

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 ΔH , change of entropy ΔS 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. ΔH_e^0 and ΔS_e^0 as well as the relations between ΔH_e^0 , ΔS_e^0 of the electrochemical reaction and gaseous ΔH_p^0 , ΔS_p^0 have also been derived on the basis of the Nernst equation. Much more accurate results have thus been assured. © 1997 International Association for Hydrogen Energy

NOMENCLATURE

$\alpha_{\text{H}_2\text{O}}$	The activity of water
γ_{H_2}	Activity coefficient of hydrogen
C_{aff}	Maximum hydrogen concentration of α phase
$C_{\beta\alpha}$	The hydrogen concentration of β phase equilibrating with α phase
E	Electrode potential
E_1	Experimental value of potential
E_t, E_d	Plateau potential for hydride formation and decomposition
E_{eq}	Equilibrium plateau potential
ΔE	Electrochemical potential error
F	Faraday constant
$F_{\Delta H}, F_{\Delta S}$	ΔH function and ΔS function
Δ	The change of enthalpy
$\Delta H_p^0, \Delta H_e^0$	The change of enthalpy of gaseous process and electrochemical process
K_1, K_2	Reaction constants
m	Concentration of KOH (mol/kg electrolyte)
P_{eq}	Equilibrium plateau pressure
P_t, P_d	The hydride formation and decomposition plateau pressure
$P(\text{H}_2)$	The hydrogen pressure
P_1	Experimental values of hydrogen pressure
$\Delta P/P$	Relative error for hydrogen pressure
R	Faraday constant
$\Delta S_p^0, \Delta S_e^0$	The change of entropy, of gaseous process and electrochemical process
T	Temperature (K)

INTRODUCTION

Hydrogen storage alloys such as $\text{LaNi}_{2.5}\text{Co}_{2.5-x}\text{M}_x$ ($\text{M} \equiv \text{TMn, Cr, Al, or Ti}$) 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 inter-metallic 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 ΔH , the change of entropy ΔS , the maximum hydrogen concentration of α phase, C_{aff} and the hydrogen concentration of β phase equilibrating with α phase $C_{\beta\alpha}$. 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 ΔH 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 $\text{LaNi}_{2.5}\text{Co}_{2.5}$ 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 $\text{LaNi}_{4.9}\text{Sn}_{0.1}$ 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 ΔH_e^0 and the change of entropy ΔS_e^0 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 5 mm diameter by a shrink sleeve and positioned in a three-compartment glass open cell using a Hg/HgO electrode as the reference electrode. To reduce the ohmic drop between the working electrode and the reference electrode a Luggin capillary was located close to the hydride electrode in the working electrode compartment. A sintered nickel cathode was placed in the counter electrode compartment separated by porous glass filters. The electrodes were charged and discharged electrochemically in 6.25 M KOH. As the positive electrode was made to have an excess capacity, the charging/discharging capacity was limited by the negative electrode. The discharge cut-off potential was set at -0.6 V with respect to the Hg/HgO reference electrode. The electrochemical reaction was thermostated within an accuracy of 1°C by means of a temperature control unit.

Conventionally electrochemical p - c - T curves were obtained by converting equilibrium potential to pressure on the basis of Nernst equation using electrochemical data [3]. The equilibrium charge (or discharge) potential curves were obtained by alternating the following two processes: (1) a pulse charge or discharge of

$25\text{ mA/g} \times 0.25\text{ h}$ and (2) a rest period until the potential remained unchanged. Charging was stopped when the electrode potential reached the potential corresponding to 1 atm hydrogen pressure and discharging stopped when the potential dropped to -0.6 V with respect to Hg/HgO. A rest time of 0.5 h between the charge and discharge was adopted. The accuracy of potential measurement was within 0.5% i.e. 5 mV.

Gaseous p - c - T curves were determined by the conventional constant volume and pressure differential method [4]. Fig. 1 is the schematic diagram of the p - c isotherm measuring system. Alloy of about 10 g in weight was put into a stainless steel reactor which was immersed in a thermostatic water bath. After more than 10 absorption/desorption cycles, the data for p - c isotherms were determined. The absorption isotherms are obtained by passing hydrogen into the reactor from the reservoir of known volume in small increments, measuring each subsequent equilibrium pressure. The desorption isotherms were obtained as follows. For hydrogen pressure above 1 atm, the water displaced in an inverted scaled cylinder was a direct measure of the total quantity of hydrogen released. For hydrogen pressure below 1 atm the reservoir of known volume is first evacuated by a vacuum pump to a definite vacuum and then the hydrogen was withdrawn from the alloy in the reactor in small aliquots until no more hydrogen was evolved. The hydrogen released in each test was calculated, and the hydrogen capacity was the sum of the aliquots. The hydrogen used had a purity of 99.999%. A typical p - c - T curve of actual electrode material is shown in Fig. 2.

The hydride formation plateau pressure P_f and hydride decomposition plateau pressure P_d were determined at the midpoint of hydrogen content of the alloy at each temperature. Presently $H/M = 2.5$ was chosen as shown in the above plots.

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

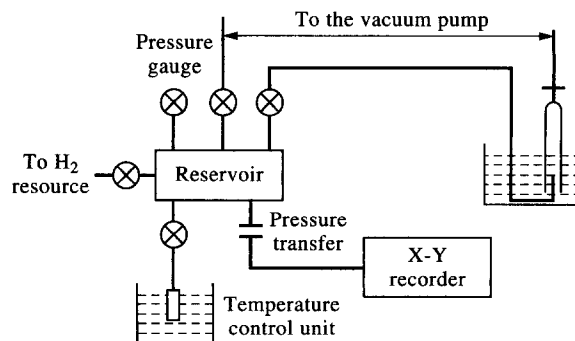


Fig. 1. The schematical diagram of p - c isotherm measuring system.

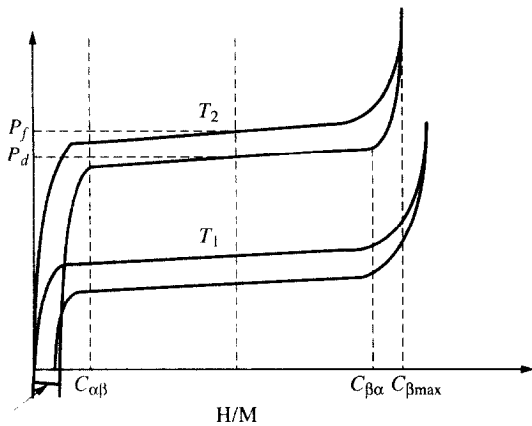


Fig. 2. The typical p - c - T curve.

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].

$$E = E_{\text{H}}^0 - E_{(\text{HgO}:\text{Hg})}^0 + \frac{RT}{2F} \ln \left(\frac{\alpha_{(\text{H}_2\text{O})}}{\gamma_{(\text{H}_2)} P_{(\text{H}_2)}} \right) \quad (1)$$

Here $\alpha_{(\text{H}_2\text{O})}$ is the activity of water and $P_{(\text{H}_2)}$ is the hydrogen pressure.

$$E_{(\text{H})}^0 - E_{(\text{HgO}:\text{Hg})}^0 = -1.18041 + (4.4666 \times 10^{-3} - 6.93606 \times 10^{-4} \ln T)T + 1.0788 \times 10^{-6} T^2 - 4.512 \times 10^{-10} T^3 + 5.232/T \quad (2)$$

$$\log \alpha_{\text{H}_2\text{O}} = -0.0225m + 0.001434m^2 + (1.38m - 0.9254m^2)/T \quad (3)$$

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

$$\ln \gamma_{(\text{H}_2)} = \frac{20.5T - 1857}{83.1447T^2} + \frac{-351T^2 + 12760T^{1.5} - (20.5T - 1857)^2}{1.4009 \times 10^4 T^4} \quad (4)$$

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:

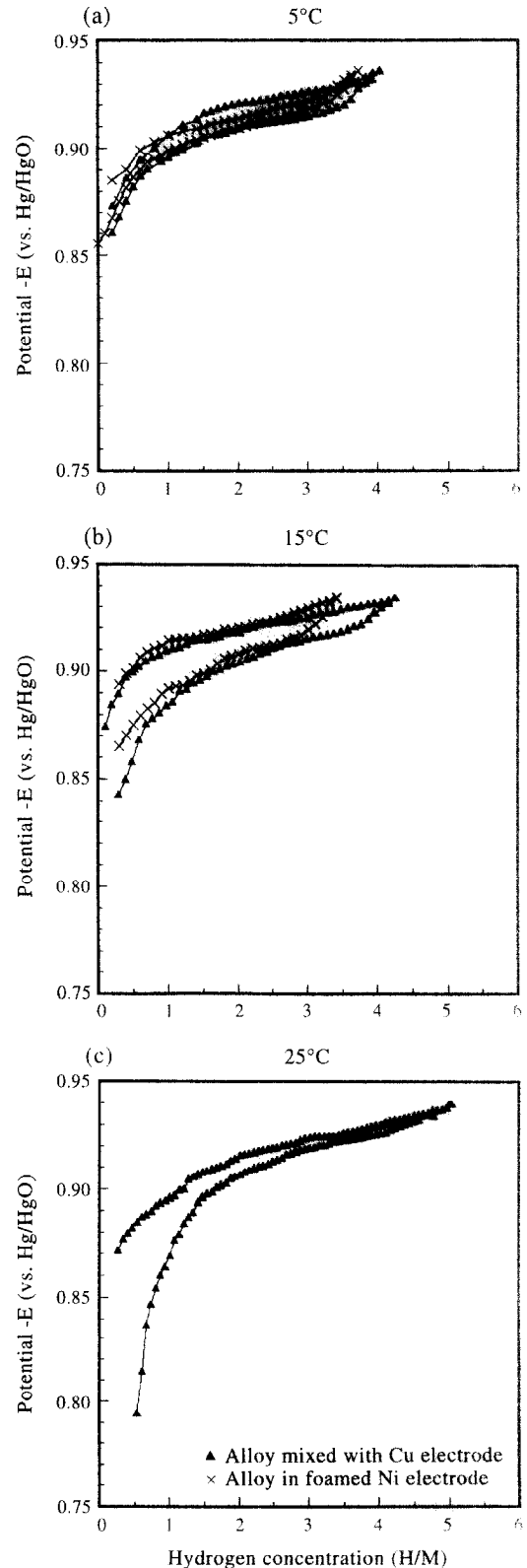


Fig. 3. The e - c - T curves for $\text{MINi}_{0.75}\text{Mn}_{0.2}\text{Co}_{0.75}\text{-H}$ system: (a) 5°C, (b) 15°C, (c) 25°C (the data of alloy in foamed Ni electrode is not indicated in (c)).

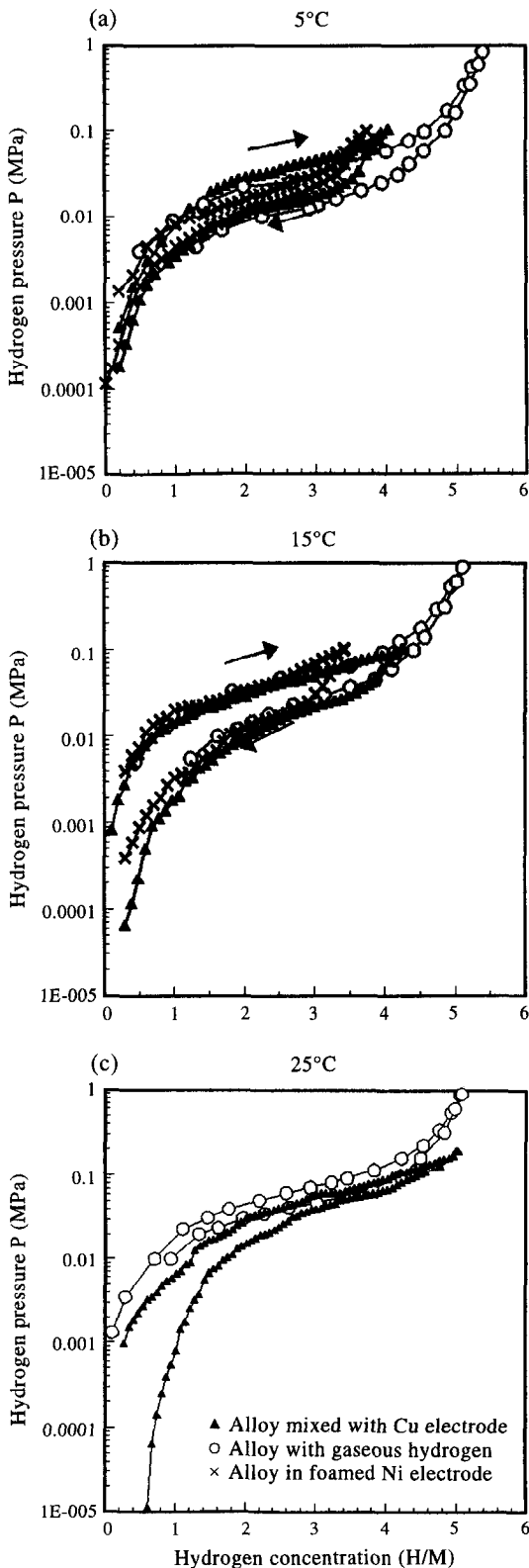


fig. 4. the p - c - T curves for $\text{MINi}_{3.75}\text{Mn}_{0.5}\text{Co}_{0.75}\text{-H}$ system: (a) 5°C , (b) 15°C , (c) 25°C (the data of alloy in foamed Ni electrode is not indicated in (c)).

Table 1. Parameter values in 6.25 M KOH solutions

T (K)	$(E_{(\text{H})}^0 - E_{(\text{H}_2\text{O}/\text{H}_2)})/V$	$\alpha_{(\text{H}_2\text{O})}$	$\gamma_{(\text{H}_2)}$
278	-0.931317	0.670768	1.0006
288	-0.928375	0.675615	1.00059
298	-0.925493	0.68168	1.00058
308	-0.922669	0.684453	1.00057

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, $E = -0.9361 - 0.02756 \log P_{\text{H}_2}$

at 288 K, $E = -0.93325 - 0.028556 \log P_{\text{H}_2}$

at 298 K, $E = -0.93045 - 0.029547 \log P_{\text{H}_2}$

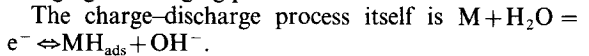
at 308 K, $E = -0.9277 - 0.03054 \log P_{\text{H}_2}$.

Gas method > alloy mixed with Cu

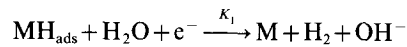
> alloy in foamed Ni plate.

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

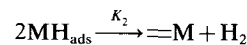
With increasing temperature, the difference between the electrochemical charge capacities and hydrogen absorption capacities decreased but the difference between charge capacity and discharge capacity increased. We believe that these are for the following two reasons: The first one is that there exists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



The parallel electrochemical process is either



or



(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.

Table 2. The utilization factor of alloy (%)

	Gas method	Alloy mixed with Cu	Alloy in foamed Ni plate
Utilization factor of alloy	100	90	78.5

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 5×10^{-7} 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 ΔH_p^0 and ΔS_p^0 of gaseous reaction from electrochemical reaction

ΔH_p^0 and ΔS_p^0 can be determined by reaction calorimeter or interpreted from the slope and intercept of the van't Hoff equation

$$\ln P_{\text{eq}} = \frac{\Delta H_p^0}{RT} - \frac{\Delta S_p^0}{R}$$

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 $P_{\text{eq}} = \sqrt{P_f P_d}$, 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 $P_{\text{eq}} = \sqrt{P_f P_d}$, 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 ΔH_p^0 and ΔS_p^0 thus determined are shown in Table 3.

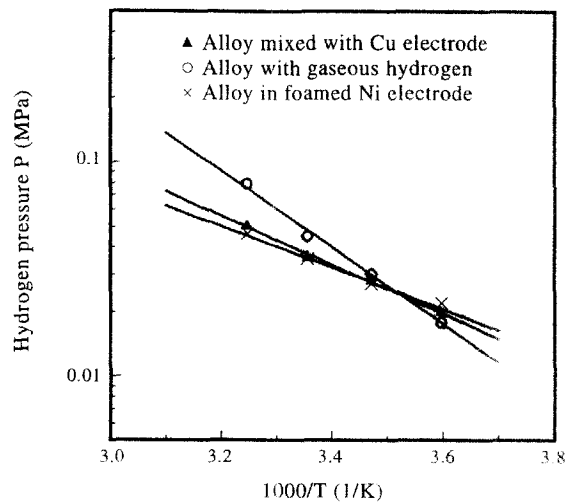
From this table, we can see that the disparities (or errors) are large for both ΔH_p^0 and ΔS_p^0 determined by the two methods. The authors believe the result is understandable and the errors are mainly due to the intrinsic mathematical relation between potential and pressure. According to the Nernst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

$$\Delta E = E_1 - E = \frac{RT}{2F} \ln \left(\frac{P_1}{P} \right) = \frac{RT}{2F} \ln \left(1 + \frac{\Delta P}{P} \right) \quad (5)$$

where E_1 and P_1 are experimental values of potential and pressure respectively, and E and P are the actual values.

The relative error for pressure is:

$$\frac{\Delta P}{P} = \exp \left(\frac{2F}{RT} \Delta E \right) - 1 \quad (6)$$



electrochemical methods

Fig. 5. The van't Hoff plots determined by gaseous and electrochemical methods.

Table 3. The values of ΔH_p^0 and ΔS_p^0 determined by the two methods

	Method	ΔH_p^0 (kJ/mol)	ΔS_p^0 (J/mol)	Relative error	
				ΔH_p^0	ΔS_p^0
Electrochemical	Alloy mixed with Cu electrode	-21.2	-62.9	37.7%	41.8%
Electrochemical	Alloy in foamed Ni electrode	-18.0	-51.6	47.1%	52.2%
Gaseous		-34.0	-108.0		

with $F = 23\,060 \text{ cal} \cdot \text{v}^{-1} \cdot \text{mol}^{-1}$, $R = 1.986 \text{ cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, we obtained from [6]

$$\frac{\Delta P}{P} = \exp\left(23\,223 \frac{\Delta E}{T}\right) - 1$$

The $\Delta P/P$ varies exponentially with $\Delta E/P$. At 298 K the variation of $\Delta P/P$ with ΔE 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 ΔP and ΔE leads to a large relative error. So a new electrochemical reaction, in which ΔH and ΔS are calculated directly from potential should be used to reduce the relative errors.

Determination of ΔH_c^0 and ΔS_c^0 directly from electrochemical reaction

For the electrode with flat plateaus the potential E can be taken as the mean value of the E_r and E_d , i.e., $E_{\text{eq}} = (E_r + E_d)/2$ where E_r 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. $P_{\text{eq}} = \sqrt{P_r P_d}$.

For $\text{Mn}_{1.75}\text{Ni}_{3.75}\text{Co}_{0.75}$ alloy the plateau is sloped, however, from Fig. 3 we can see that the plateau increases

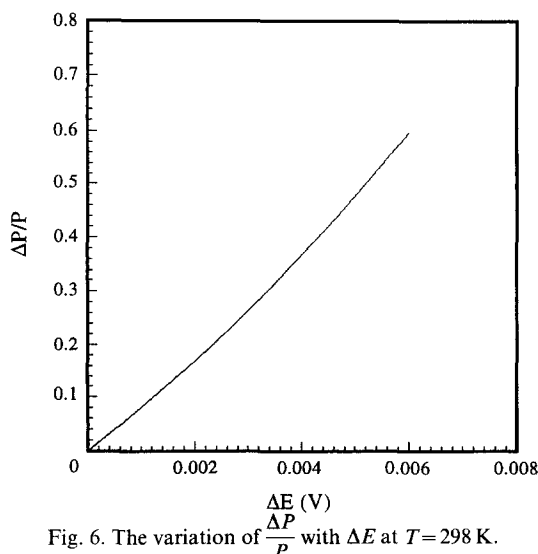


Fig. 6. The variation of $\frac{\Delta P}{P}$ with ΔE at $T = 298 \text{ K}$.

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 $E_{\text{eq}} = (E_r + E_d)/2$ a reasonable approximation. Our test results indicate that the measured equilibrium plateau potential is proportional to the temperature for $\text{Mn}_{1.75}\text{Ni}_{3.75}\text{Co}_{0.75}$ mixed with Cu electrode as shown in Fig. 7.

The relation of potential and temperature for $\text{Mn}_{1.75}\text{Ni}_{3.75}\text{Co}_{0.75}$ mixed with Cu electrode can be expressed as follows

$$E_{\text{eq}} = -0.914 - 2.5 \times 10^{-4}(T - 273). \quad (7)$$

According to the electrochemical principle

$$\Delta H_c^0 = 2F \left[E_{\text{eq}} - T \left(\frac{\partial E_{\text{eq}}}{\partial T} \right)_P \right] \quad (8)$$

$$\Delta S_c^0 = 2F \left(\frac{\partial E_{\text{eq}}}{\partial T} \right)_P. \quad (9)$$

Substituting equation (7) into equations (8) and equation (9) and taking $R = 8.314 \text{ J/mol} \cdot \text{K}$, $F = 96.548$

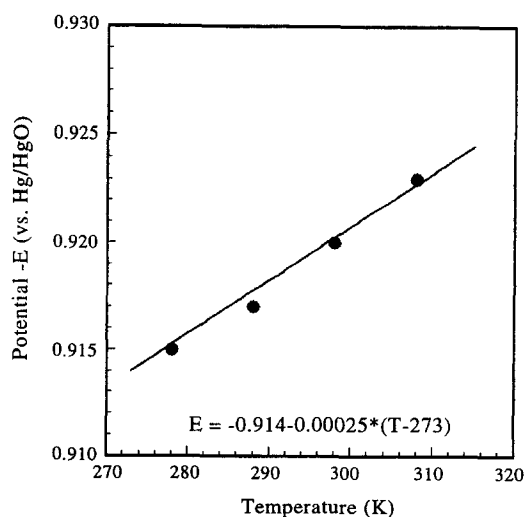


Fig. 7. The relation between the equilibrium potential and the temperature for $\text{Mn}_{1.75}\text{Ni}_{3.75}\text{Co}_{0.75}$ mixed with Cu electrode in the range of 278–308 K.

kJ/v * mol, we obtained: $\Delta H_c^0 = -163.07 \text{ kJ/mol}$,
 $\Delta S_c^0 = -48.274 \text{ J/mol} \cdot \text{K}$.

The relation between $\Delta H_c^0, \Delta S_c^0$ of the electrochemical reaction and $\Delta H_p^0, \Delta S_p^0$ of the gaseous reaction

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

$$E_{\text{eq}} = -1.1804 + (4.4666 \times 10^{-3} - 6.93606 \times 10^{-4} \ln T)T + 1.0788 \times 10^{-6} T^2 - 4.512 \times 10^{-10} T^3 + \frac{5.232}{T} - \frac{RT}{2F} \times \left(0.19198 - \frac{57.64383}{T} \right) - \frac{RT}{2F} \ln(\gamma_{(\text{H}_2)} P_{\text{eq}}) \quad (10)$$

$$\begin{aligned} \frac{\partial(E_{\text{eq}})}{\partial(T)} &= 4.4666 \times 10^{-3} - 6.93606 \times 10^{-4} \ln T - 6.93606 \times 10^{-4} + 2.157 \times 10^{-6} T - 1.3536 \times 10^{-9} T^2 - \frac{5.232}{T^2} \\ &- 0.19198 \times \frac{R}{2F} - \frac{R}{2F} \ln(\gamma_{(\text{H}_2)} P_{\text{eq}}) - \frac{RT}{2F} \times \frac{\partial(\ln \gamma_{(\text{H}_2)} P_{\text{eq}})}{\partial(T)} \\ \Delta H_c^0 &= 2F \left[E_{\text{eq}} - \left(\frac{\partial(E_{\text{eq}})}{\partial(T)} \right)_P \right] = 2F \left(-1.18041 + 6.93606 \times 10^{-4} T - 1.0788 \times 10^{-6} T^2 + 9.024 \times 10^{-10} T^3 + \frac{10.464}{T} \right) \\ &- 57.64383 R + RT^2 \left(\frac{\partial(\ln \gamma_{(\text{H}_2)} P_{\text{eq}})}{\partial(T)} \right) \end{aligned}$$

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 $0 \sim 200^\circ \text{C}$, 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't Hoff equation we get

$$\begin{aligned} \Delta H_p^0 &= R \times \frac{\partial(\ln P_{\text{eq}})}{\partial\left(\frac{1}{T}\right)} = -RT^2 \frac{\partial(\ln P_{\text{eq}})}{\partial(T)}, \\ \Delta S_p^0 &= -\frac{\partial(RT \ln(P_{\text{eq}}))}{\partial(T)} \end{aligned}$$

Then

$$\begin{aligned} \Delta H_c^0 &= 2F \left(-1.18041 + 6.93606 \times 10^{-4} T - 1.0788 \times 10^{-6} T^2 + 9.024 \times 10^{-10} T^3 + 10. \frac{464}{T} \right) - 57.64383 R \\ &- \Delta H_p^0 = F_{\Delta H} - \Delta H_p^0 \end{aligned}$$

$$\Delta S_c^0 = 2F \left(\frac{\partial(E_{\text{eq}})}{\partial(T)} \right)_P = 2 \times 96390$$

$$\times \left(4.4666 \times 10^{-3} - 6.93606 \times 10^{-4} \ln T - 6.93606 \right.$$

$$\left. \times 10^{-4} + 2.157 \times 10^{-6} T - 1.3536 \times 10^{-9} T^2 - \frac{5.232}{T} \right)$$

$$- 0.19198 \times R - \frac{\partial(RT \ln(\gamma_{(\text{H}_2)} P_{\text{eq}}))}{\partial(T)} = F_{\Delta S} + \Delta S_p^0$$

Functions $F_{\Delta H}$ and $F_{\Delta S}$ change with temperature very little as shown in Fig. 8. For $T = 298 \text{ K}$.

$$\Delta H_p^0 = -195.28724 - \Delta H_c^0 \text{ kJ/mol} \quad (11)$$

$$\Delta S_p^0 = -53.45 + \Delta S_c^0 \text{ J/mol} \cdot \text{K}. \quad (12)$$

For $\text{MnNi}_{3.75}\text{Mn}_{0.5}\text{Co}_{0.75}$ electrode mixed with Cu electrode, with $\Delta H_c^0 = -163.07 \text{ kJ/mol}$ and $\Delta S_c^0 = -48.274 \text{ J/mol} \cdot \text{K}$ (see Section 3.3), substituting the above two values into equation (11) and (12) we obtained

$$\Delta H_p^0 = -195.28724 + 163.07 = -32.22 \text{ kJ/mol}$$

$$\Delta S_p^0 = -48.274 - 53.45 = -101.724 \text{ J/mol} \cdot \text{K}.$$

Comparing the above data with the values of $\Delta H_p^0, \Delta S_p^0$ measured by gaseous method (see Table 3), we find the relative error is much smaller.

Relative error

$$\eta_{\Delta H} = \frac{34.2 - 32.22}{34.2} = 5.8\%$$

$$\eta_{\Delta S} = \frac{102.3 - 101.724}{102.3} = 5.6\%$$

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

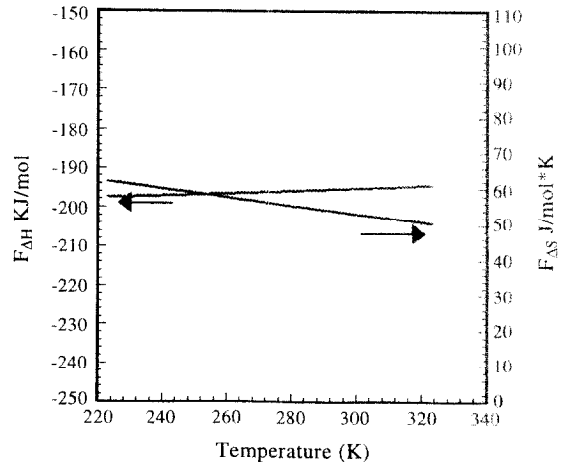


Fig. 8. The relation of ΔH function and ΔS function with temperature.

CONCLUSION

1. The accuracy of enthalpy change ΔH and entropy change ΔS 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 α phase and β 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 (ΔH_e^0) and entropy change (ΔS_e^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 ΔH_e^0 and ΔS_e^0 calculated directly from the e - c - T curve has been developed. For the electrode $\text{MnNi}_{3.75}\text{Mn}_{0.5}\text{Co}_{0.75}$ mixed with Cu: $\Delta H_e^0 = -163.07 \text{ kJ/mol}$, $\Delta S_e^0 = -48.274 \text{ J/mol} \cdot \text{K}$.
4. The relation between electrochemical ΔH_e^0 , ΔS_e^0 and gaseous reaction ΔH_p^0 , ΔS_p^0 has been deduced as $\Delta H_p^0 = -195.28724 - \Delta H_e^0$ (kJ/mol), $\Delta S_p^0 = -53.45 + \Delta S_e^0$ (J/mol * K). The accuracy of ΔH_p^0 ,

ΔS_p^0 calculated from ΔH_e^0 , ΔS_e^0 is much higher (with relative error within 7%) than those from conventional methods.

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REFERENCES

1. Sakai, T., Miyamura, H., Kuriyama, N., Akihikokato, Ogvro, K. and Ishikawa, H., *Journal of Less-common Metals*, 1990, **159**, 127.
2. Zhou, Z. X., He, C. H., Wang, Y. Q. and Wang, C. M., *Acta Physico-chimica Sinica (in Chinese)*, 1992, **4**, 558.
3. Balei, J., *International Journal of Hydrogen Energy*, 1985, **10**, 365.
4. Wang, X. H., Chen, C. P., Wu, J. and Wang, Q. D., *Journal of Rare Earths (English edition)*, 1994, **12**, 193.
5. Iwakura, C. and Asaoha, T., *Nippon Kagaku Kaishi*, 1988, **8**, 1482.
6. Wang, C. S., Lei, Y. Q., Wu, J. and Wang, Q. D., *Journal of Synthetic Crystals (in Chinese)*, 1994, **1**, 50.
7. Wang, C. S., Yan, M., Lei, Y. Q., Wu, J. and Wang, Q. D., *Journal of Synthetic Crystals (in Chinese)*, 1994, **3**, 60.
8. Conway, B. E. and Wojtowicz, J., *Journal of Electroanalytical Chemistry*, 1992, **326**, 227.
9. Flanagan, T., Clewley, J., Kuji, T., Park, C.-N. and Everett, D. H., *Journal of the Chemical Society, Faraday Transactions I*, 1986, **82**, 2589.
10. Flanagan, T., Park, C.-N., *Materials Science Forum*, 1988, **31**, 297.
11. Flanagan, T., Luo, W. and Clewley, J., *Journal of Less-common Metals*, 1991, **42**, 172-174.