A NEW METHOD OF DETERMINING THE THERMODYNAMIC PARAMETERS OF METAL HYDRIDE ELECTRODE MATERIALS

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Abstract—Thermodynamic parameters of the hydriding reaction of a hydride electrode can be obtained by two different methods. The results show that the change of enthalpy $\Delta H$, change of entropy $\Delta S$ and hydrogen pressure calculated from $e-c-T$ curves of electrochemical reactions have much larger inherent errors compared with those obtained from $p-c-T$ curves of alloys in hydriding reactions with hydrogen gas (gaseous method). The hydrogen storage capacities determined by gaseous and electrochemical methods are also different, owing to the low utilization factor, and diffusion of hydrogen into air and formation of hydrogen gas bubbles in electrolyte in an unsealed battery. $\Delta H_e$, $\Delta S_e$ also as well as the relations between $\Delta H_e$, $\Delta S_e$ of the electrochemical reaction and gaseous $\Delta H_p$, $\Delta S_p$ have also been derived on the basis of the Nernst equation. Much more accurate results have thus been assured.

A. Wang et al. determined the $p-c-T$ curves of LaNi$_5$,Co$_{1-x}$-M$_x$ (M = TMn, Cr, Al, or Ti) as promising materials for reversible hydrogen storage negative electrode because of their high energy densities, their free from poisonous Cd, higher tolerance to over-charge and over-discharge, and absence of memory effect. The suitability of intermetallic compounds used as hydride electrodes rests principally on their thermodynamic and kinetic properties. Thus the determination of these properties is of importance for electrode evaluations.

Hydrogen storage alloys such as LaNi$_5$,Co$_{1-x}$-M$_x$ (M = TMn, Cr, Al, or Ti) are promising materials for reversible hydrogen storage negative electrode because of their high energy densities, they are free from poisonous Cd, higher tolerance to over-charge and over-discharge, and absence of memory effect. The suitability of intermetallic compounds used as hydride electrodes rests principally on their thermodynamic and kinetic properties. Thus the determination of these properties is of importance for electrode evaluations.

INTRODUCTION

NOMENCLATURE

$z_{H2O}$ The activity of water
$\gamma_E$ Activity coefficient of hydrogen
$C_{e\gamma}$ Maximum hydrogen concentration of $\alpha$ phase
$C_{e\beta}$ The hydrogen concentration of $\beta$ phase equilibrating with $\alpha$ phase
$E$ Electrode potential
$E_i$, $E_d$ Plateau potential for hydride formation and decomposition
$E_{eq}$ Equilibrium plateau potential
$\Delta E$ Electrochemical potential error
$\Gamma$ Faraday constant
$F_{\Delta H}$, $F_{\Delta S}$ $\Delta H$ function and $\Delta S$ function
$\Delta$ The change of enthalpy
$\Delta H_p$, $\Delta H_e$ The change of enthalpy of gaseous process and electrochemical process
$K_{eq}$, $K_i$ Reaction constants
$\mu$ Concentration of KOH (mol/kg electrolyte)
$P_{eq}$ Equilibrium plateau pressure
$P_0$, $P_d$ The hydride formation and decomposition plateau pressure
$P_{H2}$ The hydrogen pressure
$P_1$ Experimental values of hydrogen pressure
$\Delta P/P$ Relative error for hydrogen pressure
$R$ Faraday constant
$\Delta S_p$, $\Delta S_e$ The change of entropy, of gaseous process and electrochemical process
$T$ Temperature (K)

Hydrogen storage alloys such as LaNi$_5$,Co$_{1-x}$-M$_x$ (M = TMn, Cr, Al, or Ti) are promising materials for reversible hydrogen storage negative electrode because of their high energy densities, they are free from poisonous Cd, higher tolerance to over-charge and over-discharge, and absence of memory effect. The suitability of intermetallic compounds used as hydride electrodes rests principally on their thermodynamic and kinetic properties. Thus the determination of these properties is of importance for electrode evaluations.

The important thermodynamic properties are the change of enthalpy $\Delta H$, the change of entropy $\Delta S$, the maximum hydrogen concentration of $\alpha$ phase, $C_{e\alpha}$ and the hydrogen concentration of $\beta$ phase equilibrating with $\alpha$ phase $C_{e\beta}$. All these parameters can be determined from the pressure–composition isothermal ($p-c-T$ curves) at different temperatures. However, as the plateau pressure of hydride electrode materials at room temperature is generally lower than 1 atm, the $p-c-T$ data determination needs a specially designed high vacuum equipment and the experiment is difficult and sometimes even impossible when the plateau pressure is much lower than 1 atm. Presently, in the pressure range from $10^{-10}$ atm to 1 atm, the $\Delta H$ value is calculated from the van’t Hoff plot constructed from $p-c-T$ curves calculated from electrochemical determination ($e-c-T$) on the basis of the Nernst equation. The accuracy of the values thus obtained are inherently low. Although Sakai et al. [1] determined the $p-c-T$ curves of LaNi$_5$,Co$_{1-x}$ alloy by both
the electrochemical method and the gaseous hydrogen method and reported that the pressures calculated from the electrochemical data agreed well with the equilibrium pressures obtained from the gaseous method with the values obtained by electrochemical method some 10% higher. Zhou et al. [2] on comparing the $p-c-T$ curves of LaNi$_5$Sn$_3$, alloy obtained by both gaseous hydrogen and electrochemical methods, regarded that the difference between the results of the two methods at low temperature was small, but at high temperatures became larger, due to the escape of hydrogen in form of gas bubbles in the electrochemical method. The present authors, however, believe the errors incurred from calculations directly from the Nernst equation in its common form are, as a rule, much bigger. A new approach can greatly improve the accuracy. In this paper, the new approach of calculating the gaseous $p-c-T$ curve from electrochemical $p-c-T$, and the determination of the change of enthalpy $\Delta H^\circ$ and the change of entropy $\Delta S^\circ$ of an electrochemical process are discussed in detail. The difference in hydrogen contents is also studied.

EXPERIMENTAL DETAILS

Alloys were prepared by arc melting metallic elements under argon atmosphere. The alloy powder was obtained by passing the powder through a 300 mesh sieve after mechanical pulverization. Negative electrodes were prepared by the following two methods. (A) 100 mg alloy powder was mixed with copper powder (below 300 mesh) in a weight ratio of 1.2 and cold pressed into pellets (d=10 mm). (B) copper-free pellets were prepared by mixing the alloy particles (900 mg) with 3 wt% polyvinyl alcohol (PVA) solution and then pressing the mixture onto a highly porous foamed nickel plate. For electrochemical measurements each pellet was attached to a copper rod of 5mm diameter by a shrink sleeve and positioned in a three-compartment glass open cell using copper powder (below 300 mesh) as the counter electrode and a Luggin capillary was located close to the ohmic drop between the working electrode and the reference electrode a Hg/HgO electrode as the reference electrode. To reduce bubbles in the electrochemical method. The present authors, however, believe the errors incurred from calculations directly from the Nernst equation in its common form are, as a rule, much bigger. A new approach can greatly improve the accuracy.

RESULTS AND DISCUSSION

The difference in hydrogen content between the hydrogen absorption and desorption determined from electrochemical $p-c-T$ and gaseous $p-c-T$ curves

The $e-c-T$ curves and $p-c-T$ plots converted from electrochemical data and those obtained by the gaseous

Fig. 1. The schematical diagram of $p-c$ isotherm measuring system.
method were determined at 5, 15, 25 and 35°C. For a clear presentation, only those determined at 5, 15 and 25°C are presented in Figs 3 and 4. The pressures (in atm) at different temperatures are calculated from potentials according to the Nernst equation using parameters adopted by Iwakura and Asaoha [5].

\[
E = E_{\text{H}_2}^0 - E_{\text{H}_2O}^0 + \frac{RT}{2F} \ln \left( \frac{a_{\text{H}_2O}}{P_{\text{H}_2}} \right).
\]  

(1)

Here \(a_{\text{H}_2O}\) is the activity of water and \(P_{\text{H}_2}\) is the hydrogen pressure.

\[
E_{\text{H}_2}^0 - E_{\text{H}_2O}^0 = -1.18041 + (4.4666 \times 10^{-2} - 6.93606 \\
\times 10^{-4} \ln T)T + 1.0788 \times 10^{-6} T^2 - 4.512 \times 10^{-10} T^3 \\
+ 5.232/T.
\]  

(2)

\[
\log a_{\text{H}_2O} = -0.0225m + 0.001434m^2 + (1.38m - 0.9254m^2)/T.
\]  

(3)

where \(m\) is the concentration of KOH (mol/kg electrolyte) and here \(m = 6\) (mol/kg).

\[
\ln \frac{\eta_{\text{H}_2}}{i_{\text{H}_2}} = \frac{20.5T - 1857}{83.1447T^2} \\
+ \frac{-351T^2 + 12760T^{1.5} - (20.5T - 1857)^2}{1.4009 \times 10^4 T^4}.
\]  

(4)

Table 1 lists the values of the parameters calculated from above equations [3].

From the plots it can be seen that the discharge capacity of electrode formed by mixing with Cu is larger than that of the electrode formed by putting the alloy mixture into porous foamed Ni plate, and both of them are less than that obtained by gaseous methods. We believe that the difference is due to different utilization factors of alloy in different electrodes as the charging-discharging of some alloy particles are obstructed by oxide films or PVA (polyvinyl alcohol) on their surfaces. The utilization factor is the ratio of the amount of alloy participating hydrogen absorption/desorption according to the following order:

![Fig. 3. The e–c–T curves for MnNi_{1-x}Mn_{x}Co_{0.5-x}H system: (a) 5°C, (b) 15°C, (c) 25°C (the data of alloy in foamed Ni electrode is not indicated in (c)).](image-url)
Substituting the above values into Nernst equation (1), the relation between equilibrium potential of the electrode and pressure at different temperatures is as follows:

- at 278 K, \( E = -0.9361 - 0.02756 \log P_{H_2} \)
- at 288 K, \( E = -0.93325 - 0.028556 \log P_{H_2} \)
- at 298 K, \( E = -0.93045 - 0.029547 \log P_{H_2} \)
- at 308 K, \( E = -0.9277 - 0.03054 \log P_{H_2} \)

Gas method > alloy mixed with Cu

From Fig. 4a we estimated the utilization factors of the alloy in different electrodes as tabulated in Table 2.

With increasing temperature, the difference between the electrochemical charge capacities and hydrogen absorption capacities decreased but the difference between charge capacity and discharge capacity increased. We believe that these are for the following two reasons: The first one is that there exists a parallel electrochemical process in conjunction with the charging-discharging process.

The charge-discharge process itself is \( M + H_2O = e^- + \text{MH}_{\text{ads}} + OH^- \).

The parallel electrochemical process is either

\[ \text{MH}_{\text{ads}} + H_2O + e^- \xrightarrow{k_1} M + H_2 + OH^- \]

or

\[ 2\text{MH}_{\text{ads}} \xrightarrow{k_2} M + H_2 \]

(a chemical catalytic hydrogen gas desorption process).

In the parallel \( H_2 \) formation reaction during the charging process, the rate of hydrogen gas formation is controlled by the rate of nucleation and growth of hydrogen gas, which is determined by the hydrogen pressure, and the surface condition of the substrate [6, 7]. When the equilibrium pressure plus the overpressure caused by pulse charge current is less than 1 atm, the nucleation and growth of gas is relatively slow. In our experiments the overall pressure at two phase regions was less than 1 atm after activation, so \( K_1 \) and \( K_2 \) were small, and the efficiency for charge-discharge was high [8]. But at the later period of charging, the overall pressure was larger than 1 atm, so \( K_1 \) and \( K_2 \) increased, and these two parallel reactions caused the apparent hydrogen absorption capacity to appear higher than the actual value as some hydrogen atoms were combined into gas molecules and escaped to the electrolyte. At the discharging process, the overall pressure was lower than 1 atm during the discharging process, the efficiency in the discharge is higher than that in the charging process.
The other reason is the diffusion of hydrogen atom from the electrode surface into the electrolyte and subsequently to the surface of the electrolyte and escapement into air. The partial pressure of hydrogen in air is around $5 \times 10^{-5}$ atm, which is much less than the actual pressure of hydrogen in the electrode. The diffusion rate of hydrogen increases with increasing temperature due to a higher hydrogen diffusion coefficient. In our experiment, the time for determining one $e-c-T$ curve was around 50 h. So the amount of hydrogen diffused and transformed into gaseous hydrogen was noticeable.

From this point of view, we believe that the discharge capacity in a sealed battery should be higher than that in an open battery. From the above analysis, we believe that the capacity difference between the electrochemical method and gaseous method depends on two factors: one is the utilization factor of the alloy, which is determined by the oxidation property of the electrode, the kind and amount of binder, and the other is the rate of formation of hydrogen gas and of hydrogen diffusion. Lower utilization factor decreases the charge and discharge capacity, while a higher hydrogen diffusion rate increases the apparent charging capacity but decreases the discharging capacity. At low temperature, the utilization factor of alloy is the main factor affecting the capacity of electrode, so the capacity determined by different method are in the order of:

gaseous method > alloy mixed with Cu

> alloy in foamed Ni plate.

With increasing temperature, the hydrogen escape rate becomes faster. This results in a larger charging capacity and smaller discharging capacity. When the temperature is high enough, the apparent charging capacity of the electrode may even be higher than that obtained from gaseous method (see Fig. 3c), but the discharge capacity may be much lower than that in gaseous method.

The error in calculating $\Delta H^0$ and $\Delta S^0$ of gaseous reaction from electrochemical reaction

$\Delta H^0$ and $\Delta S^0$ can be determined by reaction calorimeter or interpreted from the slope and intercept of the van't Hoff equation

$$\ln P_{eq} = \frac{\Delta H_0}{RT} - \frac{\Delta S_0}{R}$$

constructed on the basis of $p-c-T$ curves obtained from gaseous reaction. The plateau pressure which should be employed in van't Hoff equation is subject to some uncertainty because of hysteresis. It has been proposed that for this purpose the geometric mean plateau pressure should be employed [9, 10], namely $P_{eq} = \sqrt{P_fP_d}$, where $P_f$ and $P_d$ are the hydride formation and decomposition plateau pressures respectively. Experimental evidence has been given that this is the correct choice [11].

On adopting $P_{eq} = \sqrt{P_fP_d}$, we first calculated the pressures for the constructed $p-c-T$ curves from electrochemical curves ($e-c-T$) and then plotted the van’t Hoff’s equations (Fig. 5). The $\Delta H^0$ and $\Delta S^0$ thus determined are shown in Table 3.

From this table, we can see that the disparities (or errors) are large for both $\Delta H^0$ and $\Delta S^0$ determined by the two methods. The authors believe the result is understandable and the errors are mainly due to the intrinsic mathematical relation between potential and pressure. According to the Nernst [1], the error in converting electrochemical potential to pressure is:

$$\Delta E = E_1 - E = \frac{RT}{2F} \ln \left( \frac{P_f}{P_d} \right) = \frac{RT}{2F} \ln \left( 1 + \frac{\Delta P}{P} \right)$$

where $E_1$ and $P_f$ are experimental values of potential and pressure respectively, and $E$ and $P$ are the actual values.

The relative error for pressure is:

$$\frac{\Delta P}{P} = \exp \left( \frac{2F}{RT} \Delta E \right) - 1$$

Table 2. The utilization factor of alloy (%)

<table>
<thead>
<tr>
<th>Method</th>
<th>Utilization factor of alloy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas method</td>
<td>100</td>
</tr>
<tr>
<td>Alloy mixed with Cu</td>
<td>90</td>
</tr>
<tr>
<td>Alloy in foamed Ni plate</td>
<td>78.5</td>
</tr>
</tbody>
</table>

The utilization factor of alloy (5')

The error in calculating $\Delta H^0$ and $\Delta S^0$ of gaseous reaction from electrochemical reaction.

The error in calculating $\Delta H^0$ and $\Delta S^0$ of gaseous reaction from electrochemical reaction.

The error in calculating $\Delta H^0$ and $\Delta S^0$ of gaseous reaction from electrochemical reaction.

Fig. 5. The van’t Hoff plots determined by gaseous and electrochemical methods.
Table 3. The values of $\Delta H_p^0$ and $\Delta S_p^0$ determined by the two methods

<table>
<thead>
<tr>
<th>Method</th>
<th>$\Delta H_p^0$ (kJ/mol)</th>
<th>$\Delta S_p^0$ (J/mol)</th>
<th>Relative error $\Delta H_p^0$</th>
<th>Relative error $\Delta S_p^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrochemical</td>
<td>-21.2</td>
<td>-62.9</td>
<td>37.7%</td>
<td>41.8%</td>
</tr>
<tr>
<td>Electrochemical</td>
<td>-18.0</td>
<td>-51.6</td>
<td>47.1%</td>
<td>52.2%</td>
</tr>
<tr>
<td>Gaseous</td>
<td>-34.0</td>
<td>-108.0</td>
<td>41.1%</td>
<td>52.2%</td>
</tr>
</tbody>
</table>

with $F = 23060 \text{cal} \cdot \text{v}^{-1} \text{mol}^{-1}$, $R = 1.986 \text{cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, we obtained from [6]

$$\frac{\Delta P}{P} = \exp\left(\frac{23223 \cdot \Delta E}{T}\right) - 1$$

The $\Delta P/P$ varies exponentially with $\Delta E/P$. At 298 K the variation of $\Delta P/P$ with $\Delta E$ is shown in Fig. 6, when $\Delta E = 5 \times 10^{-3} \text{V}$, $(\Delta P/P) = 47.6\%$.

From the above analysis, we can see that the exponential relation between $\Delta P$ and $\Delta E$ leads to a large relative error. So a new electrochemical reaction, in which $\Delta H$ and $\Delta S$ are calculated directly from potential should be used to reduce the relative errors.

Determination of $\Delta H_p^0$ and $\Delta S_p^0$ directly from electrochemical reaction

For the electrode with flat plateaus the potential $E$ can be taken as the mean value of the $E_i$ and $E_d$, i.e., $E_{eq} = (E_i + E_d)/2$ where $E_i$ and $E_d$ are the plateau potential for hydride formation and decomposition respectively, because the amount of escaped hydrogen in a two phase range does not affect the plateau potential, i.e., plateau potential does not vary with the hydrogen concentration of alloy in a two phase range. This method of determining $E_{eq}$ is in principle the same as that of determining plateau pressure. $P_{eq} = \sqrt{P_iP_d}$.

For M1Ni3.75Mn0.5Co0.75 mixed with Cu electrode the plateau is sloped, however, from Fig. 3 we can see that the plateau increases only by 2 mV when the hydrogen concentration increases by 1 H/M and the maximum hydrogen concentration changes only 1 H/M from 5°C to 35°C. In our experiment, we adopt the potential with the hydrogen concentration fixed at 2.5 H/M, the potential error caused by hydrogen escape is within 1 mV, so it is reasonable to adopt $E_{eq} = (E_i + E_d)/2$ a reasonable approximation. Our test results indicate that the measured equilibrium plateau potential is proportional to the temperature for M1Ni3.75Mn0.5Co0.75 mixed with Cu electrode as shown in Fig. 7.

The relation of potential and temperature for M1Ni3.75Mn0.5Co0.75 mixed with Cu electrode can be expressed as follows

$$E_{eq} = -0.914 - 2.5 \times 10^{-4}(T - 273).$$

According to the electrochemical principle

$$\Delta H_e^0 = 2F \left[ E_{eq} - T \left( \frac{\partial E_{eq}}{\partial T} \right)_p \right]$$

$$\Delta S_e^0 = 2F \left( \frac{\partial E_{eq}}{\partial T} \right)_p.$$
kJ/mol, we obtained: $\Delta H^o = -163.07 \text{ kJ/mol}$, $\Delta S^o = -48.274 \text{ J/mol} \cdot \text{K}$.

The relation between $\Delta H^o$, $\Delta S^o$ of the electrochemical reaction and $\Delta H^g$, $\Delta S^g$ of the gaseous reaction

Combining equations (2)–(4) we obtain the relation between potential and hydrogen pressure

$$E_{\text{eq}} = -1.1804 + (4.4666 \times 10^{-3} - 6.93606 \times 10^{-4} \ln T) + T \frac{5.232}{7} - \frac{RT}{2F} \times \left(\frac{0.19198 - 57.64383}{T}\right) - \frac{RT}{2F} \ln (\gamma_{\text{H}_2}, P_{\text{eq}}) \quad (10)$$

From Table 1 we find the change of $\gamma_{\text{H}_2}$ with the temperature is very small under our experimental conditions. When the temperature change is in the range 0–200°C, the $\gamma_{\text{H}_2}$ changes from 1.0006 to 1.00042 [7]. So we can adopt the $\gamma_{\text{H}_2} \approx 1$. From the Van’ Hoff equation we get

$$\Delta H^o = R \times \frac{\partial (\ln P_{\text{eq}})}{\partial (T)} = -RT \frac{\partial (\ln P_{\text{eq}})}{\partial (T)}$$

$$\Delta S^o = -\frac{\partial (RT \ln (P_{\text{eq}}))}{\partial (T)}$$

Then

$$\Delta H^o = 2F \left(1.1804 + 6.93606 \times 10^{-4} T - 1.0788 \times 10^{-3} - 4.512 \times 10^{-10} T^3 + \frac{5.232}{T} - \frac{RT}{2F} \times \left(\frac{0.19198 - 57.64383}{T}\right) - \frac{RT}{2F} \ln (\gamma_{\text{H}_2}, P_{\text{eq}}) \right)$$

$$\Delta S^o = 2F \left(\frac{\partial (\ln P_{\text{eq}})}{\partial (T)} \right) P = 2 \times 96390$$

$\Delta H^o = -195.28724 + 163.07 = -32.22 \text{ kJ/mol}$

$\Delta S^o = -53.45 + 53.45 = -101.74 \text{ J/mol} \cdot \text{K}$

Comparing the above data with the values of $\Delta H^o$, $\Delta S^o$ measured by gaseous method (see Table 3), we find the relative error is much smaller.

Relative error

$$\eta_H = \frac{34.2 - 32.22}{34.2} = 5.8\%$$

$$\eta_S = \frac{101.724 - 101.74}{101.724} = 0.1\%$$

The accuracy is eight times higher than that calculated from the electrochemical $p-c-T$ method.

Fig. 8. The relation of $\Delta H$ function and $\Delta S$ function with temperature.
CONCLUSION

1. The accuracy of enthalpy change $\Delta H$ and entropy change $\Delta S$ obtained from $p-c-T$ calculated from electrochemical measurement is very low, due to error amplification in converting the potential to hydrogen pressure.

2. Owing to the low utilization factor of the alloy in an open cell, at low temperatures the maximum hydrogen concentration of $\alpha$ phase and $\beta$ phase (hydride) are smaller than that obtained in gaseous reaction, but at higher temperatures the concentrations obtained from electrochemical reaction is close to or even larger than that obtained from gaseous reactions, due to the parallel hydrogen evolution reaction and hydrogen lost by diffusion through the electrolyte. These two factors also lead to concentration hysteresis, i.e., discharge capacity is less than charge capacity.

3. The enthalpy change ($\Delta H^0$) and entropy change ($\Delta S^0$) of hydride electrodes in cell reactions can be used to evaluate the stability of the electrodes by electrochemical $e-c-T$ method with Hg/HgO as the reference electrode. A method of evaluating $\Delta H^0$ and $\Delta S^0$ calculated directly from the $e-c-T$ curve has been developed. For the electrode $\text{MnNi}_{3.75}\text{Mn}_{0.75}\text{Co}_{0.75}$ mixed with Cu: $\Delta H^0 = -163.07 \text{ kJ/mol}$, $\Delta S^0 = -48.27 \text{ J/mol} \cdot \text{K}$.

4. The relation between electrochemical $\Delta H^0$, $\Delta S^0$ and gaseous reaction $\Delta H_p$, $\Delta S_p$ has been deduced as $\Delta H^0 = -195.28724 - \Delta H_p$ (kJ/mol), $\Delta S^0 = -53.45 + \Delta S_p$ (J/mol $\cdot$ K). The accuracy of $\Delta H^0$, $\Delta S^0$ calculated from $\Delta H_p$, $\Delta S_p$ is much higher (with relative error within 7%) than those from conventional methods.

Acknowledgement—This program is supported by the National Advanced Science and Technology Foundation of China.

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