Investigation of La$_{0.8}$Ce$_{0.2}$Ni$_4$Co$_{0.4}$Mn$_{0.3}$Al$_{0.3}$ for possible use as a metal hydride fuel cell anode

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Abstract. The low-Co AB5-type La$_{0.8}$Ce$_{0.2}$Ni$_4$Co$_{0.4}$Mn$_{0.3}$Al$_{0.3}$ alloy was investigated as a potential material for a metal hydride fuel cell anode. The intermetallic compound was prepared by arc melting in argon atmosphere followed by annealing at 1223 K and hardening in cold water. According to XRD analysis, the alloy has the hexagonal CaCu5 type structure without inclusions of secondary impurities. Electrodes were prepared by cold pressing of alloy powder (20%) with carbonyl nickel (80%). Activation at 100 mA/g was almost done in 3 charge/discharge cycles. Full capacity was 340 mAh/g at current density 300 mA/g. The metal hydride electrodes demonstrate stable high rate dischargeability dropping to 317 mAh/g (-7%) at 1000 mA/g. The electrodes have shown high values of the hydrogen diffusion coefficient, with a maximum of 9×10$^{-11}$ cm$^2$/s at 10% SOC.

1. Introduction

Metal hydrides are efficient materials for the electrochemical storage of energy, they are used as anodes for Ni-MH alkaline batteries and Li-ion batteries [1]. Besides, particularly promising electrochemical applications combine the functions of the hydrogen storage medium and anode catalyst [2]. The rare-earth-based AB5-type electrodes showed good catalytic activity for hydrogen oxidation in alkaline fuel cells, and results indicated that hydrogen storage alloys can replace the expensive Pt catalyst [3]. Metal hydride fuel cells are known since the 1980s, and their advantage is that the system can be recharged in two ways: either electrochemically or by hydrogen pressure [4]. Thus, the MHFC is the fuel cell with built-in charge storage, which can operate reversibly as an electrolyzer, and hydrogen is absorbed by the metal alloy, i.e. as unitized regenerative fuel cells [5]. An MHFC was demonstrated in 320 W stacks and 500 W systems by Ovonic Fuel Cell Company [2].

LaNi$_5$-type materials are mainly used as anodes of Ni-MH batteries, they are effective, though their intrinsic capacity is restricted to 300 mAh/g [1]. Anode materials for metal hydride fuel cells and hybrid batteries are also generally chosen from the LaNi$_5$ family [4, 6-13]. It was found, that LaNi$_5$ is too unstable and too corrosion sensitive for use as a battery electrode, and La is often substituted by mischmetal (Mm), while the B component remains primarily Ni, but is substituted in part with Co, Mn, Al, etc. [3]. Published compounds include: Ml(NiCoMnCu)$_5$ [6] (Ml – La-rich mischmetal),
MmNi$_{3.5}$Co$_{0.7}$Al$_{0.7}$Mn$_{0.1}$ [7], LmNi$_{4.1}$Co$_{0.4}$Mn$_{0.4}$Al$_{0.3}$ (Lm – La-based mischmetal) [9], MlNi$_{3.6}$Ce$_{0.85}$Al$_{0.15}$Mn$_{1.8}$ [10], MmNi$_{3.38}$Co$_{0.85}$Mn$_{0.39}$Al$_{0.4}$ [11].

We chose La$_{0.8}$Co$_{0.2}$Ni$_{0.4}$Mn$_{0.3}$Al$_{0.3}$ as a possible anode material by a notion to increase stability and cycle life of the electrode, keeping electrochemical capacity and activity. The addition of Ce is known to increase corrosion stability in the presence of KOH aqueous solution, moreover, Ce increases cyclic stability for the gas phase reaction [14]. For the use in electrochemical applications AB5 alloys usually contain Co, which is the key element to maintain cycle life materials, but it greatly increases the total cost of the alloy. Partial or complete substitution of Co by cheaper metals, such as Fe, Mn, Al, etc. to reduce material cost is investigated widely [15-19]. Aluminum is widely used because it is a thermodynamically stable and anti-corrosion element, though it slows the charge transfer process that was shown by the recent comprehensive investigation on low-Al alloys [20].

In the present work, to create a useful low-Co AB5-type anode material La$_{0.8}$Co$_{0.2}$Ni$_{0.4}$Mn$_{0.3}$Al$_{0.3}$ for a metal hydride fuel cell, we investigated hydrogen diffusion, electrode discharge performance, and cyclic stability of electrodes.

2. Experiment

Laboratory 50 g samples of intermetallic compounds were prepared by arc melting in an argon atmosphere from commercial source materials La (99.9%), Ce (99.5%), Ni (99.95%), Co (99.5%), Al (99.9%) and Mn (99.9%) in a stoichiometric composition. To compensate evaporation, ca. 2% was added to the calculated weight of Al and Mn. The mixture was melted three times to ensure homogeneity of the final composition, and the samples were annealed at 1223 K for 20 hours and hardened in cold water. The loss of the mass was less than 0.5% comparing to the initial mixture. Structure and phase composition of the samples were checked by X-ray diffraction (XRD) using D8 Advance (Bruker) diffractometer with Cu K-alpha radiation. Samples for XRD analysis were prepared by mechanical grinding to a fine powder. Angles 2θ were scanned within 0.02° and the exposition time of 1 s. Diffractograms were analyzed by Jana2006 and Crystal Impact Match software using JCPDS PDF-2 Data Base.

Metal hydride electrodes were prepared by mixing of a 40-60 μm intermetallic powder fraction with a mean particle size of 50 μm (20%) and carbonyl nickel (80%) powder followed by a cold pressing at 25 MPa into pellets 10 mm in diameter. The pellets were placed between two nickel foam plates and connected to current collectors. Measurements were performed at ambient temperature (ca. 20°C) in a conventional three-electrode open-air cell coupled directly with Potentiostat P-40X and controlled by ES8 software (Electrochemical Instruments). A high capacity Ni(OH)$_2$ counter electrode and a Hg/HgO reference electrodes were used. The electrolyte was a KOH (6 M) aqueous solution without any stirring and flow.

Activation of the MH electrodes was performed by charging and discharging of the electrodes at 100 mA/g during 10-20 cycles to cut-off discharge potential of 0.6 V.

Hydrogen diffusion was measured by potentiostatic intermittent titration technique (PITT) [21, 22]. Electrode discharge performance at current densities from 100 to 1000 mA/g and cyclic stability at 300 mA/g (1C) current density were also measured. Measurements were performed using different samples to exclude the influence of charge/discharge history.

3. Results and discussion

The results of XRD have demonstrated that the alloy samples have the hexagonal CaCu5 type structure. Unit cell parameters are $a = 5.029$ Å, $c = 4.042$ Å, $c/a = 0.804$, $V = 88.5$ Å$^3$. There were no observable impurities.

The activation of the electrodes was almost complete in 3-10 cycles. Figure 1 (inside graph) shows the evolution of the discharge curves of one electrode for the first 10 cycles. The electrode capacity was within 328–339 mAh/g (within 3%) for the 3rd cycle, and discharge potential at SOC=50% was $-E = 0.877$ V for the 4th cycle and $-E = 0.883$ V for the 10th cycle (within 0.7%). In our opinion, fast
activation can be contributed to the initial preparation of the alloy powder and high activation current density. Besides, the studied electrodes show good cyclic stability. Figure 1 (outside graph) shows 1C (300 mA/g) cyclic stability of an electrode. At high current density, the electrode was activated faster, and after 50 cycles the discharge capacity reached 92% of the maximum capacity.

Figure 1. Activation and cyclic stability of the MH electrodes. Inside: activation discharge curves at 100 mA/g for one electrode. Outside: 1C (300 mA/g) cyclic stability for another electrode.

The hydrogen diffusion coefficient shows a decrease as far as the alloy is saturated with hydrogen from $9 \times 10^{-11}$ to $2 \times 10^{-13}$ cm$^2$/s (Figure 2). Meanwhile, there is some kink at 40% SOC. Obviously, this kink is associated with the transition of $\alpha$-H solid solution to the $\beta$-hydride phase. Such behavior is typical for many intermetallic compounds.

Metal hydride electrodes demonstrate high performance at different current densities. High rate dischargeability is presented in Figure 3. Electrode capacity at 300 mA/g is 340 mAh/g, and only slightly decreases to 317 mAh/g (-7%); 303 mAh/g (-11%) for electrode potentials of -0.5 V and -0.6 V, respectively. Performance measured on different electrodes was within 5%.

Our results on $La_{0.8}Ce_{0.2}Ni_4Co_{0.4}Mn_{0.3}Al_{0.3}$ are comparable to other investigations with AB5-type electrodes (see e.g. a survey of low-temperature and high-power electrochemical properties of MH electrode [20]). Decreased concentration of Co in favor of other metals, for example, Fe, could lead to slow activation [23]. In our case, the high activation current densities and preparation of initial alloy powder result in the fast activation of the electrodes. Our results on the diffusion coefficient show the same behavior as the results measured by the galvanostatic intermittent titration technique (GITT) [24] and chronopotentiometric experiments and chronoamperometry [25].

Further investigations will include use of $La_{0.8}Ce_{0.2}Ni_4Co_{0.4}Mn_{0.3}Al_{0.3}$ both as anode and hydrogen storage material for an MH fuel cell with intrinsic hydrogen storage ability. Indeed, new materials with larger capacity and cyclic performance will be investigated, for example, costly rare-earths can be partially replaced by additions of magnesium [1]. The AB5-type anode could be a good reference point for further development of MH fuel cells with the use of other metal hydrides as anode materials.
**Figure 2.** Hydrogen diffusion coefficient at different states of charge.

**Figure 3.** High rate dischargeability of the electrodes. Outside: discharge curves for current densities from 100 to 1000 mA/g. Inside: Capacity at -0.6 V and electrode potential for SOC = 50%.
### Conclusions

AB5-type alloy \( \text{La}_{0.8}\text{Ce}_{0.2}\text{Ni}_{4}\text{Co}_{0.4}\text{Mn}_{0.3}\text{Al}_{0.3} \) was investigated as a potential anode material for an MH fuel cell. Our investigations have shown the following:

- electrodes prepared by the cold pressing of alloy powder (40-60 μm) and carbonyl nickel (20%/80%) have shown good activation characteristics at high current densities (>100 mA/g);
- the low-Co alloy has a capacity of 340 mAh/g at current density 300 mA/g, and shows good HRD and adequate cycle life, which is very important for high-power devices;
- the electrodes have high values of the hydrogen diffusion coefficient (9×10−11 cm²/s at 10% SOC).

The investigated alloy can be used as an anode material for metal hydride fuel cells.

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