

SHORT COMMUNICATION

Electrocatalytic activity of LaNi_{4.9}Si_{0.1}-Ni/Mo composite electrode for hydrogen evolution in alkaline solution

L. BING

Department of Applied Chemistry, Tianjin University, Tianjin 300072, China

H. WEI-KANG

Institute of New Energy Material Chemistry, Nankai University, Tianjin 300071, China

Received 15 November 1996; revised 24 February 1997

Keywords: *Metal hydride alloys, hydrogen evolution, water electrolysis***1. Introduction**

Metal hydride alloys have received wide attention due to their various applications such as in hydrogen storage, in heat pumps, as negative electrodes in nickel/metal hydride batteries, in hydrogen purification and in isotope separation. In recent years, study of the electrocatalytic activities of metal hydride alloys in alkaline solution has also attracted great interest [1–10]. Kitamura and coworkers [2–4] studied the hydrogen evolution reaction (HER) on LaNi₅, MmNi₅ etc. ingot-electrodes and found these ingot-electrodes to have highly electrocatalytic activities for hydrogen evolution, almost comparable to Pt and Pd electrodes. Hall and coworkers [5–6] also investigated the catalytic activities of the AB₅-type porous electrodes in 30 wt % KOH at 80 °C. Their experimental results indicated that the AB₅-catalysed electrodes had highly electrocatalytic properties. The NiTi and NiZr alloys also exhibited good catalytic activities for HER after surface treatments with 1 M HF aqueous solution [7–10]. However, hydrogen storage alloys easily suffered from hydrogen-caused embrittlement during cathodization due to absorbing amounts of hydrogen and lattice expansion, especially during long-term polarization under high current density. In recent years, Ni–Mo alloys have been proved to be effective as electrocatalysts for HER in alkaline solution. However, the activity for HER on the Ni–Mo alloy electrodes is easily lost during intermittent electrolysis, especially after cell short-circuiting cases for more than two weeks. The reasons for degradation may be ascribed to the oxidized dissolution of the Mo component because of a reverse current caused by the cell short circuit [17, 18]. Hydrogen storage alloys can absorb amounts of hydrogen during electrolysis and release the hydrogen reversibly when oxidation current pass through the cathode. Therefore, development of a new class of cathode, which can overcome the above defects of Ni–Mo alloys and hydrogen storage alloys, is very important. The purpose of this work was to develop a new composite electrode composed of LaNi_{4.9}Si_{0.1} hydride alloy and Ni/Mo alloy, and then evaluate its electrochemical properties such as activity for HER,

durability under long-term electrolysis and stability against cell short-circuiting situations.

2. Experimental details*2.1. Electrode structure*

To ensure that the new cathode has highly catalytic activity for HER, excellent stability against cell short circuit and durability for long-term electrolysis, a cathode with multilayer structure was designed. Figure 1 shows the schematic diagram of the cross-section of this kind cathode. The cathode consists of three main parts; Part A consists of a Ni–Mo alloy coating which provides for a fast electrochemical hydrogen evolution reaction and guarantee higher activity for HER. In addition, the Ni–Mo coating can effectively protect the inner LaNi_{4.9}Si_{0.1} alloys from hydrogen-caused embrittlement. Part B consists of hydrogen storage alloys, responsible for hydrogen absorption and desorption. In a period of short circuit, they release absorbed hydrogen by a electrochemical discharge reaction ($\text{MH}_{\text{ab}} + \text{OH}^- + \text{e}^- = \text{M} + \text{H}_2\text{O}$). Part C is a nickel foam, serving as the electrode skeleton.

2.2. Electrode preparation and electrochemical measurement

LaNi_{4.9}Si_{0.1} alloy powders as hydrogen storage alloys, which were prepared by arc melting and then mechanically pulverized, were screened to 300 mesh by passing through sieves. Before cathode preparation, the alloy particles (between 0.15–0.30 g) were first mixed with a small amount of poly(vinyl alcohol) (PVA) solution. The mixture was then pressed into a nickel foam substrate (size: 0.998 cm × 0.936 cm × 0.188 cm) and dried in air at 50–60 °C. Surface modification of the electrode was then conducted by plating a Ni–Mo alloy coating. The bath composition and deposition conditions were presented in a previous paper and a Chinese patent [11, 12].

The electrochemical measurement of the cathode was performed in a three-compartment conventional double-walled thermostat glass cell. The cathode was

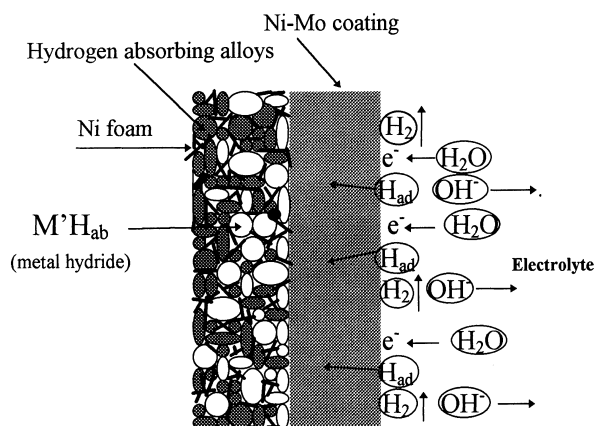


Fig. 1. Schematic diagram of the cross-section of the new cathode.

used as the work electrode. The counter electrode was a nickel foil with a large surface area. The reference electrode was of the type Hg/HgO (30 wt % KOH) and was linked to the main compartment by a Luggin capillary. The electrolyte was a 30 wt % KOH solution prepared from KOH (analytical purity) and distilled water. The hydrogen overpotential was measured by a steady-state galvanostatic method. The reversible potential for HER in 30 wt % KOH at 70 °C is -0.960 V vs the Hg/HgO electrode. During long-term electrolysis experiments, the cathode was polarized with a constant current density of 200 mA cm^{-2} at 70 °C and at certain intervals the hydrogen overpotential was measured.

3. Results and discussion

This new class of cathode is a hybrid electrode with LaNi_{4.9}Si_{0.1} hydrogen storage alloy and a Ni-Mo alloy coating. It is well known that Ni-Mo alloy electrodes have highly catalytic properties, but easily

lose activity during intermittent electrolysis. Hydrogen storage alloy electrodes have good resistance against intermittent electrolysis, but are easily pulverized. To overcome the individual drawback, a multilayer structure electrode was made as shown in Fig. 1. During electrolysis, the catalytic activity of the new cathode was determined by the Ni-Mo alloy coating on the surface. The electrocatalytic activity of electrodes mainly depends on the surface properties (not the bulk properties). After measurement, the hydrogen overpotential of the cathode at 200 mA cm^{-2} and 70 °C was about 84 mV in this work. The coating (about 12–15 μm thickness) can also effectively prevent the hydrogen embrittlement of the LaNi_{4.9}Si_{0.1} alloys under conditions of long-term continuous electrolysis at a current density of 200 mA cm^{-2} . Figure 2 shows the results obtained for the new cathode under conditions of continuous electrolysis in 30 wt % KOH at 200 mA cm^{-2} and 70 °C. The hydrogen overpotential remained between 84–86 mV after 4000 h of electrolysis and no hydrogen-caused embrittlement of the cathode was observed. This indicates that the new cathode possesses very good activity and excellent durability after long-term continuous electrolysis.

In the course of practical electrolysis, cell power shutdowns or cell short circuits, which result from maintenance or unpredicted problems may occur. Thus, to estimate this case, a short-circuiting test was carried out. During a period of short circuit, the electrolyte temperature was cooled from 70 °C to room temperature (20 °C) in 2 h. Electrolysis was then resumed and the electrolyte temperature increased to 70 °C from room temperature in 2 h. The result of the short-circuiting test is shown in Fig. 3. The activity of the new cathode remained practically unchanged after a short-circuiting test of 552 h (23 d). These results demonstrate that the new cathode not

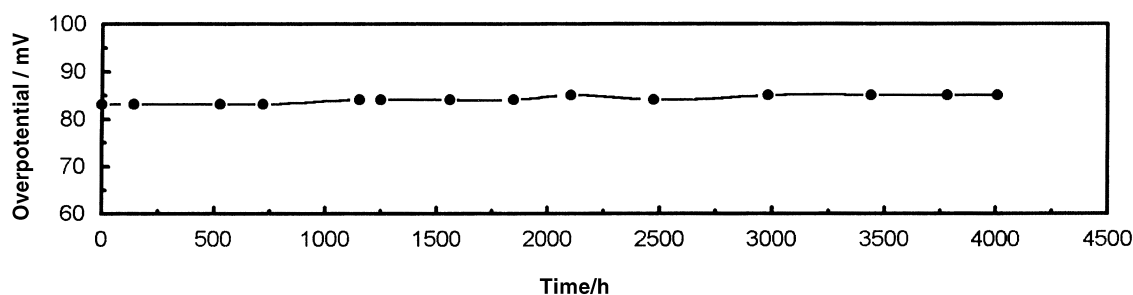


Fig. 2. Durability of the cathode during continuous electrolysis in 30 wt % KOH at 200 mA cm^{-2} and 70 °C.

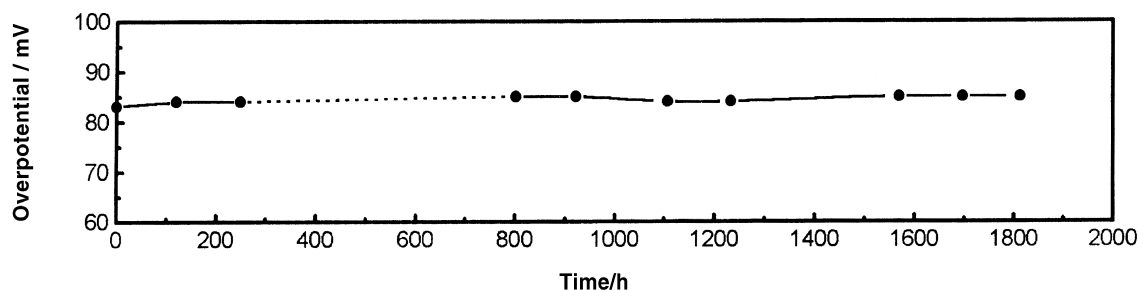
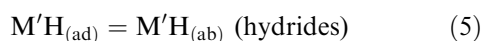
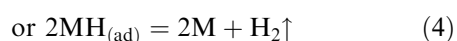
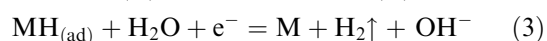
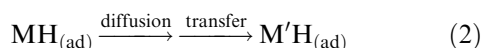
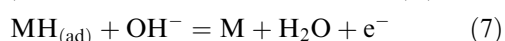
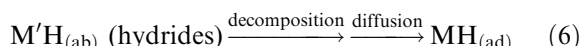


Fig. 3. The stability of the cathode during intermittent electrolysis with short-circuiting for 552 h (from 250 h to 802 h).

only had high activity for HER and durability under conditions of long-term continuous electrolysis, but also had excellent stability against short circuit for a long period. In contrast, conventional nickel-based electrocatalysts such as Raney nickel and Ni–Mo alloy electrodes were usually oxidized and deactivated after a cell short circuit of 14 d [15–19]. The reasons for the excellent stability against cell short circuit of the new cathode may be explained as follows. During cathodic polarization, the internal LaNi_{4.9}Si_{0.1} alloys can absorb the hydrogen diffused from the cathode surface where a large amount of atomic and molecular hydrogen is generated. When the cell short circuit occurs, the metal hydrides release the absorbed hydrogen and the hydrogen transports to the electrode surface by diffusion, then the hydrogen is oxidized by the reverse current caused by the short circuit through electrochemical reaction. This process is similar to the discharge process of the metal hydride electrodes in alkaline solution. The electrode reactions may be expressed as follows: During continuous electrolysis:



During power interruption shutdown:



Where M and M' represent, respectively, the Ni–Mo alloy and the LaNi_{4.9}Si_{0.1} hydrogen absorbing alloy of the electrode. MH_(ad) and M'H_(ab) denote the electrochemical adsorption of hydrogen on the electrode surface and the hydrogen absorbed by the LaNi_{4.9}Si_{0.1} alloys, respectively. Thus, the interior hydrogen storage alloys can effectively prevent the surface Ni–Mo catalyst from deteriorative oxidation by desorbing hydrogen electrochemically.

4. Conclusion

A new class of hydrogen cathode which consists of hydrogen storage alloys and Ni–Mo alloys was developed. The new cathode had not only highly catalytic activity and durability under conditions of continuous electrolysis in 30 wt % KOH at 70 °C and 200 mA cm⁻², but also excellent stability in the case of cell short circuit. The new electrode is an ideal candidate as a cathode material for alkaline water electrolysis.

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