

CALCULATION OF ELECTROCHEMICAL OVERPOTENTIAL AND CONCENTRATION OVERPOTENTIAL BASED ON CURVE OF ANODIC POLARIZATION IN HYDROGEN STORAGE ALLOY ELECTRODE^①

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ABSTRACT It was investigated in detail how to calculate the electrochemical polarization overpotential V_e and concentration polarization overpotential V_c based on anodic polarization curve in hydrogen storage alloys electrode. The results show that the experimental anodic polarization curve should be divided into three regions to discuss according to discharge current density J_d , namely, $J_d < J_p$, $J_p < J_d < J_f$, and $J_d > J_f$. In different regions, the calculation for V_e and V_c should use different formulas. When discharge current density J_d is smaller than J_p , the traditional equation used to calculate the electrochemical overpotential can't be used, when J_d is between J_p and J_f , both equations used to calculate the electrochemical overpotential and concentration overpotential can be used, and when J_d is larger than J_f , because there exists absorption and adsorption of hydrogen, the traditional equation used to calculate concentration overpotential can't be used in the system of hydride electrodes.

Key words electrochemical overpotential concentration overpotential anodic polarization
hydrogen storage alloy

1 INTRODUCTION

Metal hydrides have been used as negative electrodes of nickel/metal hydride batteries in place of cadmium, because of their high energy density, high charge and discharge ability, long charge-discharge cycle life, and environmental compatibility^[1-3].

The performance of a hydride electrode is mainly determined by the thermodynamic properties, such as plateau pressure p_{plat} , the hydrogen concentration of α phase and β phase at the interface between α and β phase, $c(\alpha\beta)$, $c(\beta\alpha)$; and corrosion resistance in the alkaline solution, and the kinetic properties, i.e., exchange current density J_0 , diffusion coefficient

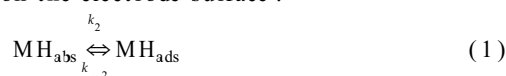
of hydrogen in the α phase D_α , and the geometric parameter r_0 .

The hydrogen desorption process during discharge in an alkaline solution is composed of several steps^[4,5]:

(1) Nucleation and growth of α phase from β phase.

(2) Diffusion of hydrogen from α phase through the oxide film to the near-surface region of the particle.

(3) Transfer of the hydrogen from the absorbed site in the near surface to the adsorbed site on the electrode surface.

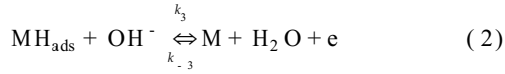


(4) Electrochemical oxidation of hydrogen,

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namely, occurring electrochemical reaction at the electrode surfaces.



The polarization overpotential of hydride electrode is composed of two parts, electrochemical polarization V_e and concentration polarization V_c . Electrochemical polarization V_e and concentration polarization V_c are very important kinetic parameters, but it is apparent, from the hydrogen desorption process mentioned above, that the traditional equations can't be used to calculate V_e and V_c in hydride electrode because there exists the process of absorption and adsorption of hydrogen. Yang *et al*^[6] use traditional equation to calculate the electrochemical overpotential V_e and concentration overpotential V_c in the entire polarization process is incorrect. In this paper, how to calculate the electrochemical polarization V_e and concentration polarization V_c based on anodic polarization curve in hydrogen storage alloy electrode system has been studied in detail.

2 EXPERIMENTAL

Hydrogen storage alloy of composition $\text{Ml-Ni}_{3.8}\text{Co}_{0.5}\text{Al}_{0.7}$ was prepared by arc melting under an argon atmosphere. The Ml stands for lanthanum-rich misch metal, which contains 74.50% La, 21.95% Ce, 2.40% Pr, and 1.15% Nd. and the purity of the other metals is at least 99.9%. The ingots were turned over and remelted five times for homogeneity, and then the ingots were mechanically pulverized and ground into fine powders with an average size of 15 μm as electrode materials.

The metal hydride electrode was made by firstly mixing 0.5 g of alloy powder with 0.2 g of carbonyl nickel powder and then 3% PVA solution was added to the mixture as binder. Finally, the mixture was cold pressed onto a Ni mesh under pressure of 20 MPa to make the electrode materials. The effective surface area of the electrode was 15.0 mm \times 15.0 mm and the thickness of the electrode was about 1.5 mm.

The electrochemical cell for electrochemical

measurement consisted of a working electrode (metal hydride electrode), a counterelectrode ($\text{NiOOH}/\text{Ni}(\text{OH})_2$ electrode), and a reference electrode (Hg/HgO electrode). Before polarization measurements, the hydrogen storage hydride electrode was activated completely (10 cycles).

3 THEORY

When the absorption and adsorption process exists, The concentration overpotential can be expressed as^[7]:

$$V_c = \frac{RT}{\beta F} \ln \frac{\theta_0}{\theta} \quad (3)$$

where R is gas constant, T is temperature, F is Faraday constant, β is symmetry factor, θ_0 and θ are the hydrogen surface coverage at $J = 0$ and $J = J_d$, respectively.

The θ_0 and θ can be expressed as^[7]

$$\theta_0 = \frac{k_2 c_a}{(k_2 - k_{-2}) c_a + k_{-2} N_m} \quad (4)$$

$$\theta = \frac{k_2 c_s - \frac{J_d}{F} N_m}{(k_2 - k_{-2}) c_s + k_{-2} N_m} \quad (5)$$

where k is rate constant, N_m is the total number of interstitial sites available for hydrogen per unit volume of the host metal, c_s is the near surface concentration of hydrogen in the α phase, c_a is the concentration of hydrogen in α phase, and J_d is discharge current density.

The c_s can be expressed as^[4]

$$c_s = c_a - \frac{J_d r_0^2 \rho}{3 D_a F} \left(\frac{r_0}{r_a} - 1 \right) \quad (6)$$

where D_a is the diffusion coefficient of hydrogen in the α phase, r_0 is the average radius of the particle, and r_a is radius of unreacted β phase in discharge process.

Letting $c_s = 0$ in Eqn.6, the diffusion limiting current density J_{LD} can be obtained

$$J_{LD} = \frac{3 D_a F c_a}{\rho r_0^2 \left(\frac{r_0}{r_a} - 1 \right)} \quad (7)$$

Substituting Eqn.7 into Eqn.6, the c_s can be rewritten as

$$c_s = c_a \left(1 - \frac{J_d}{J_{LD}} \right) \quad (8)$$

The limiting current density can be written as

$$J_L = Fk_2c_s/N_m \quad (9)$$

Substituting Eqn.8 into Eqn.9, the following relationship can be rewritten as

$$\frac{1}{J_L} = \frac{1}{J_{LD}} - \frac{N_m}{Fk_2c_a} \quad (10)$$

Substituting Eqn.10 into Eqn.8, the relationship between c_s and J_L can be rewritten as

$$c_s = c_a \left[1 - \left(\frac{1}{J_L} - \frac{N_m}{Fk_2c_a} \right) J_d \right] \quad (11)$$

Combining Eqn.3, 4, 5 and 11, the concentration overpotential V_c can be expressed as

$$V_c = \frac{RT}{\beta F} \ln \frac{J_L}{J_L - J_d} - \frac{RT}{\beta F} \ln \frac{1}{1 - \frac{(k_2 - k_{-2})c_a}{(k_2 - k_{-2})c_a + k_{-2}N_m} \left(\frac{J_d}{J_L} - \frac{J_d N_m}{Fk_2c_a} \right)} \quad (12)$$

When $J_d \ll J_L$, J_d is also much smaller than Fk_2c_a , therefore, absorption and adsorption of hydrogen (the second term on the right side of Eqn.12) can be neglected, the Eqn.12 can be simplified as

$$V_c = \frac{RT}{\beta F} \ln \left(\frac{J_L}{J_L - J_d} \right) \quad (13)$$

The electrochemical overpotential V_e can be expressed as

$$V_e = V - \frac{RT}{\beta F} \ln \frac{J_L}{J_L - J_d} \quad (14)$$

where V is the total overpotential and it can be obtained by the anodic polarization curve. Under this condition, the following traditional equation used to calculate electrochemical overpotential V_e can't be used because the J_d is not large enough.

$$V_e = \frac{RT}{\beta F} \ln \left(\frac{J_d}{J_0} \right) \quad (15)$$

where J_0 is the exchange current density.

When the discharge current density J_d is large enough, Eqn.14 and Eqn.15 can be used to calculate electrochemical overpotential V_e , Eqn.13 can be used to calculate the concentration overpotential V_c .

When the discharge current density J_d is too large, Eqn.12 can't be simplified as Eqn.13. Therefore, Eqn.13 can't be used to calculate the

concentration overpotential V_c , but Eqn.15 can be used to calculate electrochemical overpotential V_e . Under this condition, generally speaking, Eqn.12 can be used to calculate the concentration overpotential V_c . Because Eqn.12 is too knotty, the following equation can be used as long as the anodic polarization curve is available.

$$V_c = V - \frac{RT}{\beta F} \ln \left(\frac{J_d}{J_0} \right) \quad (16)$$

4 RESULTS AND DISCUSSION

In order to determine the exchange current density J_0 , the linear polarization experiment was conducted at 50 % SOD and scanning rate of 5 mV/s. Fig.1 shows the linear polarization curve of $M\text{Ni}_{3.8}\text{Co}_{0.5}\text{Al}_{0.7}$ hydride electrode. The exchange current density J_0 can be calculated according to the following formula^[8]:

$$J_0 = \frac{J_d RT}{FV} \quad (17)$$

where V is the total polarization at the discharge current density J_d . The exchange current density J_0 calculated by Eqn.17 is 233 mA/g.

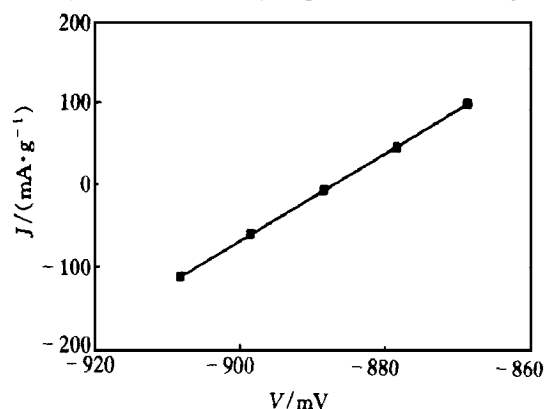


Fig.1 Linear polarization curve of $M\text{Ni}_{3.8}\text{Co}_{0.5}\text{Al}_{0.7}$ hydride electrode

Fig.2 shows the anodic current in response to the overpotential of the $M\text{Ni}_{3.8}\text{Co}_{0.5}\text{Al}_{0.7}$ hydride electrodes at 50 % SOD. The limited current density determined by anodic polarization is 1 295 mA/g.

When the discharge current density is large enough, according to Eqn.13 and Eqn.15, the total anodic polarization V can be calculated by

the following equation :

$$V = \frac{RT}{\beta F} \ln\left(\frac{J_L}{J_0}\right) + \frac{RT}{\beta F} \ln\left(\frac{J_d}{J_L - J_d}\right) \quad (18)$$

A plot of V vs $\ln(J_d/(J_L - J_d))$ should be a straight line with $RT/\beta F$ as its slope. Therefore, symmetry factor in the oxidation direction can be calculated from data of J_L and T . The calculated β is 0.74.

The electrochemical polarization V_e calculated by Eqn.14, which is stood by circles, and V_e calculated by Eqn.15, which is stood by up triangles, and the concentration polarization V_c calculated by Eqn.13, which is stood by rhombs, and V_c calculated by Eqn.16, which is stood by down triangle, are presented in Fig.3.

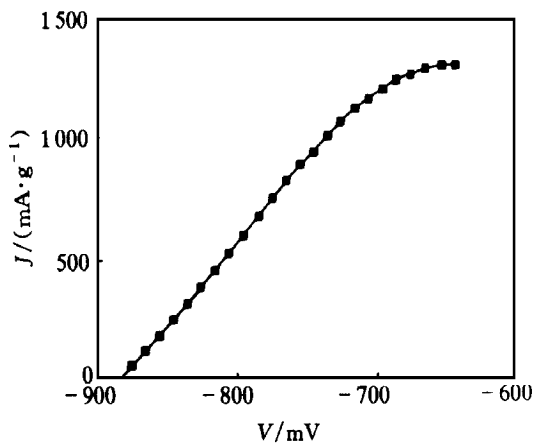


Fig.2 Anodic polarization of $\text{MnNi}_{3.8}\text{Co}_{0.5}\text{Al}_{0.7}$ hydride electrode

It can be seen from Fig.3 that, when $J_p \leq J_d \leq J_f$, the electrochemical polarization V_e calculated by Eqn.14 and Eqn.15 and the concentration polarization V_c calculated by Eqn.13 and Eqn.16 fit very well, respectively.

When the discharge current density $J_d \leq J_p$, the difference between the value of V_e calculated by Eqn.14 and 15, and the value of V_c calculated by Eqn.13 and 16, respectively, becomes much larger with decreasing discharge current density J_d . Under this condition, because the discharge current density J_d is not very large, Eqn.12 can be simplified as Eqn.13, which can be used to calculate the value of V_c as long as the SOD is constant, but when we use Eqn.15 to calculate the value of V_e , the condi-

tion $V \geq RT/\beta F$. Therefore, when $J_d \leq J_p$, only Eqn.13 can be used to calculate the concentration polarization and Eqn.14 can be used to calculate the electrochemical polarization, respectively.

Fig.3 Electrochemical overpotential V_e and concentration overpotential V_c in $\text{MnNi}_{3.8}\text{Co}_{0.5}\text{Al}_{0.7}$ hydride electrodes calculated by different expressions

When the discharge current density is close to the limiting current density J_L , or $J_d \geq J_f$, it can be seen that from Fig.3, the V_e calculated by Eqn.14 increases with increase of the discharge current density, passes through a maximum $V_{e\max}$, and then decreases. This result is unreasonable because the larger the J_d , the higher the V_e . Therefore, Eqn.13 can't be used to calculate the concentration overpotential V_c . When the discharge current density J_d is very large, i.e., $J_d \rightarrow J_L$. The exchange current density J_0 are constant during the anodic polarization, so V_e can be calculated by Eqn.15, and V_c can be obtained by experimentally determined value of V minus that of V_e calculated by Eqn.15. The calculated V_e and V_c by this way are also shown in Fig.3 (up triangles for V_e and down triangles for V_c). Why Eqn.13 can't be used to calculate the concentration polarization is that, when the discharge current density J_d is close to the limiting current density J_L , Eqn.12 can't be simplified as Eqn.13, because, under this condition, there exists the absorption and adsorption of hydrogen.

5 CONCLUSIONS

The traditional equations can't be used to calculate the electrochemical polarization V_e and concentration polarization V_c in the entire anodic polarization process in the hydride electrode system. The anodic polarization curve should be divided into three regions to discuss according to discharge current density J_d , namely, $J_d < J_p$, $J_p < J_d < J_f$, and $J_d > J_f$. In different regions, the calculation for V_e and V_c should use different formulas. When discharge current density J_d is smaller than J_p , the traditional equation used to calculate the electrochemical overpotential can't be used, when J_d is between J_p and J_f , both equations used to calculate the electrochemical overpotential and concentration overpotential can be used, and when J_d is larger than J_f , because there exists absorption and adsorption of

hydrogen, the traditional equation used to calculate concentration overpotential can't be used in the system of hydride electrodes.

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