An improved analysis method of constant-current charge/discharge curves and its application to nickel hydroxide electrode [①]

PAN Tao(潘　滔)[1], WANG Jian-ming(王建明)[1], CHEN Hui(陈　惠)[1],
ZHAO Yan-lin(赵彦琳)[1], XIAO Hui-ming(肖慧明)[1], ZHANG Jian-qing(张鉴清)[1, 2]
(1. Department of Chemistry, Zhejiang University, Hangzhou 310027, China;
2. State Key Laboratory for Corrosion and Protection, Institute of Metal Research,
Chinese Academy of Sciences, Shenyang 110015, China)

Abstract: The derivative of charge and discharge curves (dt/dE vs E plot) can be used to describe the charge and discharge process more exactly. The $dt/dE - E$ plots of nickel hydroxide electrode at different charge/discharge rates and intermittent discharge experiment are discussed. Though the $dt/dE - E$ plot is affected by many factors, it clearly has intrinsic relation with the nature of active material such as conductivity and thermodynamic potential of active material, which changes with the state of charge. The $dt/dE - E$ plot can also be applied to other electrochemical active materials, especially to those having several phases during charge or discharge.

Key words: nickel hydroxide electrode; constant-current charge/discharge curve; derivative

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1　INTRODUCTION

The constant-current charge and discharge curves are widely used to describe the electrochemical characteristic of active material of batteries. Several parameters can be obtained from these curves, such as total discharge time, discharge capacity and half-discharge potential. These parameters give out a rough view of total charge/discharge process.

The charge/discharge curve is affected by many factors, such as the thermodynamic potential of active material, the exchange current density of redox reaction, the porosity and tortuosity of electrode, the current density and temperature. Many papers [1⁻5] have been published dealing with the mathematical model of discharge curve of simple active material using a lot of parameters, but these models still have some discrepancies to the actual curves. The charge process is more complex than discharge because it is accompanied by the evolution of gas and is difficult to describe with simple function. If the electrode consists of active materials with multiphase, its charge and discharge curves are impossible to be described by mathematical model.

Guerlou-Demourgues et al[6] used the derivatives of discharge curve ($dt/dE - E$ plot) to give an overview of the curve shape modifications in the cycle test of the manganese-substituted nickel hydroxide electrodes. The peak in the $dt/dE - E$ plot comes from the pseudo plateau on the discharge curve displaying potential vs time, and is considered to correspond to a certain redox system. They also implied that during the charge-discharge cycle test of beta nickel hydroxide the different peaks at $dt/dE - E$ plot are related to β-NiOOH and γ-NiOOH respectively[7].

In this paper, the $dt/dE - E$ plot is discussed in detail, and it is also used to interpret the charge-discharge behavior of alpha nickel hydroxide electrodes.

2　EXPERIMENTAL

The active materials were home-made Al-stabilized alpha Ni(OH)$_2$. The molar ratio of Ni: Al is 85: 15 in sample A and 90: 10 in sample B. The preparation and test details were described elsewhere[8]. In discharge experiment, the electrodes were usually discharged to 0.1 V (vs Hg/HgO) continuously, except for the constant-current intermittent discharge experiment. The intermittent discharge experiment was done in this way: a fully charged electrode made of sample B was discharged for 6 min at 1 C rate, rest 40 min, then was discharged for another 6 min at 1 C rate, and so on.

3　RESULTS AND DISCUSSION

3.1　Theoretical analysis on $dt/dE - E$ plot

The discussion in this paper focuses on the usage of dt/dE plot of positive electrode. The situation is similar for negative electrode.

The characteristic values of dt/dE —E plot of positive electrode include: $E_{p,a}$, the potential where the charge curve has maxim and $t_{p,a}$, the corresponding time; $E(O_2)$, the potential of oxygen evolution; $E_{p,c}$, the potential where the discharge curve has maxim and $t_{p,c}$, the corresponding time; the difference between $E(O_2)$ and $E_{p,a}$; the difference between $E_{p,a}$ and $E_{p,c}$. The dt/dE value is negative at discharge and positive at charge. In order to simplify the expression, usually the absolute value of dt/dE was used and was still called as dt/dE. $t_{p,a}$ and $t_{p,c}$ have relationship with the state of charge (SOC), and will not be discussed further in this paper.

Guerlou-Demourgues et al[6] and Tessier et al[7] did not give the dt/dE —E plot of charge process. Since the potential of electrode changes little or even keeps constant at the later part of charge process due to oxygen evolution, the dt/dE value is very large or becomes infinite. In order to avoid this trouble and understand the peak of active material, the charge curve is derived from the start of charge to the beginning of oxygen evolution. The plateau potential of oxygen evolution can be noted out alone on the graph if needed.

The dt/dE —E plot and its characteristic values are affected by those factors that have influences on the charge/ discharge curves. There are no mathematical models that can describe the constant-current charge/ discharge performance of practical electrode accurately and there are not any accurate functions between electrode potential and the parameters of active material and electrode. Therefore it is impossible to give out the relation between the peak potential in dt/dE —E plot and the parameters of active material and electrode. The peak potential of dt/dE —E plot of different electrodes made by the same active material varies about 10 mV or more. The change of peak potential in the dt/dE —E plot is caused by the change of macroscopic characteristics in electrode and inherent properties of active material.

Mao et al[5] pointed out that a discontinuity in the conductivity of nickel hydroxide will give rise to a secondary plateau on the discharge curve. In that paper, the conductivity function was selected to produce the secondary discharge plateau appearing at − 0.1 V vs Hg/ HgO reference electrode. It is clear that a small change in conductivity will lead to another discharge plateau close to the first one. It also implies that in constant charge/ discharge experiment when the dt/dE value reaches a maximum, the conductivity of active material may change most slowly with the state of charge of electrode.

3.2 Application of dt/dE —E plot to study of α-Ni(OH)₂

Fig. 1(a) shows the E —r curves of sample A in cycles 1 and 150. Here "r" is the ratio of charge/ discharge coulomb to the discharge capacity of electrode. These two curves have very similar shape though the half-discharge potential increases from 310 mV in cycle 1 to 338 mV in cycle 150 and the oxygen evolution potential also increases. Fig. 1(b) gives the dt/dE —E plots of each case. It clearly shows that after hundreds of charge/ discharge cycles besides the rise of the main peak from 322 to 355 mV which relates to the long discharge plateau, another peak in dt/dE —E is forming ranging between 280 and 260 mV, which implies the appearance of a new phase. It is interesting that the dt/dE plots of charge and discharge process are very similar except for the last part of charge plot corresponding to oxygen evolution. This implies that the peaks in dt/ dE plot has relation with redox reaction system in the electrode.
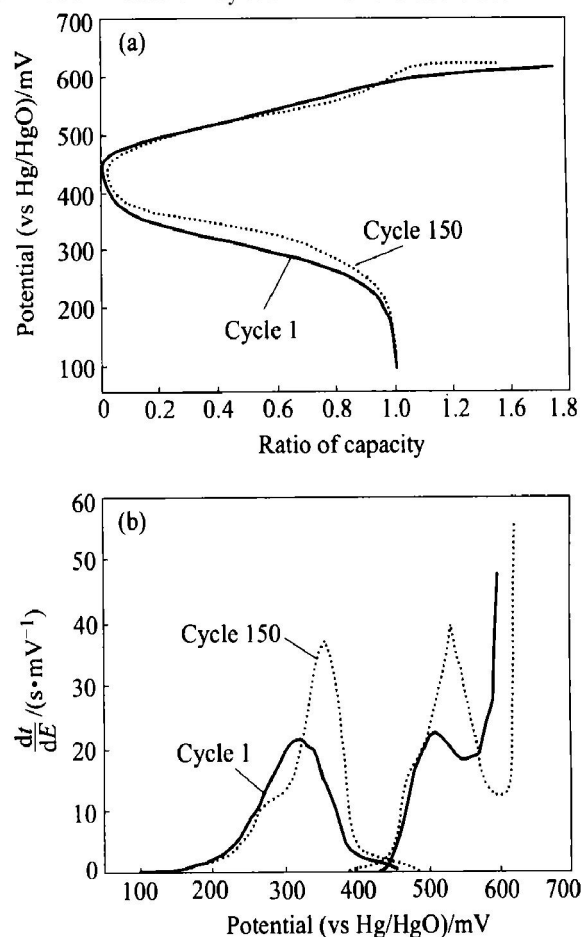

Fig. 1 E —r plots of sample A at cycle 1 and cycle 150(a) and dt/dE —E plots of sample A at cycle 1 and cycle 150(b)

In this experiment, the E —r curves and dt/dE —E plots show that the SOC when the dt/dE value in discharge reaches a maximum is 85%~ 60%. So, if there is only one discharge plateau in E —t plot, the half-discharge potential is lower than the peak potential of dt/dE plot. The SOC when the dt/dE value in charge reaches a maximum is 20%~ 50%. These SOC values were also affected by the

property of active material, the manufacture detail and the operation condition.

Fig. 2(a) shows the $E—r$ curves of sample B at cycles 1 and 100. The curve of cycle 100 is different from that of cycle 1, showing two discharge plateaus. Fig. 2(b) gives the $dt/dE—E$ plots of each case in which the change of electrode behavior after 100 cycles can be seen more clearly. After cycles, there are two split peaks in $dt/dE—E$ plot. In $E—r$ curve, one can only say that charge plateau becomes lower and half-discharge potential rises from 285 to 292 mV. While in $dt/dE—E$ plot, one can point out that the charge peak decreases from 502 to 490 mV and the shape of discharge plots change from one peak at 292 mV to two peaks at 347 mV and 284 mV. The dt/dE plot of charge process of sample B does not show two split peaks, but shows a high peak, which seems to be an overlap of two peaks.
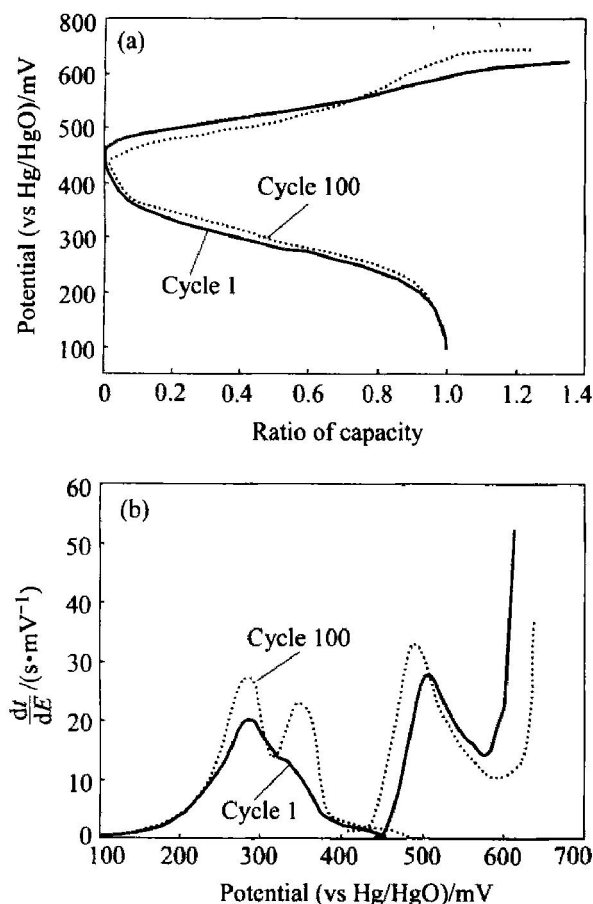

Fig. 2 $E—r$ plots of sample B at cycle 1 and cycle 100(a) and $dt/dE—E$ plots of sample B at cycle 1 and cycle 100(b)

It is well known that the α-Ni(OH)$_2$ is labile in alkaline media and easy to revert to β-Ni(OH)$_2$. Partial substitution of nickel ion in the lattice of nickel hydroxide by other metal ions such as Al can stabilize alpha structure[8]. In this experiment, the results of Figs. 1 and 2 show that sample A in which more Ni atoms are substituted by Al is much more stable than sample B. But after hundreds of charge and dis-

charge, sample A also has the trend of changing to a mixture of two phases. These phase changes lead to small shape changes in $E—r$ or $E—t$ curves and are easy to be ignored, but cause distinct differences in $dt/dE—E$ plots.

Fig. 3(a) shows the XRD pattern of sample A, and Fig. 3(b) shows the XRD pattern of aged sample A having been placed in 6 mol/L KOH for a month. The in situ XRD research of nickel hydroxide electrode had been carried out by Dai et al[10], but the XRD pattern of pasted nickel hydroxide electrode is too complex to distinguish those phases in the electrode. When nickel hydroxide is aged in KOH, it obeys a dissolution-nucleation-growth process, whether it is charged or not[6]. In this paper, the XRD graphs of un-cycled nickel hydroxide are used. Fig. 3(a) shows a typical α-Ni(OH)$_2$ pattern, and Fig. 3(b) shows the characteristic of mixed α- and β-Ni(OH)$_2$. Fig. 3(b) also shows that after ageing the XRD peaks related to α phase of sample A become sharper, which means the increase of crystallinity. According to the conclusion of Sugimoto et al[9], the utilization and half-discharge potential of Al-stabilized alpha Ni(OH)$_2$ will increase as the sample crystallinity improves. Both the $E—r$ curve and $dt/dE—E$ curve show the rise of discharge plateau in this experiment. The XRD pattern of cycled electrode is very complex and difficult to identify different materials because there are too many phases in the electrode.
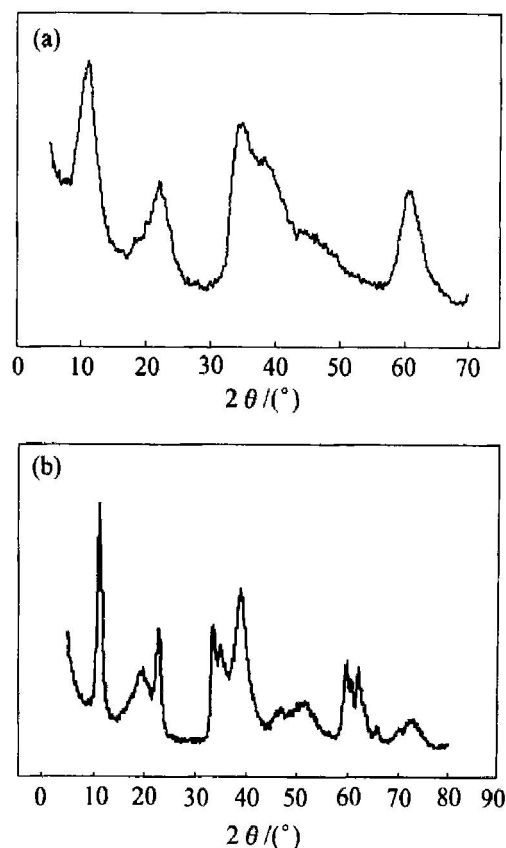

Fig. 3 XRD patterns of sample A (a) and aged sample A (b)

Fig. 4(a) gives a set of dt/dE —E plots in a constant-current intermittent discharge experiment of sample B. Fig. 4(b) is the dt/dE —E plot of the same electrode in a 1 C rate continuous discharge experiment. Fig. 4(c) gives the E —t curves of intermittent discharge experiment and open circuit potentials (OCP) at different SOC. The OCP was measured after 40 min rest. Fig. 4(c) shows the E-t plots, and hence the dt/dE plots, were affected by OCP. However, the most interesting thing in this experiment is the relation between Figs . 4 (a)
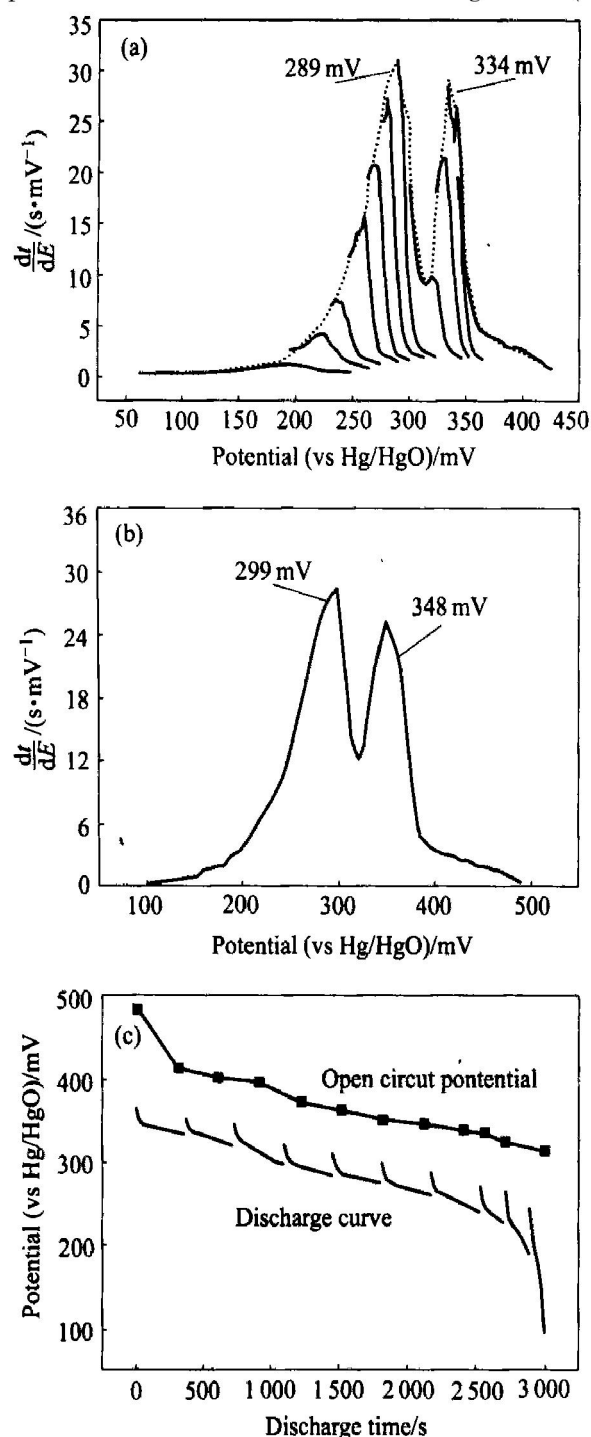

and (b). In the constant-current intermittent discharge experiment, the total shape of those dt/dE — E plots is similar to that of continuous discharge experiment. In the intermittent discharge case the half-discharge potential has no meaning. It clearly shows that the dt/dE —E plot is a good way to describe the electrode behavior and the values of $E_{p, a}$, $E_{p, c}$ and dt/dE have intrinsic relation with the nature of active material such as OCP and conductivity, though this relation may be too complex to be exactly defined.

Fig. 5 shows how the characteristic values of dt/dE plot of sample B change with different charge/discharge rates. Here $E(O_2)$ is oxygen-evolution potential, $E_{p, a}$ the peak potential of dt/dE —E plot in charge, $E_{p, c1}$, $E_{p, c2}$ two peak potentials of dt/dE —E plot in discharge, E_{mid} the half-discharge potential. The three lines of $E_{p, c1}$, $E_{p, c2}$ and E_{mid} are almost parallel. The slope of E_{mid} is – 49 mV/ C and the slope of E_{c1} and E_{c2} is about – 44 mV/ C. The slope of $E_{p, a}$ is about 44 mV/ C and the slope of E (O_2) is 76 mV/ C. E_{mid} is affected by OCP, liquid polarization and electrochemical polarization. It is clear that $E_{p, a}$ and $E_{p, c}$ in dt/dE plot is also affected by those factors.
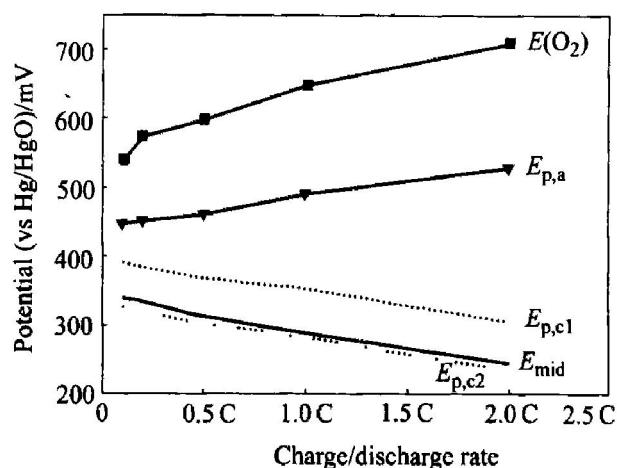

Fig. 5 Characteristic values of dt/dE plot
at different rates

Fig. 4 dt/dE plots in 1 C rate intermittent discharge (a), dt/dE plot in 1 C rate continuous discharge (b), and E —t curves of intermittent discharge experiment and OCP (c)

The total dt/dE —E plot of constant-current charge and discharge cycle (here the negative dt/dE value in discharge process is adopted) has similar shape with that of cyclic voltammetry experiment. Fig. 6(a) shows the dt/dE plots when the electrode was charged and discharged at 1 C rate; Fig. 6(b) shows the CV curve of the same electrode scanning between 100 and 650 mV at 0. 1 mV/ s rate so that both experiments spent about 3 h. The reduction peak in CV graph is much cathodic than that in dt/dE —E plot and the oxidation peak in CV graph is much positive than that in dt/dE —E plot. When the oxidation potential of active material is close to oxygen-evolution potential, the oxidation peak in CV graph is not clear, or even
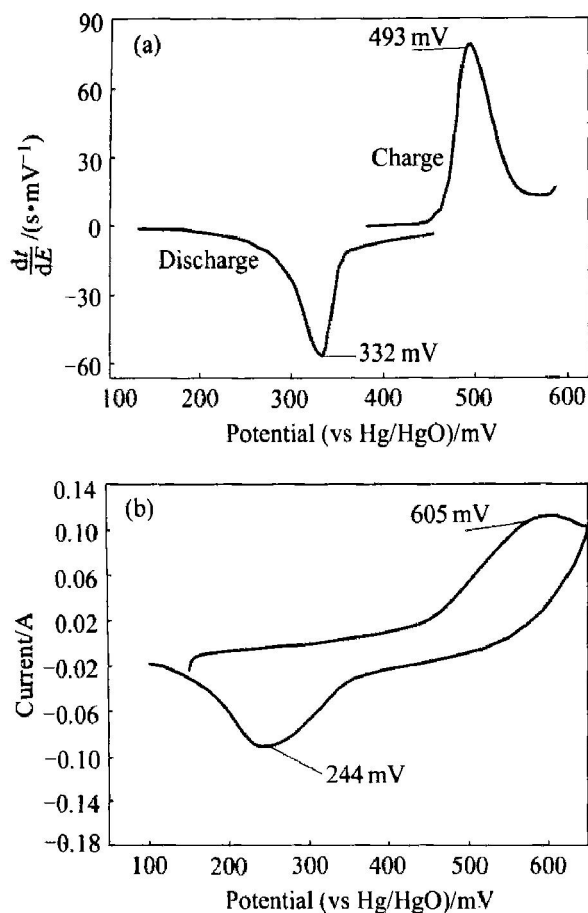
Fig. 6 Total dt/dE —E plot of constant-current charge and discharge cycle (a) and CV curve, scan at 0.1 mV/s (b)

covered by the oxygen-evolution current. While the oxidation peak in dt/dE —E plot is always distinct. There may be two reasons that cause the difference between those peaks in dt/dE —E curves and CV curves. First, the dt/dE plot is obtained from constant-current experiment, when the electrode is in the SOC range where the thermodynamic potential changes slightly, it can keep its polarization potential and get a dt/dE maximum value. While the CV curve is obtained from potential-scanning experiment, when the electrode is in the SOC range where the thermodynamic potential changes slightly, the current may not reach a maximum value and will be larger with the electrode

becoming more positive/ negative potential. Second, the peak currents in CV are much higher than ordinary charge/ discharge rate. In this experiment, 1 C rate is 40 mA, while anodic peak current in CV is about 103 mA and cathodic current is 90 mA. When the current is larger, the over-potential is larger too.

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