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The electrolyte temperature dependence of the electrochemical hydrogen storage property of Mg–Ni alloy codeposited from aqueous solution

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Abstract

The temperature dependence of the electrochemical property of Mg–Ni alloy codeposited from aqueous solution was studied. Results show that not only solvating temperature, deposition temperature but also temperature variation in deposition temperature controlling will affect Mg–Ni codeposition and electrochemical hydrogen storage property of the Mg–Ni deposit synthesized.

The temperature combination of solvating temperature 87.9 ± 1.2 °C and deposition temperature 47.9 °C is favourable for Mg–Ni codeposition, deposit synthesized under this temperature combination has a electrochemical capacity of 67 mAh/g.

Keywords: Temperature dependence; Electrochemical hydrogen storage; Mg–Ni alloy; Codeposition

1. Introduction

Mg-based alloy has much higher hydrogen storage ability compared with other hydrogen storage alloys, thus it has attracted attentions of many scientists, whereas, casting Mg-based alloy has low activity, and high temperature and high hydrogen pressure condition is needed for the alloy to absorb hydrogen. In 1990s [1–4], Mg-based alloy was synthesized by mechanical alloying, researches found that the alloy synthesized by mechanical alloy has high activity, it can absorb and desorb hydrogen electrochemically at room temperature, and no activation process is needed for the hydride electrode to arrive at its maximum capacity, and the alloy has much higher capacity compared with other hydride material, but the stability of the alloy is poor, its capacity degrades rapidly, and as Mg is quite soft, it sticks on the milling tin and milling balls used and cannot be got rid of, thus the alloy composition is hard to control, and the synthesis process needs high energy consumption.

Electrochemical metal deposition is one of the oldest methods within the framework of electrochemistry. The electrodeposition takes place at electrode/electrolyte interfaces under the influence of an electric field including a number of phase formation phenomena. Comparing to other methods of alloy preparation, it has the merit of simplicity in synthesis, easiness in alloy composition controlling, and by changing the electrolyte composition and deposition rate, alloy with different structure can be obtained [5].

It is known [6] that, owing to the very large negative normal redox potential of Mg element, it is difficult for Mg to be electrodeposited from aqueous solution even the concentration of Mg^{2+} ion is increased to shift the equilibrium potential of Mg reduction to positive direction, the electrochemical reaction that occurred at the negative electrode is hydrogen evolution. And the redox potential of Mg and Ni differs more than 2 V, thus it is difficult for Mg and Ni to codeposit together. Whereas, in a former study we found [7] that Mg can be codeposited with Ni from a chloride–sulfate aqueous solution.

Mg–Ni alloy can form crystal Mg, Ni, Mg_2Ni and $MgNi_2$ phases or amorphous phase, but only Mg, Mg_2Ni and amorphous Mg–Ni phase can absorb and desorb hydrogen. Thus, only alloy which has high Mg, Mg_2Ni and/or amorphous Mg–Ni phase content will review a high electrochemical hydrogen storage capacity.

In the present study, electrodeposition of Mg–Ni alloy from a chloride–sulfate aqueous electrolyte was performed,

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and the synthesized alloy deposit was used as the negative electrode of a Ni-MH battery and its electrochemical performance was studied by a three-pole battery method. The influence of deposition temperature and electrolyte solvating temperature to the electrochemical property of deposit synthesized was correlated, and the effects of deposition temperature and electrolyte solvating temperature on Mg–Ni codeposition is deduced based on its influence on the electrochemical property of the deposit synthesized.

2. Experimental

The Mg–Ni alloys were deposited under constant current density of 80 mA/cm^2, in a conventional three-electrode cell in which the working and counter electrode were oil-removed and polished (with energy paper) red copper, reference electrode is 3 M KCl/Hg/HgCl$_2$, the electrolyte used is of the following composition: NiSO$_4$·6H$_2$O, 32.5 g/L; NiCl$_2$·6H$_2$O, 32.5 g/L; MgSO$_4$·7H$_2$O, 100 g/L; MgCl$_2$·6H$_2$O, 162.5 g/L; H$_3$BO$_3$, 15 g/L; additive 1, 32.5 g/L; coumarin, 2.5 g/L; additive 2, 5 g/L; diphenylamine sulphonic acid sodium salt, 12.5 g/L; additive 3, 5 g/L; Complex 1, 12.5 g/L; Complex 2, 20 g/L; HCHO, 125 mL/L (all are analytical grade reagents) pH 2–3. Owing to the not dissolving of reagents in distilled water at room temperature, the bath is heated to 83–96 °C until all reagents are solved. Then, it is dropped and maintained at 40–57 ± 1.2 °C. The deposition takes 30 min. After deposition, the study electrode is washed by distilled water, and then dried by hot air and weighted.

The structure of the deposit was examined by means of D/Max-2c X-ray diffractionmeter with Cu Kα radiation. The composition of the deposit synthesized was analyzed by means of 3200 Atom Absorption Spectroscopy. The electrochemical characteristics of the deposits were determined in a conventional three-pole system with 6 M KOH solution. The deposit electrode was used directly as the test electrode, a nickel electrode (Ni(OH)$_2$/NiOOH) was used As the counter electrode and a mercury(II) oxide electrode (Hg/HgO, 6 M KOH) was used as the reference electrode. In the experiment for each electrode, charging was conducted at a current density of 50 mA/g for 9 h, the discharging capacity and electrochemical cycle lifetime were measured at current density of 50 mA/g at atmospheric pressure and 30 °C. The discharging end potential was fixed at −600 mV (versus Hg/HgO, 6 M KOH).

3. Results and discussion

3.1. The electrochemical property of the deposit synthesized when deposition temperature is controlled at 48 ± 0.5 °C, and solvating temperature is 79.2–90 °C

Fig. 1 is the electrochemical capacity and cycling property of Mg–Ni deposit synthesized when deposition temperature is 48 ± 0.5 °C and solvating temperature is 79.2–90 °C. Fig. 2 is the maximum capacity of deposit synthesized when deposition temperature is controlled at 48 ± 0.5 °C and solvating temperature is 79.2–90 °C. From Figs. 1 and 2, we can see that when neglecting the deposition temperature difference during the deposition procedure, the maximum capacity of deposit synthesized increased when solvating temperature increased from 79.2 to 83 °C, and do not change much when solvating temperature increased from 83 to 87 °C, and it increased to 67 mAh/g when solvating temperature increased to 88 °C, whereas it decreased to 10 mAh/g when solvating temperature increased to 90 °C. The activity of deposit increased when solvating temperature increased from 79.2 to 83 °C, the cycling number for the deposit to arrive at its maximum capacity decreased, and it do not change much when solvating temperature increased from 83 to 88 °C, deposit arrive at its maximum capacity in the first charge/discharge cycle, whereas it decreased when solvating temperature increased to temperature higher than 88 °C, the cycling number for deposit to arrive at its maximum capacity increased to 2 when solvating temperature increased to 89 °C, and it increased to 4 when solvating temperature increased to 90 °C. The cycling stability of the deposit decreased when solvating temperature increased from 79.2 to 83 °C, and it do not change much when solvating temperature increased from 83 to 87 °C, and it decreased when solvating temperature increased to 88 °C, but it increased again when solvating temperature increased to temperature higher than 88 °C. In a former study [7], we found that Mg–Ni deposit can form Mg, Ni, Mg$_2$Ni and MgNi$_2$ phases, in which Mg and Mg$_2$Ni are hydrogen-storage phase, thus alloy deposited which contain more Mg element (Mg codeposited well with Ni) may has better hydrogen storage property, And in a former study of Mg–Ni alloy synthesized by mechanical alloying [3], we found that the cycling stability

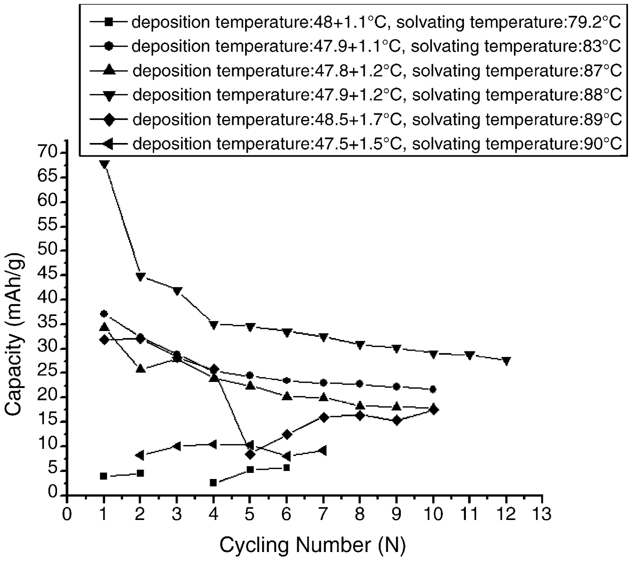

Fig. 1. The electrochemical capacity and cycling property of deposit synthesized when deposition temperature is controlled at 48 ± 0.5 °C and solvating temperature is 79.2–90 °C.

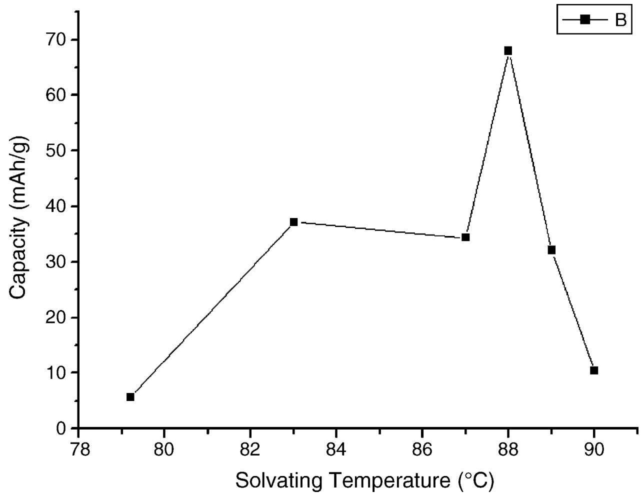

Fig. 2. The maximum capacity of the deposit synthesized when deposition temperature is controlled at 48 ± 0.5 °C with solvating temperature.

of the hydride electrode improved when alloy contained more Ni. Thus, improved capacity and decreased cycling stability may imply higher Mg/Ni ratio in the deposit synthesized. According to maximum capacity and cycling stability of the deposit, we deduce that solvating temperature accessing to 88 °C is favourable for Mg–Ni codeposition when deposition temperature is 48 ± 0.5 °C. Temperature higher or lower than it will decrease electrochemical property of the deposit synthesized, and is unfavourable for Mg–Ni codeposition. And when deposition temperature is 48 ± 0.5 °C and solvating temperature is 88 °C, Mg–Ni deposit has a electrochemical capacity of 67 mAh/g.

The reason and tendency for solvating temperature to affect the electrochemical hydrogen storage property of Mg–Ni alloy codeposited and Mg–Ni codeposition may lay in the following respect:

(1) Some component of electrolyte may be unstable and may resolve/decompose when solvating temperature increased which may be unfavourable for Mg–Ni codeposition.
(2) The solubility of component of electrolyte may increase when solvating temperature increase, thus electrolyte may have higher electrolyte concentration and higher conductance which is favourable for Mg–Ni codeposition.

As favourable and unfavourable affects may exist when solvating temperature increased, thus a promising solvating temperature exist.

3.2. *The electrochemical property of the deposit synthesized when solvating temperature is controlled at 87.9 ± 1.2 °C, and deposition temperature is 46.2–57.1 °C*

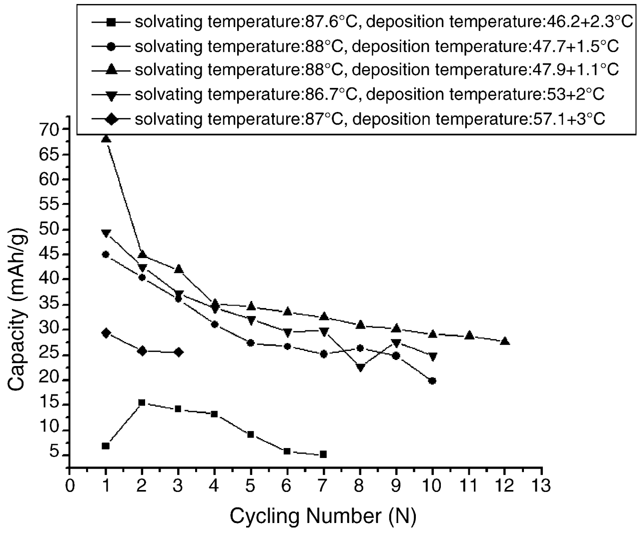

Fig. 3. The electrochemical capacity and cycling property of deposit synthesized when solvating temperature is controlled at 87.9 ± 1.2 °C and deposition temperature is 46.2–57.1 °C.

Fig. 3 is the electrochemical capacity and cycling property of Mg–Ni deposit synthesized when solvating temperature is controlled at 87.9 ± 1.2 °C and deposition temperature is 46.2 ± 2.3 °C to 57.1 ± 3.0 °C. Fig. 4 is the dependence of maximum capacity on deposition temperature. From Figs. 3 and 4, we can see that, when neglecting the difference in solvating temperature and temperature fluctuation during the deposition procedure and when solvating temperature is controlled at 87.9 ± 1.2 °C, the property of deposit changed with the change of deposition temperature in the following way. The maximum capacity of Mg–Ni deposit increased from 15 to 67 mAh/g when deposition temperature increased from 46.2 to 47.9 °C, and it decreased to 29 mAh/g when deposition temperature increased to 57.1 °C. The activity of the deposit increased when deposition temperature increased from 46.2 to 47.7 °C, and it do not change much when deposition temperature increased to temperature higher than 47.7 °C. The cycling stability of the deposit do not change much when deposition temperature increased from 46.2 to 47.7 °C, and it decreased a little bit when deposition temperature increased to 47.9 °C, but it increased again when deposition temperature increased from 47.9 to 57.1 °C. As stated in Section 3.1 [3,7], according to the electrochemical hydrogen storage property of Mg–Ni deposit, we can see that deposit exhibit better electrochemical hydrogen storage property when deposition temperature in accessing to 47.9 °C and when the solvating temperature is 87.9 ± 1.2 °C. This temperature combination is favourable for Mg–Ni codeposition. Deposit synthesized under this temperature combination has an electrochemical capacity of 67 mAh/g.

A promising deposition temperature existed, the maximum capacity of the deposit arrive at its maximum value when deposition temperature arrive at this deposition temperature, and it lowered when deposition temperature is higher or lower that this promising value. It is known that in Ni deposition [8] the rising of deposition temperature will affect

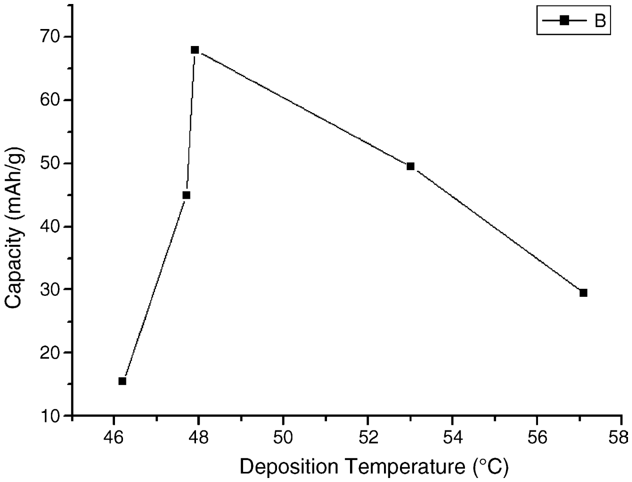

Fig. 4. The maximum capacity of the deposit synthesized when solvating temperature is controlled at 87.9 ± 1.2 °C with deposition temperature.

deposition in the following way:

1. Affect internal stress of the deposit formed, deposit with large internal stress will drop from the deposit easily. The internal stress decreased rapidly when deposition temperature rise from 10 to 55 °C, whereas, it decreased slowly when deposition temperature rise from 55 to 60 °C, and it do not change much when deposition temperature rise to temperature higher than 60 °C.
2. The solubility of component of electrolyte increase, electrolyte of high electrolyte concentration can be used.
3. Increase the conductance of solution.
4. The polarization of cathode and anode will decrease, and the current efficiency will raise.
5. The hydrolysis of salts and the of hydroxide precipitate forming tendency will increase, especially the hydrolysis of iron-impurity, small holes are easily formed.
6. The disperse ability of the electrolyte will decrease.

From the above effect, we can see that the rising of deposition temperature may have both favourable and unfavourable effect to Ni deposition. The effect of deposition temperature in Mg–Ni codeposition may have similar effect to Ni-deposition. That is why, a promising deposition temperature for Mg–Ni codeposition exist.

3.3. XRD and AAS analysis

Fig. 5 is the X-ray diffraction spectrum of the deposit synthesized when deposition temperature is 47.9 °C and the solvating temperature is 87.9 ± 1.2 °C. From Fig. 5, it can be seen that broaden peaks of Ni and Cu phase exists in the X-ray spectrum of the deposit. From the electrolyte composition, we see that no Cu^{2+} ion exists in the electrolyte, but a red cooper colour can be seen over the black deposits, and the anode we used is copper electrode, thus we believe the Cu phase in deposit is solvated anode Cu deposited in cathode as an impurity. The broaden peaks imply that amorphous phase may content in the deposit, in a former study [7] we successfully deposited crystal Mg–Ni alloy. Thus, we believe that the amorphous phase may contain Mg and Ni element, the deposit is a Mg–Ni alloy. For Ni cannot storage hydrogen, only when it is alloyed with Mg can it storage hydrogen, we believe that the electrochemical hydrogen storage property of the deposit electrode is owing to the formation of hydrogen storage amorphous Mg–Ni phase. Atom absorption analysis on the deposit show that its composition is Mg 11.35 at.%, Ni 42.93 at.%, Cu 45.72 at.%, if neglecting Cu element in the alloy, it is Mg 20.91 at.%, Ni 79.09 at.%. This confirms the synthesis of Mg–Ni alloy.

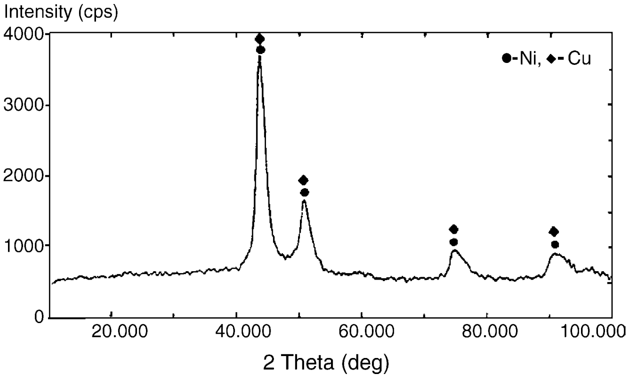

Fig. 5. The X-ray diffraction pattern of Mg–Ni deposit synthesized.

4. Conclusion

1. Not only solvating temperature, deposition temperature, but also temperature variation in deposition temperature controlling will affect Mg–Ni codeposition and electrochemical hydrogen storage property of the Mg–Ni deposit synthesized.
2. When deposition temperature is 48 ± 0.5 °C, the promising solvating temperature favourable for Mg–Ni codeposition is 88 °C. And when deposition temperature is 48 ± 0.5 °C and solvating temperature is 88 °C, Mg–Ni deposit has a electrochemical capacity of 67 mAh/g.
3. The effect of rising of solvating temperature may be: the decompose of unstable component of electrolyte, the increase of solubility of component of electrolyte, and the increase of electrolyte concentration and conductance.
4. When solvating temperature is 87.9 ± 1.2 °C, deposition temperature accessing 47.9 °C is favourable for Mg–Ni codeposition, the electrochemical property of the deposit arrive at its maximum value, and deposition temperature high or lower than this value will decrease the property of the deposit. And when solvating temperature is 87.9 ± 1.2 °C and deposition temperature is 47.9 °C, deposit has a electrochemical capacity of 67 mAh/g.
5. The effect of rising of deposition temperature may be: increase solubility of component of electrolyte, increase conductance of solution, decrease polarization of cath-

ode and anode, and raise current efficiency, increase the hydrolysis of salts and the tendency of hydroxide precipitate forming, and decrease the disperse ability of electrolyte.

(6) When solvating temperature is 87.9 ± 1.2 °C and deposition temperature is 47.9 °C, the deposit synthesized is composed of amorphous Mg–Ni phase plus crystal Ni phase. The electrochemical hydrogen storage capacity of the deposit is owing to the forming of amorphous Mg–Ni phase.

Acknowledgements

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