured from 10^4 Hz to about 10^{-3} Hz.

3. Results and discussion

3.1. EIS of a Ni/MH battery

A typical Nyquist plot of a Ni/MH battery is shown in Fig. 1. At high frequencies, the plot starts as a semicircle and, as the frequency decreases, it changes to a straight line. In our opinion, the semicircle reflects the impedance of the electrochemical reaction of the battery, while the straight line indicates diffusion of the electroactive species. Solution resistance is determined by the point of intersection of the semicircle with the real axis, including the total ohmic resistance of the solution, the separator and the electrodes. An equivalent circuit for a battery during the EIS study is shown in Fig. 2, with Q_c , R_s , R_t and Z_w designating the constant-phase element related to the surface area of the battery electrodes in order to consider semicircles with a depressed shape, the total ohmic resistance of solution and separator and electrodes, the charge-transfer resistance of the electrodes and the Warburg impedance, respectively.

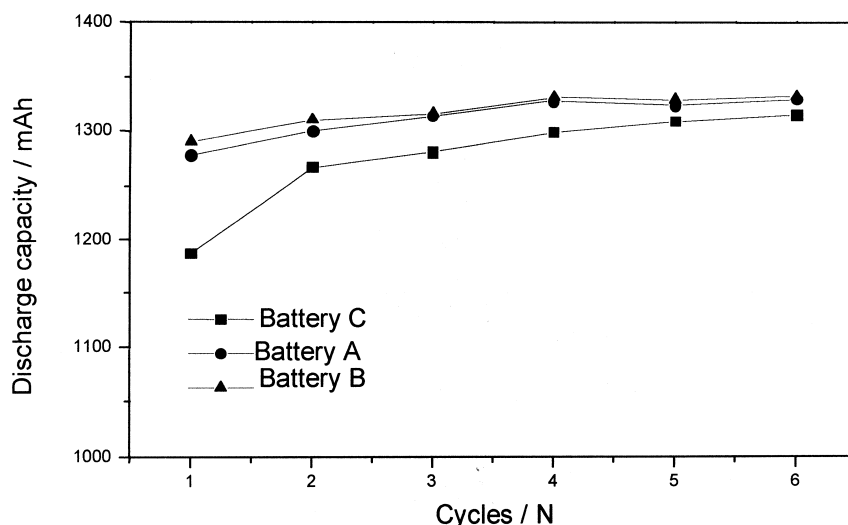


Fig. 3. Battery capacity vs. cycle number of a nickel-metal hydride battery with differently treated hydrogen storage alloy.

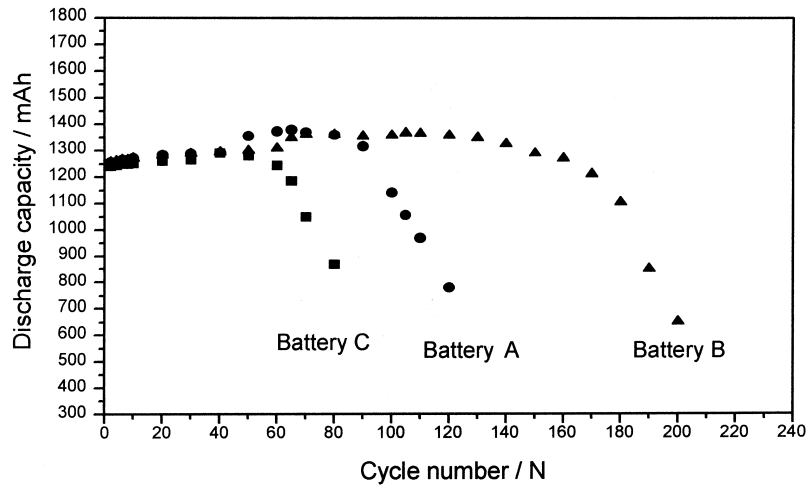


Fig. 4. Cycle-life of batteries with differently treated hydrogen storage alloy.

3.2. Effect of MH alloy surface modification on battery EIS

The hydrogen storage alloy powder of battery A was treated with alkaline solution. The alloy powder of battery B was treated with alkaline solution containing a reducing agent, and that of battery C was not treated. The effects of surface treatment on the performance of the batteries are shown in Figs. 3 and 4. It can be seen that the surface treatment of hydrogen storage alloy powder greatly improves the activation and the cycle-life of the batteries. EIS curves of the batteries after two charge/discharge activation cycles (charging at a rate of 0.1C for 15 h and discharging at a rate of 0.2C to 1.0 V) are illustrated in Fig. 5. It can be seen that the R_s values of the batteries are almost the same, while there is a large difference in R_t (the larger the diameter of the semicircle, the larger R_t) with

$R_{t,B} < R_{t,A} < R_{t,C}$. These results indicate that surface modification of MH alloy is effective in improving the electro-catalytic activity of the electrode while the electro-contact resistance of the electrodes remains the same. The values derived from the equivalent circuit of Fig. 2 are shown in Table 1. There is a marked increase in Q_c for the batteries with electrodes made of surface-modified hydrogen storage

Table 1
Parameters for Ni/MH battery EIS

Battery	Solution resistance, R_s (Ω)	Charge-transfer resistance, R_t (Ω)	Constant-phase element, Q_c (F)
Battery A	0.0289	0.104	10.4
Battery B	0.0276	0.089	11.3
Battery C	0.0302	0.117	7.8

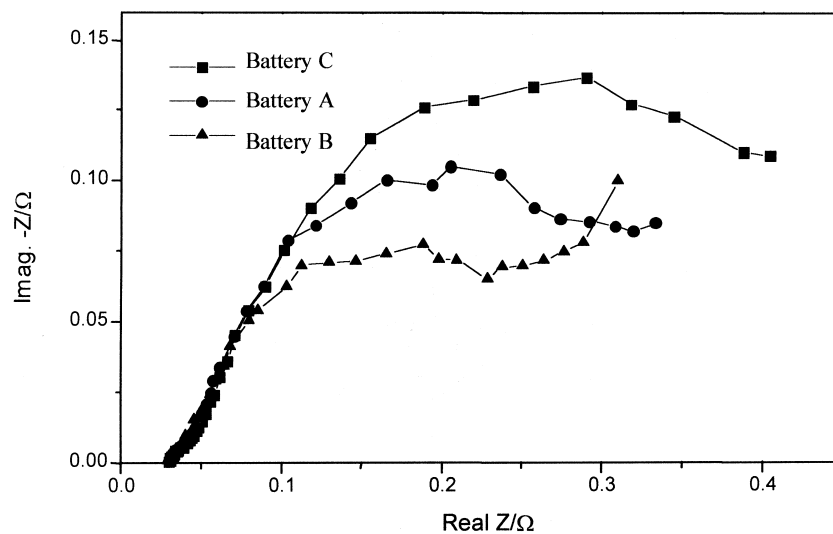


Fig. 5. EIS of batteries with MH alloy electrodes with different surface modifications.

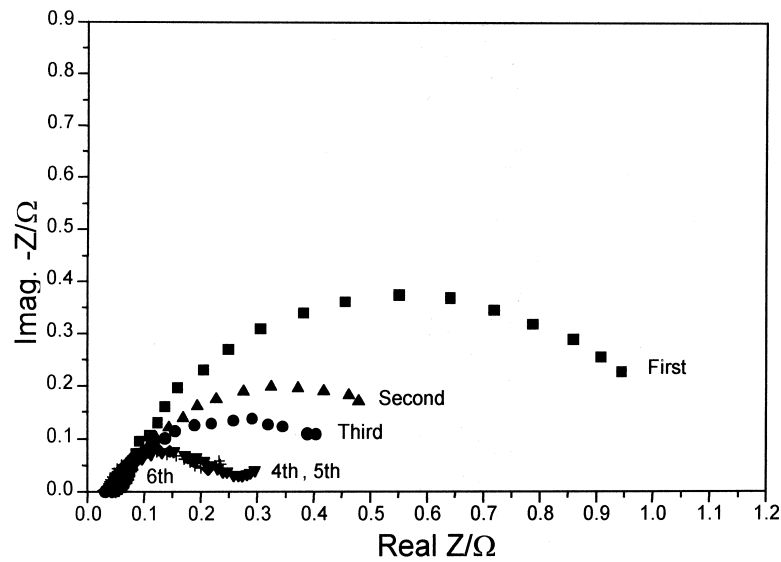


Fig. 6. EIS of battery B during activation.

alloys. This indicates that surface modification increases the effective surface area of the electrode simultaneously.

3.3. Battery EIS during activation

It can be seen from Fig. 3 that batteries A and B reached their maximum capacities on the third to fourth charge/discharge cycle, while battery C reached saturation capacity on about the fifth to sixth cycle. The EIS of battery B during activation is illustrated in Fig. 6. The diameter of the semicircle in the high frequency region decreases as the activation cycle number increases. This indicates a

decrease of battery R_t or an increase of the electro-catalytic activity of the electrode. Figs. 7–9 show the variation of, respectively, R_t , Q_c and R_s of a battery with activation cycling. The R_t of batteries A and B is much smaller in the beginning and remains stable after three to four activation cycles, while R_t of battery C is much higher in the beginning and takes five to six activation cycles to decrease. The Q_c of the three kinds of batteries show little difference in the beginning and display a large difference on the sixth cycle. This indicates that the surface modification improves the catalytic activity of the electrode surface. It can be seen from Fig. 9 that the surface modification of hydrogen storage alloy has little effect on

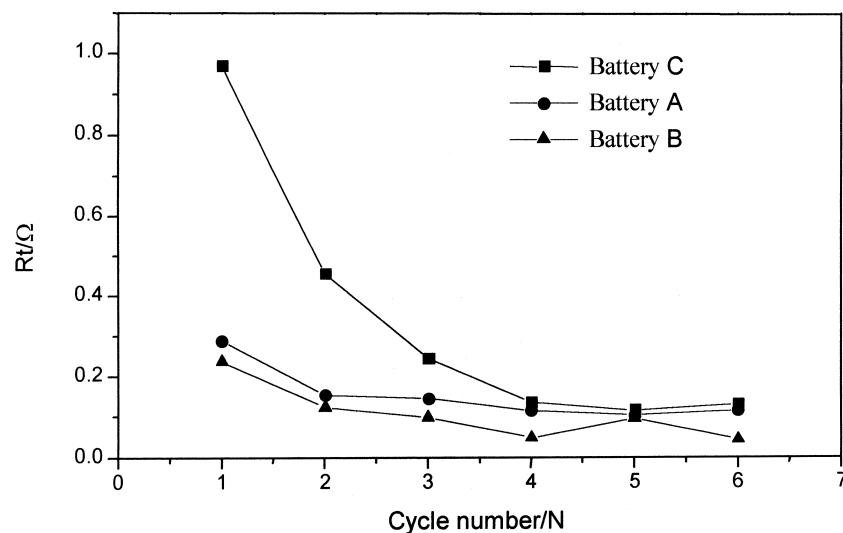


Fig. 7. R_t of a battery with different treatment and times of activation.

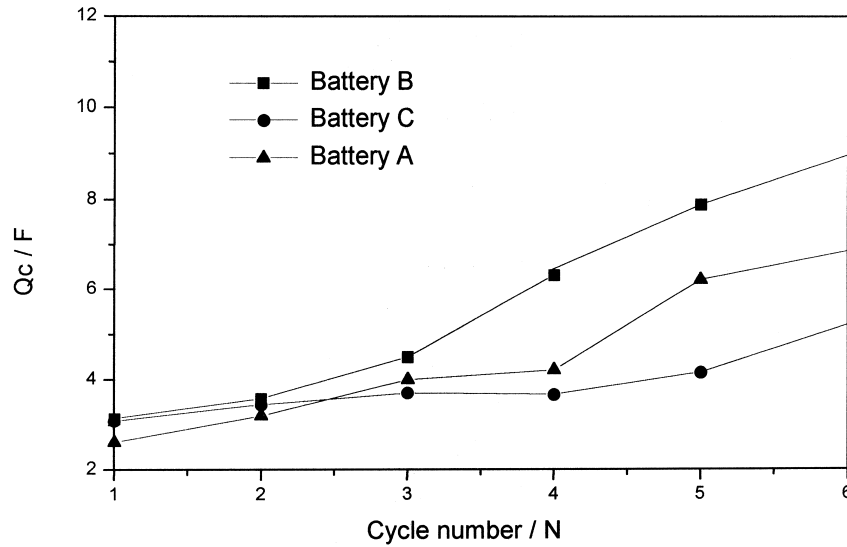


Fig. 8. Q_c of a battery with different treatment and times of activation.

the R_s value of the battery and on the electric conductivity of the negative electrode.

3.4. EIS analysis of the cyclic deterioration of batteries

There are two types of cyclic deterioration of batteries. One leads to a worsening of voltage performance in the beginning, which is reflected by an increase of the charging voltage and a decrease of the discharging voltage, while the battery capacity remains almost unchanged. After some cycles, due to the continuing increase of the

charging voltage and decrease of the charging efficiency, the battery capacity decreases sharply. The other type of deterioration leads to a gradual lowering of the battery capacity with cycling, while the voltage remains almost constant. Fig. 4 shows the effects of surface modification of hydrogen storage alloy on the cycle-life of the batteries. The cycle-lives of batteries C, A and B are around 80, 120 and 200 cycles, respectively. From the charge/discharge curves of the batteries at various cycles we find that deterioration of battery C belongs to the first type, and that of batteries A and B belongs to the second type.

Figs. 10 and 11 show EIS diagrams for the two types of

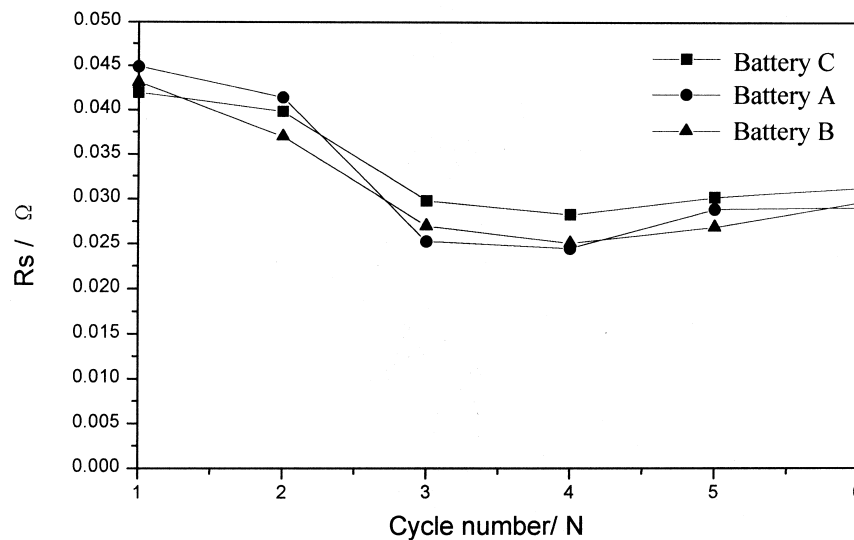


Fig. 9. R_s of a battery with different treatment and times of activation.

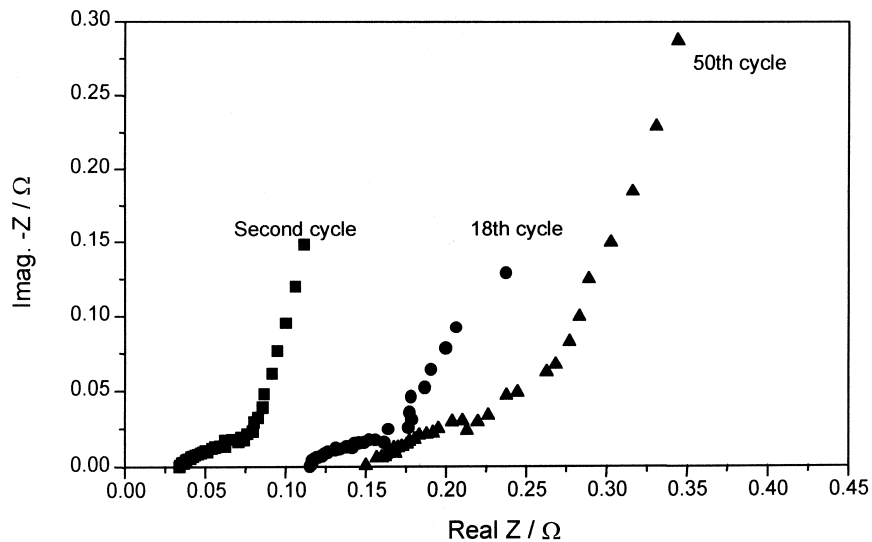


Fig. 10. EIS of battery C with voltage decay during the initial stage of cycling.

battery deterioration during cycling. Fig. 10 shows that, with an increase in the number of cycles, R_s increases gradually, which leads to a decrease in voltage. The increase of R_s is mainly due to the drying out of the separator, and thus results in an increase of the ohmic resistance of the battery. This inference is supported by the following test: dead batteries were dissected and immersed in an electrolyte of 6 M KOH solution. It was discovered that the voltage performance and capacity of the batteries almost entirely recovered. In Fig. 11, EIS indicates that, with an increase of cycling, R_s stays almost constant, while R_t increases gradually. In this case the battery performance undergoes a constant decrease of capacity with the voltage remains essentially unchanged. Hence, the voltage performance of the battery is related to R_s , while battery capacity is related to R_t .

4. Conclusions

1. The EIS of a Ni/MH battery consists of a semicircle and a sloped straight line. The semicircle reflects the electrochemical process of the battery, the diameter of which indicates the reactive impedance (R_t) of the electrode reaction. The slope of the straight line is related to the diffusion process of the protons in the electrode.
2. During activation, R_t and R_s of the battery decrease markedly, and both tend to constant values after three to five cycles.
3. There are two main types of battery deterioration. One is caused by capacity decay, and the other by voltage decay. The former is due to the increase of R_t , while the latter is caused by an increase of R_s .

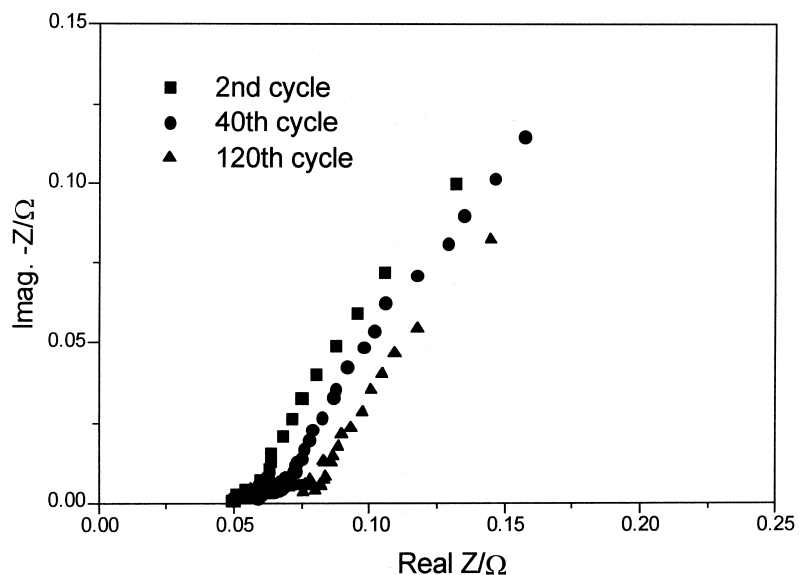


Fig. 11. EIS of battery B with capacity decay during cycling.

4. Surface treatment of hydrogen storage alloy reduces R_t remarkably, while it has little effect on R_s .

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