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Transmission electron microscope studies in the surface oxide on the La-containing AB_2 metal hydride alloy

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ABSTRACT

La-addition to a Laves-phase based AB_2 metal hydride alloy improves the high-rate discharge and −40 °C charge-transfer resistance significantly. Surface oxide formation and embedded Ni inclusions of the alloy were studied using magnetic susceptibility, BET surface area and pore size measurements, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). BET measurements correlate with the double-layer capacitance measured at −40 °C, indicating a factor 3 increase in surface area with 5 at.% La replacement of Zr. Surface catalytic ability of the same alloy improves by a factor of 13. TEM reveals the surface of the La-free sample as lightly oxidized Ni, Ti, and Zr, while the La-containing sample is randomly distributed and heavily-oxidized (Ni, Cr)O_x coating the grain/oxide channel wall. These catalytic channels are believed to be the source of improvement in the low-temperature performance of these La-containing AB_2 metal hydride alloys.

1. Introduction

The nickel/metal hydride (Ni/MH) battery has been the main power source for hybrid electrical vehicles (HEV) for more than a decade. Its superior high-rate dischargeability (HRD) with safe operation [1,2] and long cycle stability [3] have been key features enabling the more than seven million HEVs on the road today. Similar to the solid-electrolyte-interface (SEI) of the Li-ion battery's anode surface contributing to its high-rate performance and cycle stability [4–8], the Ni/MH's battery has a catalytic surface oxide layer on its anode that facilitates the electrochemical electrolyte reaction. In a conventional AB_2 metal hydride (MH) alloy, the catalytic surface oxide is formed during the activation process by removing a passivated native oxide (Fig. 1a) and replacing it with a porous surface oxide incorporating both voids and metallic inclusions (Fig. 1d and e). The surface oxides on conventional AB_2 and AB_5 MH alloys were studied [9] and the results showed both are composed of three distinct layers: i) a buffer oxide layer (about 100 and 50 nm for AB_2 and AB_5, respectively) in Fig. 1c, ii) a porous oxide layer (about 200 and 100 nm for AB_2 and AB_5, respectively) in Fig. 1d, and finally iii) a surface oxide layer that is electrochemical inactive in Fig. 1e. The porous surface oxide and its metallic inclusion (mainly Ni) has been studied by TEM [9–17] and magnetic susceptibility, which was correlated to the high-power performance of the MH alloys [18]. Voids distributed in the oxide layer, especially in the form of channels, were found to improve the low-temperature performance of Cu-containing misch-metal based AB_5 MH alloys [19].

In our continuous efforts to improve the low-temperature (especially at −40 °C) performance of Laves phase based AB_2 MH alloys, La-addition provides a large decrease in both room temperature and −40 °C charge-transfer resistance, which was attributed to the increased catalytic ability in the C14 main phase [20]. However, based on X-ray energy dispersive spectroscopy (EDS) results, the C14 main phase contains a very small amount of La (<0.1 at.%). Therefore, the increase in the surface catalytic ability of La-containing MH alloys is not a direct result of the compositional change and requires further investigation. Earlier studies of incorporating La in Laves phase MH alloys indicated the formation of a LaNi secondary phase, which absorbed a large amount of hydrogen during initial activation and contributed to a large surface area through pulverization [21–25]. We confirmed the increase in the surface area with the La-incorporation from both BET and AC impedance (surface double-layer capacitance, C2) measurements (Table 1). However, the product of R4 and C2

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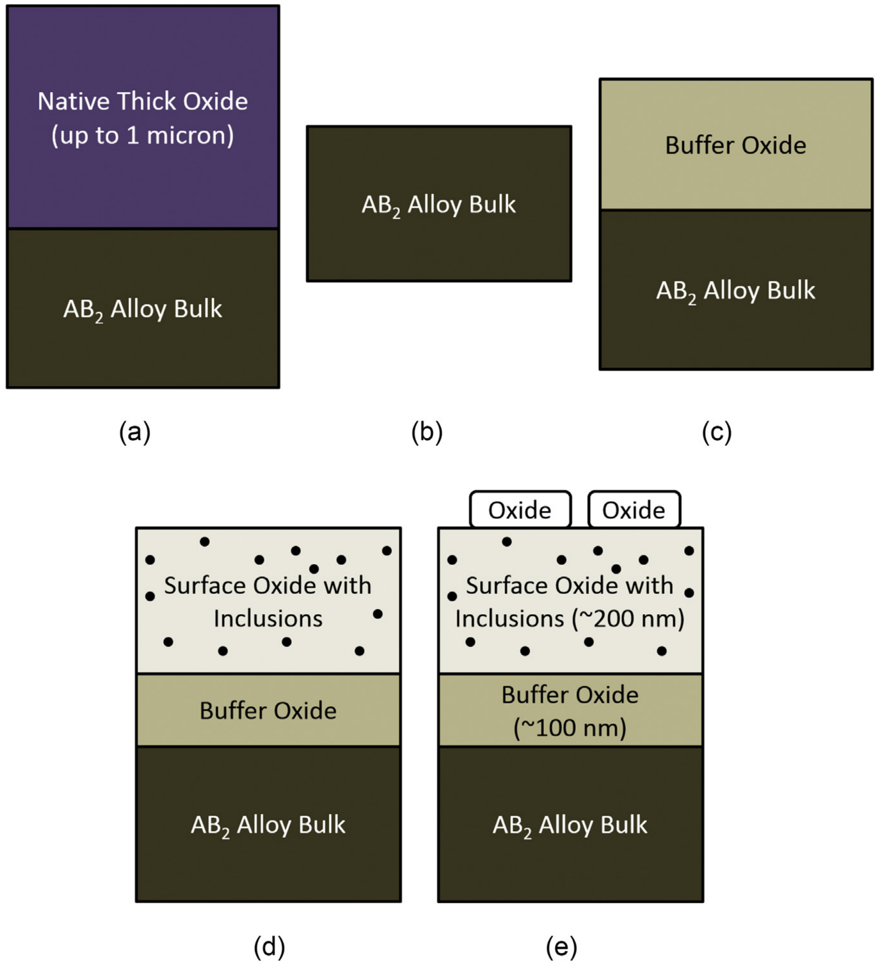

Fig. 1. Schematics of formation of surface oxide on AB_2 metal hydride alloy used as negative electrode active material in the Ni/MH battery. The surface was first covered by a native oxide formed during grinding and surface passivation (a) which was dissolved in KOH electrolyte after the cell was sealed (b); the fresh surface was first oxidized by the KOH to form a buffer oxide (c), further oxidation created a porous oxide layer with metallic inclusions embedded by precipitation, electrochemically active (d); more cycling induced oxidation promoted growth of electrochemically inert oxides on the surface (e).

(an indicator of surface catalytic ability independent of surface area [26–29]) obtained at −40 °C reduced from 28.5 to 2.1 s, which indicated that there were factors other than the increase in the surface area contributed to the improvement in the low-temperate performance of La-incorporated alloys. TEM has been extensively used to study the multi-phase nature of AB_2 MH alloys [30–34] as well as the surface oxides of conventional AB_2 and AB_5 MH alloys [9]. In this study, TEM reveals differences in the surface oxide structures of La-free and La-containing AB_2 MH alloys.

2. Experimental setup

Arc melting of the designed alloy samples was performed under a continuous argon flow with a non-consumable tungsten electrode and water-cooled copper tray. Before each run, a piece of sacrificial titanium underwent several melting–cooling cycles to reduce residual system oxygen levels. Each 12-g ingot sample was re-melted and turned over several times to ensure uniformity in chemical composition. A JEOL-*JSM6320F* scanning electron microscope (SEM) with EDS capability was used to study phase distribution and composition of the as-cast alloys. Ingots were hydrided, de-hydrided, crushed, ground, and sieved through a 200-mesh sieve. The obtained powder was etched in 100 °C 30% KOH for 4 h to emulate a lightly cycled electrode [18]. TEM analysis was done with a Philips CM200/FEG microscope. The operating voltage was 200 keV. Magnetic susceptibility was measured using a Digital Measurement Systems Model 880 vibrating sample magnetometer. BET and pore size distribution measurements were done with a Quadrasorb SI by Quantachrome.

TEM sample preparation included the following steps:

1. Mix the powders with M-Bond 610 glue and put the mixture into a 3 mm diameter copper pipe. Cure for 8 h at 150 °C.
2. Slice the copper pipe containing the glued powders into 0.5 mm thick disks using a low-speed diamond saw;
3. Polish the 3-mm-diameter disk down to about 100 μm thick using SiC media from 320 grit down to 1200 grit, then dimpling grinding;
4. Finish thinning with 5 kV ion milling (on a liquid N_2 cooled stage).
5. Insert sample into TEM to examine for electron beam transparency areas. If none are evidenced, additional ion milling time followed by TEM examination is required. This step requires