

Electrochemical properties and structure of $MINi_{5-x}Sn_x$ system

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Abstract: The electrochemical properties and structure of $MINi_{5-x}Sn_x$ ($x = 0-0.5$) hydrogen storage alloys were investigated by pressure-composition isotherms, electrochemical measurements, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and atomic parameters. With a small amount of tin substitution, the cycle life increases by 52% (0.5C) and 42% (1.0C), but maximum discharge capacity decreases only by 3.0% and 3.5%, respectively. The cycle life is obviously improved by the low volume expansion and the formed SnO_2 surface layers upon electrochemical cycling. The substitution of Ni by Sn leads to an increase of the unit cell volume and charge-discharge cycle life and decrease of the plateau pressure, hysteresis and the hydrogen storage capacity. The standard enthalpy of hydride formation decreases with increasing tin substitution. The main factor that influences the standard enthalpy of the hydriding reaction is the number of the outer orbit electrons and not the atomic size factor.

Key words: hydrogen storage alloy; $MINi_{5-x}Sn_x$; electrochemical properties; structure

The process of replacing the toxic cadmium electrodes in rechargeable Ni/Cd batteries by AB_5 -type metal hydride electrodes with higher capacity is in full progress. However the paradigm compound of the AB_5 class of alloy $LaNi_5$ is not a suitable electrode because it corrodes rapidly in the chemically aggressive battery environment. Recently some multicomponent electrode alloys with longer cycle life have been developed. For instance, substitution of nickel by tin is very effective in improving the cycle life of the negative electrode [1-3]. However, the relationship between hydriding performance and structure is still not very clear. In this work, the structure and properties of $MINi_{5-x}Sn_x$ hydrogen storage alloys were studied to improve properties and reduce cost by pressure-composition isotherms, electrochemical measurements, XRD, XPS and atomic parameters.

1 Experimental

Lanthanum or lanthanum-rich mixed metal Ml (La 80.45%, Nd 18.8%, Ce 0.28%, Pr 0.46%, in mass fraction) with Ni and Sn (with purity more than 99.9%) in stoichiometric proportion of $LaNi_{4.9}Sn_{0.1}$ and $MINi_{5-x}Sn_x$ ($x = 0, 0.1, 0.2, 0.3, 0.4, 0.5$) were melted together in a vacuum arc furnace under an Ar atmosphere. The melting process was repeated four times to ensure the constituents of the alloy were evenly distributed. The cast alloys were annealed at 950 °C for 72 h in vacuum (0.1 Pa) and activated in 4.0 MPa of hydrogen at room temperature. The resulting alloy powders were identified using a model D/MAX-RB 12 kW rotating anode

X-ray diffractometer. Pressure-composition desorption isotherms (PC isotherms) were measured for all alloy compositions according to the usual procedure [4].

Electrochemical performance was tested with plate cells. The anodes were prepared by mixing the alloy with Cu powder (mass ratio 1 : 4) and pressing into $\phi 10 \text{ mm} \times 2 \text{ mm}$ plates at $2 \times 10^7 \text{ MPa}$ pressure. The cathodes were made from $NiOOH/Ni(OH)_2$. The electrodes and separator were placed into an electrochemical cell containing 6 mol/L KOH electrolyte. The cut-off voltages for charge and discharge were 1.7 V and 0.9 V, respectively. A constant current of 180 mA/g (0.5C rate) or 360 mA/g (1.0C rate) was employed. The electrochemical activity, discharge capacity and cycle life were tested. The XPS was obtained on a VG ESCA-LAB MK-II multi-functional spectrometer using $Mg K_{\alpha}$ radiation of 1253.6 eV, C1s at 285.0 eV and 1×10^{-8} Pa base pressure.

2 Results and discussion

2.1 Electrochemical characteristics

The capacity vs charge-discharge cycle life of $MINi_{5-x}Sn_x$ electrodes is illustrated in **figure 1**. The results show that maximum discharge capacity decreases whereas cycle life and rate of initial activation increase when Sn content increases in $MINi_{5-x}Sn_x$ alloys. For a lower Sn content, such as $x = 0.2$, the cycle life increases by 52% (0.5C) and 42% (1.0C), but maximum discharge capacity decreases by only 3% and 3.5%, respectively. However, for higher Sn contents the dis-

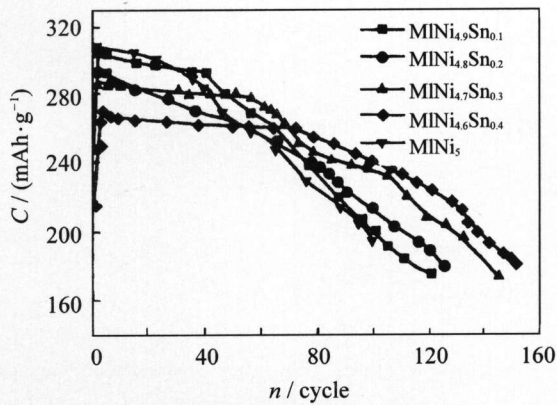


Figure 1 The capacity vs cycle life for $\text{MINi}_{5-x}\text{Sn}_x$ (0.5C) electrodes.

charge capacity and the rate of initial activation will obviously decrease. Scanning electron microscope (SEM) indicates that after 100 electrochemical cycles the grain size of alloys could be increased by 50% with tin substitution in the MINi_5 (figure 2). The substitution of Ni by Sn can decrease volume expansion and inhibit pulverization of alloy. The increase of cycle life was explained by considering the increase in unit cell volume of MINi_5 caused by tin substitution and the low volume

dilatation on hydride formation [2].

The XPS is then used to characterize the surface of the alloys. The results of XPS analysis of MINi_5 and $\text{MINi}_{4.7}\text{Sn}_{0.3}$ electrode surface indicate that after 100 cycles, Ni and La exist in the states of Ni_2O_3 , $\text{Ni}(\text{OH})_3$ and La_2O_3 (figure 3). It is just the oxidation and the loss of active material that make discharge capacity decrease continuously. And within about 200 nm and 50 nm depth Ni and La have been fully oxidized for MINi_5 and $\text{MINi}_{4.7}\text{Sn}_{0.3}$ respectively. This means that the degree of oxidation of La and Ni of $\text{MINi}_{4.7}\text{Sn}_{0.3}$ electrode are lesser than that of MINi_5 electrode. Figure 4 shows Sn 3d XPS on the surface of $\text{MINi}_{4.7}\text{Sn}_{0.3}$ alloy during charge-discharge cycles. The results indicate that after activation and 100 cycles, there are large amounts of Sn (10%-15% and 30%-38% respectively, mole fraction) in surface layer. The peak at 486.35 eV and 486.2 eV are assigned to Sn^{4+} , it means SnO_2 formation. It can be seen that tin is rapidly enriched and oxidized on the electrode surfaces and the passive tin oxide layer can inhibit further La and Ni surface segregation and oxidation. Therefore the cycle life of $\text{MINi}_{4.7}\text{Sn}_{0.3}$ electrode is obviously improved.

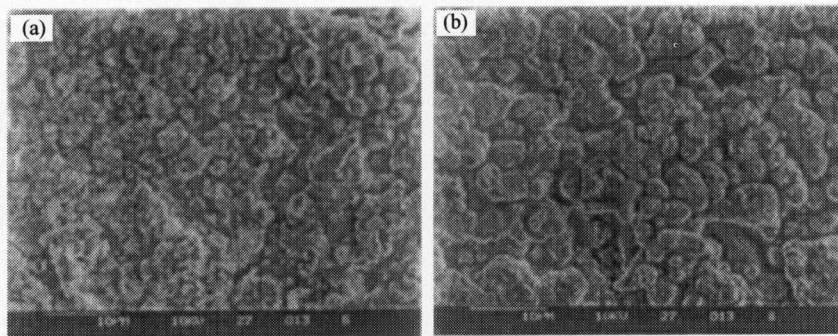


Figure 2 Comparison of the grain size of (a) MINi_5 and (b) $\text{MINi}_{4.8}\text{Sn}_{0.2}$ electrodes (100 cycles).

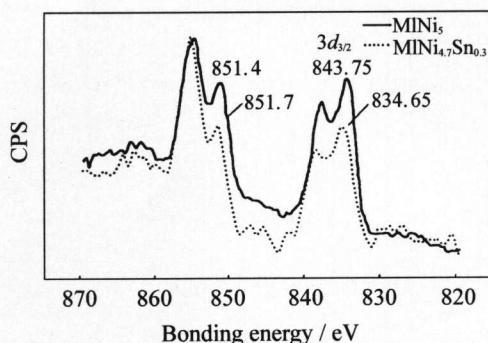


Figure 3 La 3d XPS of MINi_5 and $\text{MINi}_{4.7}\text{Sn}_{0.3}$ Electrode.

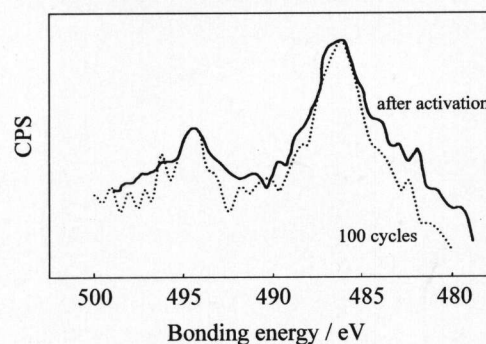


Figure 4 Sn 3d XPS of $\text{MINi}_{4.7}\text{Sn}_{0.3}$ Electrode.

3.2 Structure and hydriding performance

X-ray diffraction analysis indicates that $\text{MINi}_{5-x}\text{Sn}_x$ ($x \leq 0.5$) alloys have an hexagonal CaCu_5 crystal structure without any secondary phase. The lattice parameters and cell volumes of the alloys are presented in table 1.

The partial substitution of Ni with Sn results in an increase in the lattice parameters and cell volume of $\text{MINi}_{5-x}\text{Sn}_x$. The cell volume (V) is a linear function of Sn content (x) and is a useful check on the intermetallic composition. The equation for the cell volume as a function of x is

Table 1 Lattice parameters and cell volumes V of $\text{MgNi}_{5-x}\text{Sn}_x$ composition

Composition	a / nm	c / nm	c/a	$V / 10^{-3} \text{ nm}^3$
MgNi_5	0.497 8	0.398 2	0.7999	85.46
$\text{MgNi}_{4.9}\text{Sn}_{0.1}$	0.499 7	0.399 4	0.799 3	86.37
$\text{MgNi}_{4.8}\text{Sn}_{0.2}$	0.501 4	0.400 8	0.799 4	87.27
$\text{MgNi}_{4.7}\text{Sn}_{0.3}$	0.502 8	0.402 2	0.799 9	88.05
$\text{MgNi}_{4.6}\text{Sn}_{0.4}$	0.505 0	0.403 6	0.799 2	89.14
$\text{MgNi}_{4.5}\text{Sn}_{0.5}$	0.507 0	0.405 0	0.798 8	90.15

$$V = (85.41 + 9.280 x) \times 10^{-3} \text{ nm}^3.$$

The PC isotherms for $\text{MgNi}_{5-x}\text{Sn}_x$ alloys are shown in **figure 5**. An increase in Sn content results in a decrease in the plateau pressure and an increase in the slope of the plateau. **Table 2** lists the absorption plateau pressure (P_a), desorption plateau pressure (P_d), standard enthalpy (ΔH^\ominus) and entropy (ΔS^\ominus) (hydriding reaction), and maximum hydrogen storage capacity (g atom H/mol) of these hydrogen storage alloys. The partial substitution of Sn for Ni in MgNi_5 or LaNi_5 results in a decrease in P_a , P_d , ΔH^\ominus , ΔS^\ominus and g atom H/mol. Tin also reduces the magnitude of the hysteresis $\ln(P_a/P_d)$. The relation between the hysteresis and the unit cell volume V (nm^3) is $\ln(P_a/P_d) = 3.39 - 0.036 V$. Hysteresis is associated with plastic deformation and dislocation generation produced by the volume change on hydriding [3].

Thus the tin substitutions are efficient at decreasing the volume expansion on hydride formation. The results given by SEM indicate that the size of $\text{MgNi}_{4.7}\text{Sn}_{0.3}$ is larger than that of MgNi_5 by about 25% after activation.

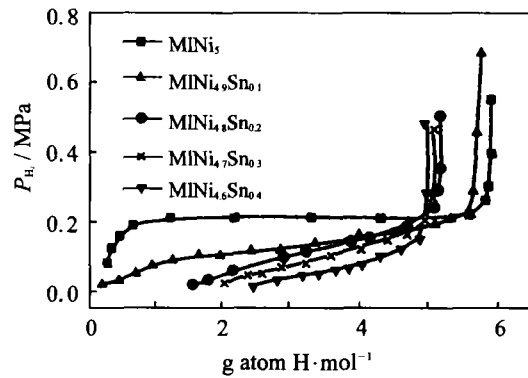


Figure 5 The PC isotherms for $\text{MgNi}_{5-x}\text{Sn}_x$ alloys.

Table 2 Thermodynamic Properties of $\text{LaNi}_{5-x}\text{Sn}_x$ and $\text{MgNi}_{5-x}\text{Sn}_x$ (298K)

Alloy	g atom H / mol	P_a / MPa	P_d / MPa	$-\Delta H^\ominus / (\text{kJ} \cdot \text{mol}^{-1})$	$-\Delta S^\ominus / (\text{kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$
MgNi_5	5.7	0.29	0.22	28.1	90.8
$\text{MgNi}_{4.9}\text{Sn}_{0.1}$	5.3	0.15	0.12	28.3	90.9
$\text{MgNi}_{4.8}\text{Sn}_{0.2}$	5.1	0.125	0.10	29.4	94.3
$\text{MgNi}_{4.7}\text{Sn}_{0.3}$	4.9	0.10	0.08	31.0	99.2
$\text{MgNi}_{4.6}\text{Sn}_{0.4}$	4.8	0.07	0.06	32.5	103.8
LaNi_5 [5]	6.0	0.20*	0.16*	30.10	105.0
$\text{LaNi}_{4.9}\text{Sn}_{0.1}$	5.8	0.12	0.09	31.7	106.1
$\text{LaNi}_{4.8}\text{Sn}_{0.2}$ [3]	—	—	0.048	34.50	109.7

Note: * 293 K.

3.3 Atomic parameters and enthalpy of hydriding reaction

The energy of alloy phases involves three factors [6].

(1) The chemical affinity factor which depends on the difference among the electronegativities of the constituent elements and illustrates the energy change to form chemical bonds.

$$(\Delta X)^2 = \sum_{i=1}^n C_i (X_i - \bar{X})^2 \quad (1)$$

where ΔX represents the difference of average electronegativities, n is the number of constituents in the alloy, C_i is the atomic proportion of the i -th element constituting the alloy, X_i is the value of electronegativity of the

i -th element, \bar{X} is the average value of electronegativity.

(2) The atomic size factor δ which depends on the atomic diameter of elements represents the space character of ions and electrons among atoms. Differences of atomic size lead to elastic strain energy.

$$\delta^2 = \sum_{i=1}^n C_i \left(\frac{d_i}{\bar{d}} - 1 \right)^2 \quad (2)$$

where d_i is the atomic diameter for a coordination number of 12 of the i -th element, \bar{d} is the average value of atomic diameter.

(3) The electron concentration factor, which depends on the number of outer orbit electrons of the element, affects the Fermi energy.

$$(e/a)^{2/3} = \sum_{i=1}^n C_i Z_i^{2/3} \quad (3)$$

where (e/a) represents the electron concentration, Z is the number of outer orbit electrons. For transition metals, post-transition metals and lanthanide's, the outer orbit electrons are $(s+d)$, $(s+p)$ and $(s+d+f)$, respectively.

Based on atomic parameters of the elements and experimental data of plateau pressures for $\text{LaNi}_{5-x}\text{M}_x$ [7], a model of the standard enthalpy of hydride formation (ΔH^\ominus) was established by a stepwise regression method. The model gives

$$\Delta H^\ominus = -1.611 \times 10^5 - 4.485 \times 10^5 (\Delta X)^2 + 3.617 \times 10^6 \delta^2 + 1.151 \times 10^4 (e/a)^{2/3} \quad (\text{J/mol}) \quad (4)$$

Equation (4) shows that lower electron concentration and atomic size factor and larger average difference of electronegativity all make the enthalpy of hydride formation more negative and the hydride more stable. The calculated enthalpy of the hydrides of $\text{LaNi}_{4.9}\text{Sn}_{0.1}$ and $\text{LaNi}_{4.8}\text{Sn}_{0.2}$ are -30.6 and -32.1 kJ/mol, which is consistent with experimental values of -31.7 and -34.5 kJ/mol, respectively.

According to the atomic parameters of La, Ni and Sn, the ΔX^2 , δ^2 and $(e/a)^{2/3}$ of $\text{LaNi}_{4.9}\text{Sn}_{0.1}$ and LaNi_5 are 0.062 35, 0.030 64 and 4.180, 0.062 45, 0.030 51, and 4.214, respectively. Because of the substitution of Sn, ΔX^2 and $(e/a)^{2/3}$ decrease and δ^2 increases. The experimental results show that the substitution of Ni by Sn in LaNi_5 leads to a lower ΔH^\ominus (table 2). According to this model, the main factor which influences ΔH^\ominus is the number of outer orbit electrons, *i.e.* electron concentration, and not atomic size factor. A lower electron concentration leads to a lower Fermi energy if electron concentration plays a main role in the alloys [6]. Thus the lower the electron concentration, the lower the enthalpy of hydride formation.

4 Conclusions

(1) With a small amount of tin substitution capacity

slightly decreases but cycle life obviously increases. The low volume dilatation and the formed passive SnO_2 surface layer cause the improved cycle life during electrochemical cycling.

(2) The partial substitution of Ni by Sn in the MNi_5 system leads to an increase of the unit cell volume and decrease of the plateau pressure. The tin substitution can decrease the enthalpy and entropy of hydride formation in the $\text{MNi}_{5-x}\text{Sn}_x$ systems.

(3) The main factor that influences the enthalpy of hydride formation is the number of outer orbit electrons, *i.e.* electron concentration, and not atomic size factor in the $\text{MNi}_{5-x}\text{Sn}_x$ system.

References

- [1] S.W. Lambert, D. Chandra, W.N. A. Cathey, F.E. Lynch, and R. C. Bowman, Investigation of hydriding properties of $\text{LaNi}_{4.8}\text{Sn}_{0.2}$, $\text{LaNi}_{4.77}\text{Sn}_{0.24}$, $\text{La}_{0.9}\text{Gd}_{0.1}\text{Ni}_5$ after thermal cycling and aging [J], *J. Alloys Comp.*, 187 (1992), p.113.
- [2] A.R. Balasubramaniam, M.N. Mungole, and K.N. Rai, Hydriding properties of MmNi_5 system with aluminium, manganese and tin substitutions [J], *J. Alloys Comp.*, 196 (1993), p.63.
- [3] R.C. Bowman, C.H. Luo, C.C. Ahn, C.K. Witham, and B. Fultz, The effect of tin on the degradation of $\text{LaNi}_{5-x}\text{Sn}_x$ metal hydrides during thermal cycling [J], *J. Alloys Comp.*, 185 (1995), p.217.
- [4] Q. Lin, R. Li, W. Ye, N. Chen, and R.M. Liu, Kinetics of hydrogen absorption in Ml-Ni-Co-Mn-Al alloys [J], *Acta Metallurgica Sinica*, 32 (1996), p.624.
- [5] C.E. Luhdin, F.E. Lurch, and C.B. Magee, A correlation between the interstitial hole sizes in intermetallic compounds and the thermodynamic properties of hydrides formed from those compound [J], *J. Less-Common Met.*, 56 (1977), p.65.
- [6] J.M. Xiao, *The Subject of Alloy Energy* [M], Metallurgy Industry Press, Beijing, 1990, p.256.
- [7] S. Zhao, Q. Lin, and N. Chan, Calculation and prediction for the hydriding properties of $\text{LaNi}_{5-x}\text{M}_x$ alloy [J], *J. Alloys Comp.*, 287 (1999), p.57.