

Influence of addition of $\text{Cu}(\text{OH})_2$ to KOH alkaline electrolyte on electrochemical properties of $\text{La}_2\text{Mg}_{0.9}\text{Al}_{0.1}\text{Ni}_{7.5}\text{Co}_{1.5}$ hydrogen storage alloy electrode

WANG Da-hui(王大辉)¹, LUO Yong-chun(罗永春)², YAN Ru-xu(阎汝煦)¹,
KANG Long(康 龙)², HOU Xin-gang(侯新刚)¹

1. State Key Laboratory of Gansu Advanced Non-ferrous Metal Materials,
Lanzhou University of Science and Technology, Lanzhou 730050, China;

2. Key Laboratory of Non-ferrous Metal Alloys, Ministry of Education,
Lanzhou University of Science and Technology, Lanzhou 730050, China

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Abstract: The influence of the addition of $\text{Cu}(\text{OH})_2$ to 6 mol/L KOH alkaline electrolyte on the electrochemical properties of $\text{La}_2\text{Mg}_{0.9}\text{Al}_{0.1}\text{Ni}_{7.5}\text{Co}_{1.5}$ hydrogen storage alloy electrode was investigated by electron probe X-ray microanalysis(EPMA), X-ray diffraction(XRD) and electrochemical measurements. EPMA micrographs and XRD patterns show that the surface of the hydride electrode is plated by metal copper film. The thickness and compactness of Cu film increase with the increment of charge-discharge cycle number. The copper film of the hydride electrode surface can keep the hydrogen storage alloy particle in the electrode interior from oxidizing availably. The addition of $\text{Cu}(\text{OH})_2$ to alkaline electrolyte lowers the activation property and the high rate dischargeability of the $\text{La}_2\text{Mg}_{0.9}\text{Al}_{0.1}\text{Ni}_{7.5}\text{Co}_{1.5}$ hydride electrode, but has no negative effect on the maximum discharge capacity of the hydride electrode. Moreover, it is effective to improve the cyclic stability of the hydride electrode utilizing electrodeposit Cu film on the $\text{La}_2\text{Mg}_{0.9}\text{Al}_{0.1}\text{Ni}_{7.5}\text{Co}_{1.5}$ hydride electrodes surface.

Key words: hydrogen storage alloy; electrodeposition; La-Mg-Ni alloy; electrochemical properties

1 Introduction

Recently, the study on the structural and electrochemical the properties of La-Mg-Ni based alloy shows that La_2MgNi_9 alloy with PuNi_3 type structure is one of the most important electrode materials substitutes for LaNi_5 based hydrogen storage alloy[1–10]. The structure of AB_3 type La-Mg-Ni alloy (PuNi_3 -type structure) is a combination of Cu_2Mg and CaCu_5 structure[11–15], the maximum electrochemical discharge capacity of $\text{La}_2\text{MgNi}_{7.5}\text{Co}_{1.5}$ hydrogen storage alloy electrode reaches above 400 mA·h/g, which is higher than that of the LaNi_5 -based alloy. However, despite the large discharge capacity, the cyclic stability of the $\text{La}_2\text{MgNi}_{7.5}\text{Co}_{1.5}$ alloy is very bad[7,16–19] and needs further improvement.

LIU et al[20] have studied the degradation behavior

of the La-Mg-Ni-Co-type metal hydride electrodes, their results show that the pulverization of the alloy particles and the oxidation/corrosion of the active components of the alloys during charge/discharge cycling in the alkaline electrolyte are the two main factors responsible for the fast capacity degradation of the alloy electrodes. For improving the cyclic stability of the $\text{La}_2\text{MgNi}_{7.5}\text{Co}_{1.5}$ alloy electrode, WANG et al[21] have studied the influence of Al substitution for Mg on structure and electrochemical properties of $\text{La}_2\text{Mg}_{1-x}\text{Al}_x\text{Ni}_{7.5}\text{Co}_{1.5}$ ($x=0.1, 0.3$ and 0.5) hydrogen storage alloy. The results show that Al substitution for Mg can improve the electrochemical cyclic stability of $\text{La}_2\text{Mg}_{1-x}\text{Al}_x\text{Ni}_{7.5}\text{Co}_{1.5}$ alloy electrode obviously. In addition, little replacement of Mg by Al ($x=0.1$) scarcely lowers the hydrogen storage capacity and the electrochemical discharge capacity of the alloy. ZHU et al[22] have studied the effects of Ni-P coatings on the electrochemical properties

of $\text{La}_2\text{MgNi}_{7.5}\text{Co}_{1.5}$ hydrogen storage alloy electrode. Their results show that the cycling stability of the electrode is also improved. However, chemical plating process to go through many working procedures can be completed, such as alloy grinding, sieving, electroless plating treatment, filtration, drying processes. This will increase the production costs of hydrogen storage alloy.

In this work, we attempt to add 0.1 g $\text{Cu}(\text{OH})_2$ to 6 mol/L KOH alkaline electrolyte, then use electro-deposition method to deposit metal Cu on the $\text{La}_2\text{Mg}_{0.9}\text{Al}_{0.1}\text{Ni}_{7.5}\text{Co}_{1.5}$ alloy electrode surface. The influence of the addition of $\text{Cu}(\text{OH})_2$ to 6 mol/L KOH alkaline electrolyte on electrochemical properties of $\text{La}_2\text{Mg}_{0.9}\text{Al}_{0.1}\text{Ni}_{7.5}\text{Co}_{1.5}$ hydrogen storage alloy electrode was investigated by electron probe X-ray microanalysis, X-ray diffraction and electrochemical measurements.

2 Experimental

$\text{La}_2\text{Mg}_{0.9}\text{Al}_{0.1}\text{Ni}_{7.5}\text{Co}_{1.5}$ alloy ingot was prepared by induction melting under Ar gas at 0.4 MPa pressure. The purity of starting elemental metals is higher than 99%. The ingot was subsequently annealed under Ar gas at 0.2 MPa and 1 123 K for 10 h. Hydride electrode was prepared by cold pressing a mixture of 0.1 g alloy powder (about 75 μm) with 0.3 g electrolytic nickel powder (about 35 μm) into a pellet of 10 mm diameter under 16 MPa pressure. Electrochemical measurements were performed at 298 K in a tri-electrode open cell. The $\text{Ni}(\text{OH})_2/\text{NiOOH}$ was adopted as the counter electrode, Hg/HgO as the reference electrode, and 6 mol/L KOH solution as electrolyte. Each hydride electrode was charged at 100 mA/g current density for 5 h. After a 10 min break, the hydride electrode was discharged at 100 mA/g. The cut-off voltage was -0.60 V vs the Hg/HgO reference electrode. The high-rate dischargeability was measured at various different discharge current densities. To investigate the structure of the alloy particles in the electrode interior after a definite number of cycles, the test electrode was prepared by cold pressing 500 mg pure alloy power under 800 MPa into a pellet of 10 mm diameter. Then the pellet was sandwiched within two foamed Ni plates (60 mm $\times$ 20 mm) with a Ni wire soldered to form a negative electrode. After a predetermined number of charging/discharging cycles (0, 20 and 40 cycles), the electrode was taken out, washed with distilled water and dried in vacuum. The experiments of X-ray powder diffraction were carried out on a D/max-3B diffractometer with Cu K_α radiation at room temperature. The microstructure of the hydride electrodes was observed electron probe X-ray microanalysis (EPMA) with JXA-8800R electron probe

microanalyzer.

3 Results and discussion

Fig.1 shows the EPMA micrographs of the $\text{La}_2\text{Mg}_{0.9}\text{Al}_{0.1}\text{Ni}_{7.5}\text{Co}_{1.5}$ alloy electrode at different cycle times with $\text{Cu}(\text{OH})_2$ added to the electrolyte. It can be seen that the hydrogen storage alloy particles are surrounded by Ni powder. After 5 charge-discharge cycles, a layer of new matter appears on the electrode surface, which is confirmed to be metal Cu by EDS analysis. Now the Cu film on the hydride electrode surface is both not smooth and not compact. The thickness and compactness of Cu film increase after 10 charge-discharge cycles. The direct contact of hydrogen storage alloy particle with the electrolyte was avoided due to the presence of copper film. The cracks in alloy particle were also observed (the 5th cycle). The result indicates that an absorption and desorption of hydrogen in hydrogen storage alloy has occurred during the charge-discharge process.

Fig.2 shows the XRD patterns of the $\text{La}_2\text{Mg}_{0.9}\text{Al}_{0.1}\text{Ni}_{7.5}\text{Co}_{1.5}$ hydride electrode without and with $\text{Cu}(\text{OH})_2$ added to the electrolyte before and after cycling. The hydrogen storage alloy for XRD analysis is derived from the inside of the alloy electrode. The characteristic peaks of Cu is not observed in the XRD patterns (Fig.2(b)), which indicates that metal copper is only coated on the surface of the hydride electrode. With increasing the number of cycles, the intensity of diffraction peaks decreases, indicating that the refinement of the crystal grains is caused by hydrogenation/dehydrogenation cycling. Moreover, the characteristic peaks of $\text{La}(\text{OH})_3$ and $\text{Mg}(\text{OH})_2$ were observed in Fig.2(a), however, the characteristic peaks of $\text{Mg}(\text{OH})_2$ are not observed in Fig.2(b). The result shows that copper film of the alloy electrode surface can keep alloy particle in the electrode interior from oxidizing availably.

Fig.3 shows the activation curves of the $\text{La}_2\text{Mg}_{0.9}\text{Al}_{0.1}\text{Ni}_{7.5}\text{Co}_{1.5}$ hydride electrode without and with $\text{Cu}(\text{OH})_2$ added to the electrolyte. It can be seen that the activation property of the hydride electrode decreases due to the addition of $\text{Cu}(\text{OH})_2$ to the electrolyte. Moreover, the first discharge capacity of the hydride electrode with the addition of $\text{Cu}(\text{OH})_2$ to the electrolyte is only 221.15 mA $\cdot$ h/g, which is obviously lower than that of the hydride electrode without addition. Fig.4 shows the charge curves of the $\text{La}_2\text{Mg}_{0.9}\text{Al}_{0.1}\text{Ni}_{7.5}\text{Co}_{1.5}$ hydride electrode with $\text{Cu}(\text{OH})_2$ added to the electrolyte. It can be seen that the first charge plateau potential is high and the plateau width is very narrow. With the

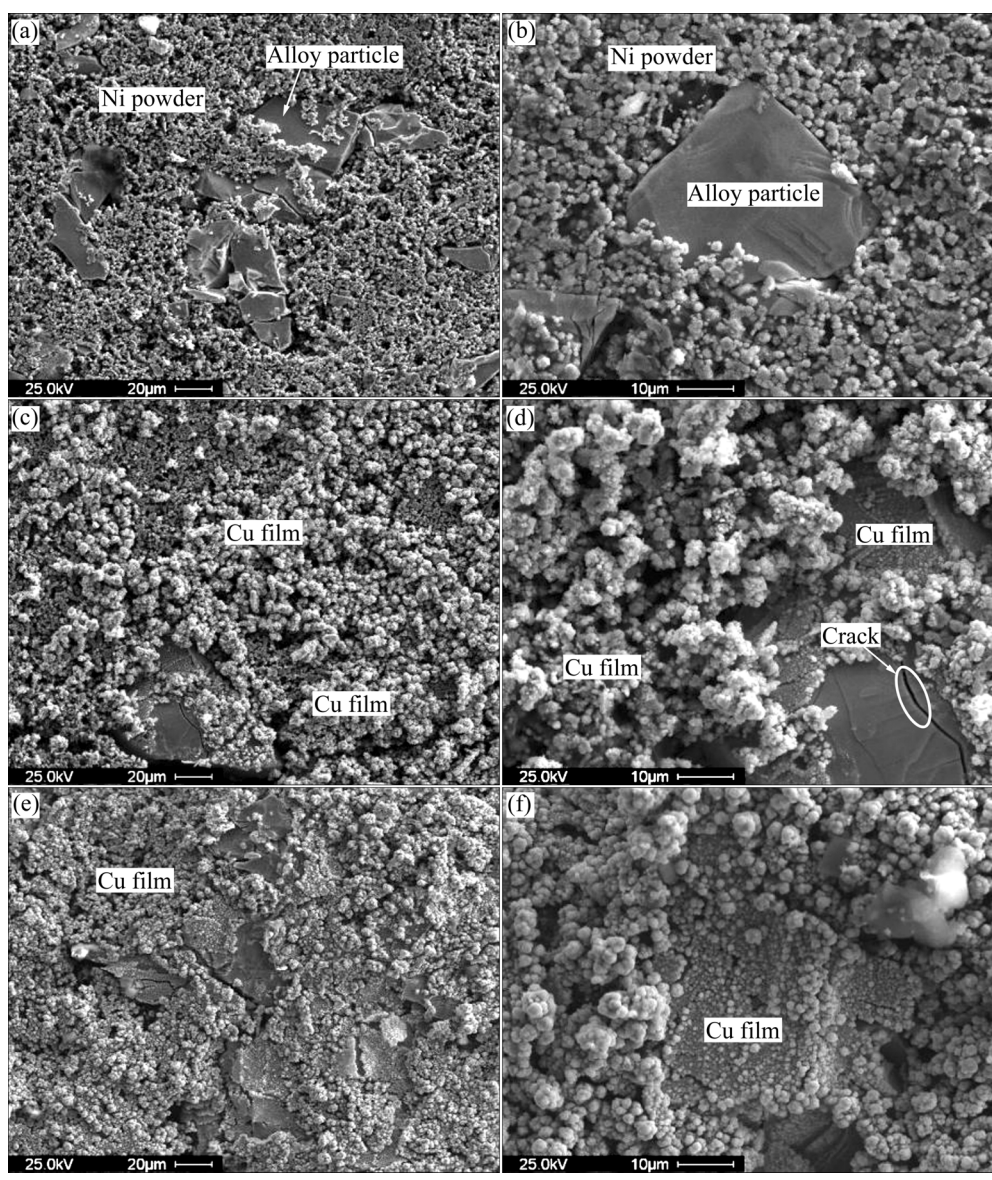


Fig.1 EPMA micrographs of $\text{La}_2\text{Mg}_{0.9}\text{Al}_{0.1}\text{Ni}_{7.5}\text{Co}_{1.5}$ alloy electrode before and after cycling with $\text{Cu}(\text{OH})_2$ added to electrolyte: (a), (b) 0 cycle; (c), (d) 5th cycle; (e), (f) 10th cycle

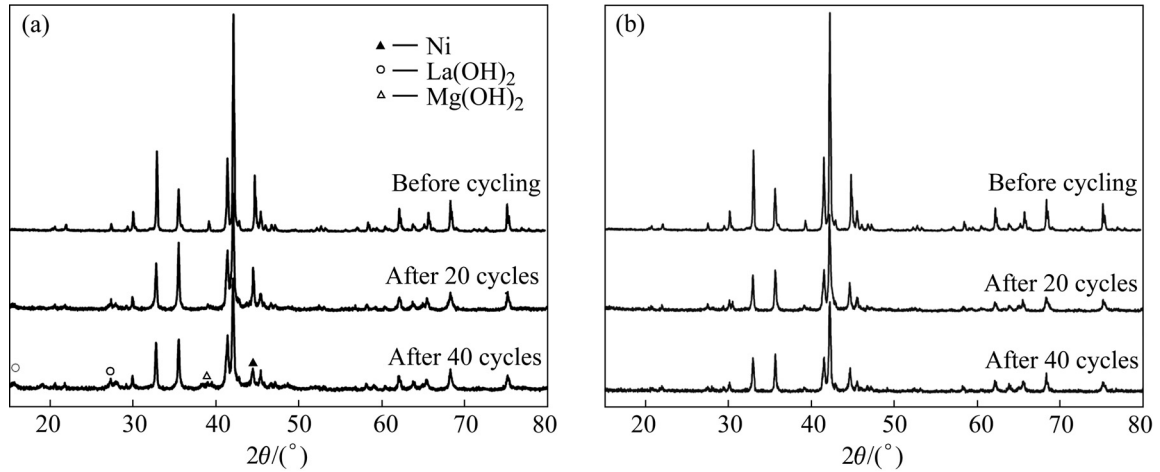


Fig.2 XRD patterns of $\text{La}_2\text{Mg}_{0.9}\text{Al}_{0.1}\text{Ni}_{7.5}\text{Co}_{1.5}$ hydride electrode without (a) and with (b) $\text{Cu}(\text{OH})_2$ added to electrolyte before and after cycling

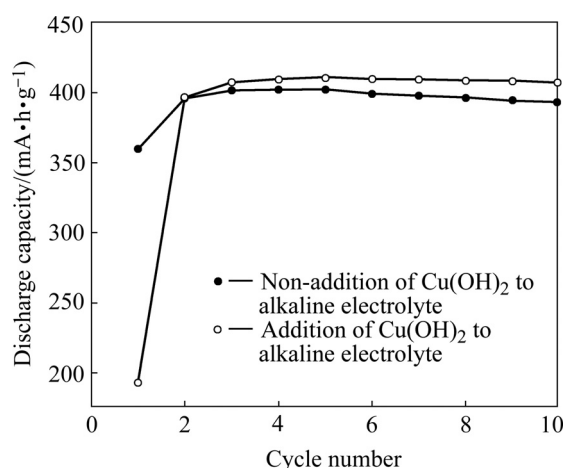


Fig.3 Activation curves of $\text{La}_2\text{Mg}_{0.9}\text{Al}_{0.1}\text{Ni}_{7.5}\text{Co}_{1.5}$ hydride electrode without and with $\text{Cu}(\text{OH})_2$ added to electrolyte

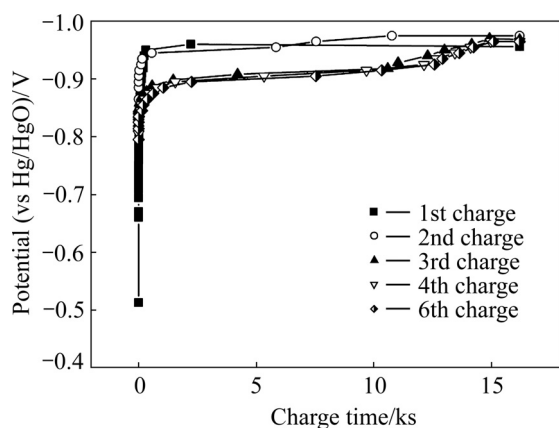


Fig.4 Charge curves of $\text{La}_2\text{Mg}_{0.9}\text{Al}_{0.1}\text{Ni}_{7.5}\text{Co}_{1.5}$ hydride electrode with $\text{Cu}(\text{OH})_2$ added to electrolyte

increment of number of charge times, the charge plateau potential gradually decreases and plateau width obviously increases.

Two electrode reactions might occur at the negative electrode with the addition of $\text{Cu}(\text{OH})_2$ to the KOH alkaline electrolyte during charging process. Namely,



EPMA results confirm that these two electrode reactions occur at the same time during earlier charging cycle. So the electricity quantity of charging don't completely supply electrode reaction (1). That is the main reason for the decrease of activation property and the first discharge capacity of the hydride electrode with the addition of $\text{Cu}(\text{OH})_2$ to the electrolyte. Electrode reaction (1) gradually becomes the main reaction at negative electrode with the increase of charging times and decrease of Cu^{2+} content in the electrolyte. The discharge capacity of the hydride electrode also increase and attain maximum value.

Fig.5 shows the discharge curves of the $\text{La}_2\text{Mg}_{0.9}\text{Al}_{0.1}\text{Ni}_{7.5}\text{Co}_{1.5}$ hydride electrode without and with $\text{Cu}(\text{OH})_2$ added to the electrolyte. It can be found that the addition $\text{Cu}(\text{OH})_2$ to the electrolyte has no negative influence on the discharge plateau potential and the maximum discharge capacity of the hydride electrode.

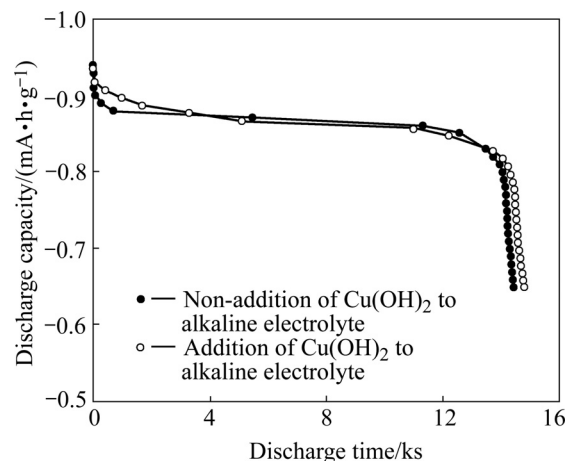


Fig.5 Discharge curves of $\text{La}_2\text{Mg}_{0.9}\text{Al}_{0.1}\text{Ni}_{7.5}\text{Co}_{1.5}$ hydride electrode without and with $\text{Cu}(\text{OH})_2$ added to electrolyte

Fig.6 shows the cycle curves of the $\text{La}_2\text{Mg}_{0.9}\text{Al}_{0.1}\text{Ni}_{7.5}\text{Co}_{1.5}$ hydride electrode without and with $\text{Cu}(\text{OH})_2$ added to the electrolyte. It can be seen that the cyclic stability of the hydride electrode is improved due to the addition of $\text{Cu}(\text{OH})_2$ to the electrolyte. For example, the discharge capacity retention (C_{120}/C_{max}) after 120 charge-discharge cycles of the hydride electrode without addition of $\text{Cu}(\text{OH})_2$ to the electrolyte is 78.53%, that of the hydride electrode with addition of $\text{Cu}(\text{OH})_2$ to the electrolyte is 82.34%. This can be attributed to the oxidation/corrosion of the hydrogen storage hydride in the electrode interior were suppressed due to the protection of the copper film.

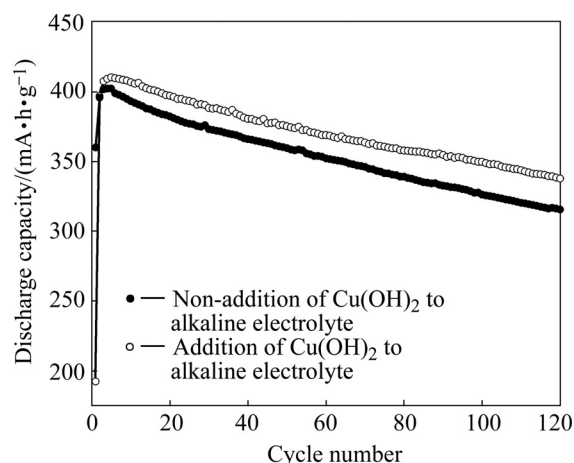


Fig.6 Cycle curves of $\text{La}_2\text{Mg}_{0.9}\text{Al}_{0.1}\text{Ni}_{7.5}\text{Co}_{1.5}$ hydride electrode without and with $\text{Cu}(\text{OH})_2$ added to electrolyte

Fig.7 shows the high-rate dischargeability of the $\text{La}_2\text{Mg}_{0.9}\text{Al}_{0.1}\text{Ni}_{7.5}\text{Co}_{1.5}$ hydride electrode without and with $\text{Cu}(\text{OH})_2$ added to the electrolyte. It can be seen that the high-rate dischargeability of the hydride electrode decreases due to the addition $\text{Cu}(\text{OH})_2$ to the electrolyte. The reason for that can be attributed to the increment of distance of H diffusion from the electrode inferior to the electrode surface due to the copper film on the electrode surface.

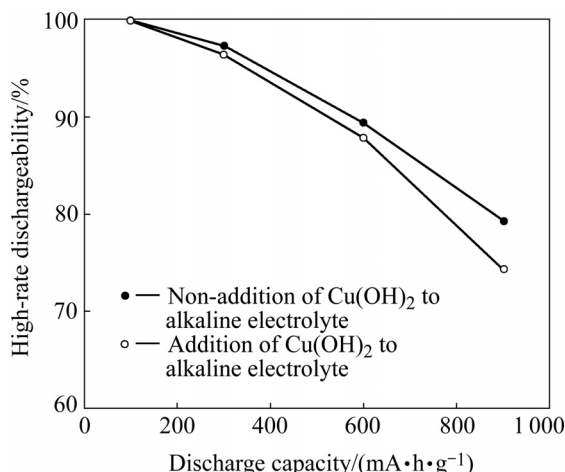


Fig.7 High-rate dischargeability of $\text{La}_2\text{Mg}_{0.9}\text{Al}_{0.1}\text{Ni}_{7.5}\text{Co}_{1.5}$ hydride electrode without and with $\text{Cu}(\text{OH})_2$ added to electrolyte

4 Conclusions

1) Metal Cu film can be formed on the hydride electrode surface by adopting electrodeposition method with the addition of $\text{Cu}(\text{OH})_2$ to the electrolyte. The thickness and compactness of Cu film increase with the increment of charge-discharge cycle. The copper film of the hydride electrode surface can keep hydride particle in the electrode interior from oxidizing available.

2) The addition of $\text{Cu}(\text{OH})_2$ to alkaline electrolyte lowers the activation property and high rate dischargeability of the $\text{La}_2\text{Mg}_{0.9}\text{Al}_{0.1}\text{Ni}_{7.5}\text{Co}_{1.5}$ hydride electrode, but has no negative effect on the maximum discharge capacity.

3) It is effective to improve the cyclic stability of the $\text{La}_2\text{Mg}_{0.9}\text{Al}_{0.1}\text{Ni}_{7.5}\text{Co}_{1.5}$ hydride electrode by utilizing electrodeposit Cu film on the electrodes surface.

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