



An electrochemical investigation of sintered thick metal hydride electrodes for oxygen-metal hydride semi-fuel cell applications

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Abstract

Based on a conventional pasting method, a sintering process was applied to fabricate thick metal hydride electrodes for oxygen-metal hydride semi-fuel cell. It was found that, after sintering, the activation and the high-rate dischargeability of the electrodes are greatly improved. The sintering parameters were optimized by measuring the electrochemical properties of the metal hydride electrode sintered in the temperature range 650–900 °C for 10–60 min under mixed argon and hydrogen gases. It was found that to make a thick metal hydride electrode, the use of perforated copper foil as a current collector is better than using perforated nickel strip and copper mesh. A new type of structure is designed for the thick metal hydride electrode, that is, by folding the perforated foil that had been prepasted with active materials into a sandwich structure. This fold-type sandwich electrode was further clamped and held together by copper mesh.

1. Introduction

The 'Partnership for a New Generation of Vehicles' (PNGV), a US government auto industry partnership initiated in 1996, has suggested that hybrid-electric vehicles (HEVs) could be the leading candidate to meet their goals of tripling auto fuel economy in the next decade [1, 2]. To realize this goal, lightweight, compact, high-power batteries or fuel cells are required. An air-metal hydride (Air-MH) semi-fuel cell for electric vehicles was developed in the Helsinki University of Technology [3,4]. The energy density of the Air-MH semi-fuel cell has already reached the level of Li-ion rechargeable batteries, exceeding conventional Ni-MH batteries [5, 6]. The main difference between this air-metal hydride semi-fuel cell from the existing Ni-MH alkaline cells was the replacement of the nickel electrode with an air gas diffusion electrode. In addition, since the commercially available thin MH electrode for Ni-MH batteries was 0.4–0.7 mm in thickness, it is not directly suitable for application in the Air-MH semi-fuel cells. For up-scale semi-fuel cells in the fields of electric vehicle application design of thick metal hydride electrodes (2–5 mm) is needed to match the relative oxygen gas diffusion electrode. However, the high power output of semi-fuel cells is limited by the increasing thickness of the metal hydride electrode. Thus, improvements in the high power output of thick MH electrodes were investigated in the present work.

During the development of high performance hydrogen storage alloys used as active materials for a negative electrode of Air-MH semi-fuel cells, considerable attention has been paid to improving the high-rate dischargeability of metal hydride electrodes. The rate-dischargeability of the MH electrode depends not only on the intrinsic properties of the hydrogen storage alloy powder, but also strongly on the manufacturing method [7], especially for thick electrodes. A process for producing a hydrogen storage alloy electrode for metal hydride alkaline batteries comprises the steps of mixing the hydrogen storage alloy powder with a binder and other ingredients to obtain a paste, scrubbing it into a current collector with the paste and solidifying the paste by low temperature heating. This process is known as the 'paste process'. However, due to the presence of binder between particles of the hydrogen storage alloy within the electrode this process has resulted in deterioration of the high-rate discharge characteristics of the electrode [8, 9]. To solve the problem, a sintering process has been developed, which has extensively been used in mass production [10]. Nevertheless, it is very difficult to sinter the hydrogen storage alloy particles, since oxidation of hydrogen storage rare earth elements in the AB₅-type mischmetal-based hydrogen storage alloy electrode may easily occur under high sintering temperature. For a thick MH electrodes, malleability is very important because of expansion and contraction of the negative electrodes during charge-discharge cycling. Packaging

becomes vital for the stability of large size electrode systems.

In this study, a new sintering technology for fabricating metal hydride electrodes has been investigated. The effect of sintering parameters on the electrochemical properties of a sintered MH electrodes has been characterized. Based on the experimental results, an advanced design concept of thick metal hydride electrodes employing the porous metal substrate as a current collector with high powder density for semi-fuel cell applications is presented.

2. Experimental details

2.1. Electrode preparation

The hydrogen storage alloy powder chosen for this study was $M\text{Ni}_{3.6}\text{Co}_{0.7}\text{Mn}_{0.3}\text{Al}_{0.4}$ (Lanthanum-rich mischmetal $M\text{l} = \text{La}_{0.58}\text{Ce}_{0.29}\text{Nd}_{0.08}\text{Pr}_{0.05}$) purchased from Höganäs AB (Sweden Company). This alloy powder was synthesized first by conventionally induction melting and then by argon gas-atomization. Argon gas-atomized (AGA) powder particles have a spherical shape and exhibit different properties compared to conventional induction melting (CIM) powder [11].

This Ar gas-atomized alloy powder was mixed with fine nickel powder, Inco T-210 (Inco Ltd, Canada: average particle size 0.5–1.0 μm , specific surface area, 1.5–2.5 $\text{m}^2 \text{g}^{-1}$) within a cylindrical stainless grinding chamber by ball milling. The resulting mixtures were pasted onto different metal substrates: nickel foam, perforated nickel strip, copper mesh and perforated copper foil. Two electrode sizes were made: thin MH electrodes using nickel foam as a current collector (10 mm width, 10 mm length, 0.7 mm thick) for measurements of cycle lifetime and thick MH electrodes (20 mm width, 30 mm length, 2 and 5 mm thick) using other metal substrates, except nickel foam, for measuring of the discharge capacity of the practical MH electrode.

2.2. Sintering technology

After pressing into sheets and drying, the prepared electrodes were placed in a tubular furnace and sintered under flow of argon–hydrogen (99/1). Sintering was carried out for various times at temperatures between 650 °C and 900 °C. From the electrochemical properties of the sintered MH electrodes, the optimum sintering technology was determined.

2.3. Structure of thick electrodes

Based on comparative experimental results of porous metal substrates, a current collector of perforated copper foil was chosen for designing a thick metal hydride electrode. A new fold-type structure electrode, employing a multilayer current collector, was developed.

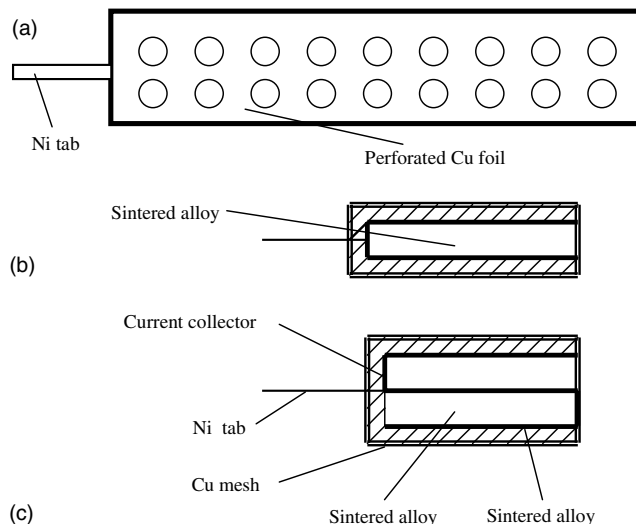


Fig. 1. Stages in making fold-type structure electrode employing multiplayer porous metal as current collector. (a) Perforated Cu foil, (b) fold-structure of sintered MH electrode with bilayer current collector, and (c) fold-structure of sintered MH electrode with trilayer current collector.

It allows assembly of plates of different heights and active mass contents.

Figure 1 shows the fold-type structure for a thick metal hydride electrode. A slurry containing active material and additives was pasted onto the porous metal substrate. Thicker electrodes were obtained by folding. The sandwiched produced is held together by means of clamping copper mesh; connections of nickel plate are used.

2.4. Electrochemical measurements

The electrodes were investigated by using an electrochemical charge–discharge method in a triple-electrode open cell. A mercury/mercury oxide electrode (Hg/HgO) was used as a reference electrode and $\text{Ni}(\text{OH})_2/\text{NiOOH}$ as a counter electrode in a 6 M KOH solution. A multiwrap separator similar to that of a commercial cell was used. This was made of a Nylon nonwoven material. Sufficient excess electrolyte was present for flooded conditions. Test conditions included a charge current rate and discharge rate. The cycle life of small sized electrode measurements was determined using a computer-controlled battery cycling. The cut-off discharge potential was fixed at -0.6 V with respect to the Hg/HgO reference electrode. The rate capacity of the electrode was also investigated by measuring the discharge capacity at the various discharge currents. The rate capacity of a thicker electrode was normalized with respect to a specific areas.

3. Results and discussion

3.1. Effect of sintering parameters on the electrochemical properties of thin MH electrode

Figure 2 shows the initial discharge capacity of thin sintered metal hydride electrodes as a function of

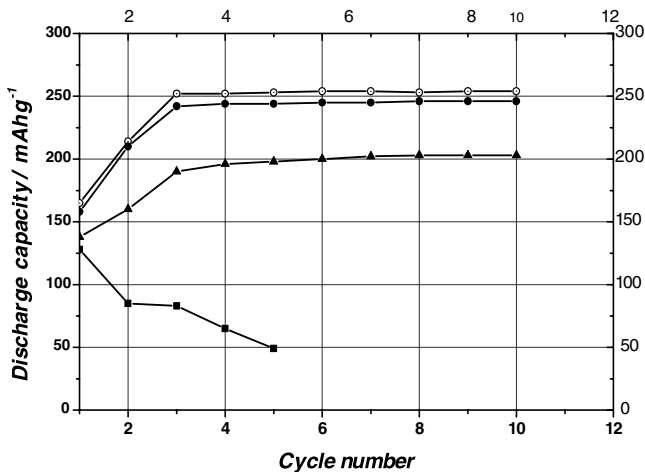


Fig. 2. Dependence of the initial discharge capacity of the thin sintered MH electrode on different sintering temperatures. Key: (▲) 650, (○) 700, (●) 800 and (■) 900 °C.

sintering temperature. As the sintering temperature increases from 650 °C to 700 °C, the initial discharge capacity of thin MH electrode increases until it reaches its maximum. However, for sintering at 900 °C, initial discharge capacity decreases again. Obviously an optimum sintering temperature (700 °C) exists for the maximum discharge capacity.

The change in particle morphology occurring during the sintering process of metal hydride powders is initially characterized by considerable neck growth between adjacent particles and by significant decrease in total surface area. After sintering at 900 °C the MH electrode is seen to be covered with an oxide film on the surface of the hydrogen storage alloy. Thus, a electron transfer reaction of sintered electrode alloys depends strongly on oxide-coverage, not on the hydride electrode itself. As known, the electron transfer of film-covered electrodes is controlled by the film thickness. For an oxide-covered alloy electrode, the exchange current

density decreases strongly and even approximately exponentially with increasing oxide film thickness [12, 13]. At higher sintering temperature the oxide films become thicker and act then as a barrier for electron transfer. As a consequence, the measured discharge capacity of a MH electrode sintered at higher temperatures is poor. In a lower sintering temperature, the film is sufficiently thin so that electron can be exchanged with the underlying alloy itself. However, for the sintering temperature of 650 °C sintering is insufficient so that the discharge capacity of the sintered MH remains lower.

The gas atomized powder alloy electrode prepared by sintering needs only a few additional activation steps unlike the MH electrode produced by traditional pasting technology, which is advantageous in application. This is because the energy change inside the gas-atomized alloy powder before and after hydriding is the main factor controlling electrochemical activation processes while the surface oxide layer has a minor effect [11].

The effect of sintering time on the cycle life of metal hydride electrode alloys sintered at 700 °C is shown in Figure 3. With increasing sintering time the maximum capacity of the sintered MH electrode decreased. For the shortest sintering time densification was very limited and behavior capacity lower than expected. It is also seen that the discharge capacity slowly decreased with increasing cycle numbers. This is caused by partial breakage during charge–discharge cycling. Therefore, the stability of a sintered MH electrode should be improved.

It is known that Co and/or Ni additives are currently used by battery manufacturers to enhance the electronic conductivity of active material [14, 15]. To investigate the effect of additives on the discharge capacity of sintered alloy, Co and Ni additives were added. Figure 4 shows the dependence of the discharge capacity of the sintered MH electrode containing different ratios of Co and Ni as a function of the cycle number for a thin

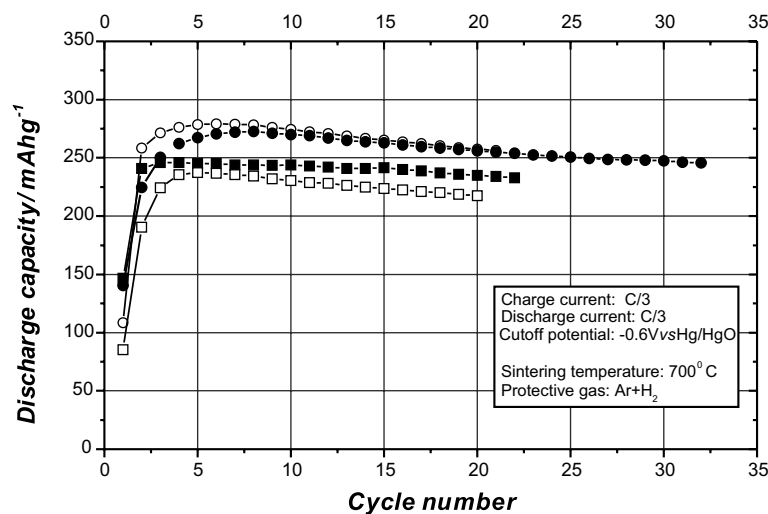


Fig. 3. Effect of sintering time at the sintering temperature of 700 °C on the cycle life of the thin sintered metal hydride electrode. Key: (○) 10, (●) 20, (■) 30 and (□) 60 min.

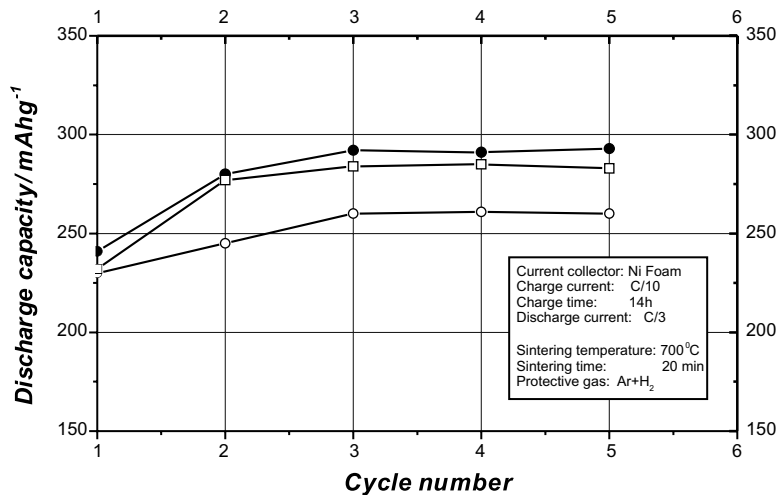


Fig. 4. Dependence of discharge capacity on the cycle number for the thin sintered MH electrode containing different ratios of Co and Ni powder. Key: (○) alloy 90%, Ni 10%; (●) alloy 85%, Ni 10%, Co 5%; (□) alloy 90%, Co 10%.

sintered MH electrode. As seen in Figure 4, suitable cobalt additions onto sintered MH electrodes can improve its discharge capacity. The improvement of discharge capacity is caused by selective formation and dissolution of a surface oxide scale on the alloy surface. Such oxide formation and dissolution decreases the corrosion rate of RE and improves the electrochemical catalytic ability and electrochemical stability of the electrode. After selective dissolution, a porous electrocatalytically active Ni layer remains on the electrode surface.

Figure 5 shows the rate-capacity change of a thin MH electrode containing Co and Ni powder additions and using a current collector of nickel foam at a discharge current density of 0.2 C and 1 C, 3 C and 5 C after three activation cycles. The rate-capacity of the sintered alloy electrode is better than that of an electrode obtained by the paste process.

However, all additions of Ni and Co onto the sintered alloy particles may not endure long charge-discharge cycling in a strong alkaline solution. Thus, one should instead consider that the conductivity of the negative electrode can be increased by increasing the conductivity of the metal substrate of the negative electrode in order to improve the high-rate-dischargeability of MH electrodes.

3.2. Selection of suitable current collector for thick sintered MH electrode

Although powder-sintered thin metal hydride electrodes with a nickel foam collector has a better rate-capacity than that of pasted electrodes, it is difficult to fabricate a thick electrode for electric vehicle battery/fuel-cell application because of the lower bending strength of nickel foam. Therefore, other current col-

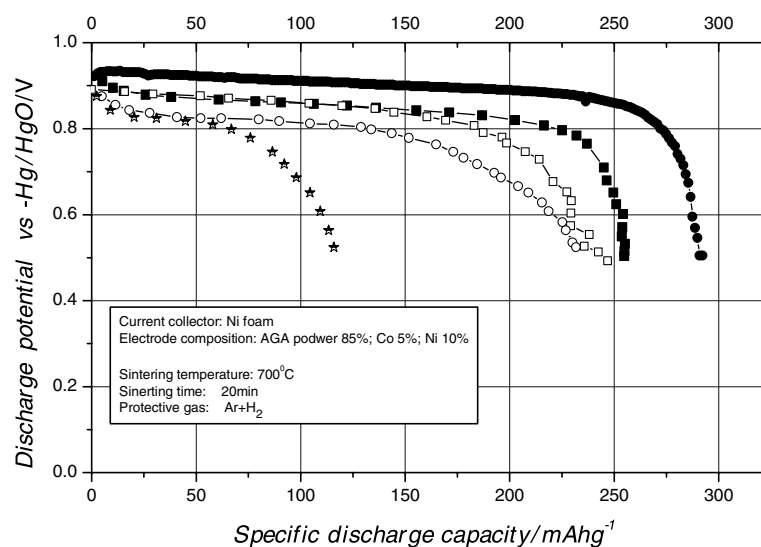


Fig. 5. Discharge potential of the thin MH electrode as a function of the rate-capacity for different discharge rates. Key: (●) 0.2 C, sintered MH; (■) 1 C, sintered MH; (□) 3 C, sintered MH; (○) 5 C, sintered MH; (☆) 5 C, pasted MH.

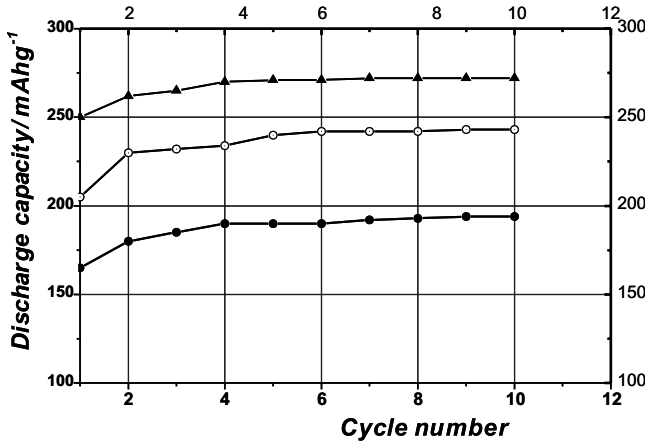


Fig. 6. Specific discharge capacity of sintered Ar-gas-atomized-powder electrodes with current collector of different porous metals. Key: (▲) perforated Cu foil; (○) Cu mesh; (●) perforated Ni strip.

lectors were considered. Generally, the porous metal substrate used for the negative electrode is a mesh, grid and foil. Figure 6 illustrates the electrochemical properties of sintered Ar-gas-atomized-powder electrodes with the different porous metals as current collector.

As can be seen from Figure 6, the initial capacity of a sintered alloy electrode using a different current collector increased in the following order: perforated nickel strip < copper mesh < perforated copper foil. Using copper to form the porous metal substrate of the negative electrode has several advantages. Copper is an excellent electrical collector. Hence its use as a substrate material decreases the resistance of the negative electrode. A considerable amount of battery power is wasted by internal dissipation, and thereby provides a MH electrode with increased output power. The copper substrate does not suffer from corrosion during normal charge–discharge cycling of the metal hydride electrode. This is because the operating potential of a sintered MH electrode (-0.85 V) is lower than the copper dissolution potential of about -0.4 V (for a pH of about 14). At the appropriate operating conditions, a copper substrate in contact with metal hydride active material is cathodically protected under the full range of operating conditions for MH electrodes. Copper is also a malleable metal. Malleability is very important because of the expansion and contraction of the negative electrodes during charge-discharge cycling of the metal hydride electrode. The increased deformability of the substrate helps prevent electrode breakage as a result of the expansion and contraction, thereby resulting in improved electrode reliability.

Based on the considerations and our experimental results, a novel electrode structure for electric vehicle application, which was composed of a stacking fold-type structure of thick metal hydride composite electrode employing multilayer copper foil as a current collector, was designed.

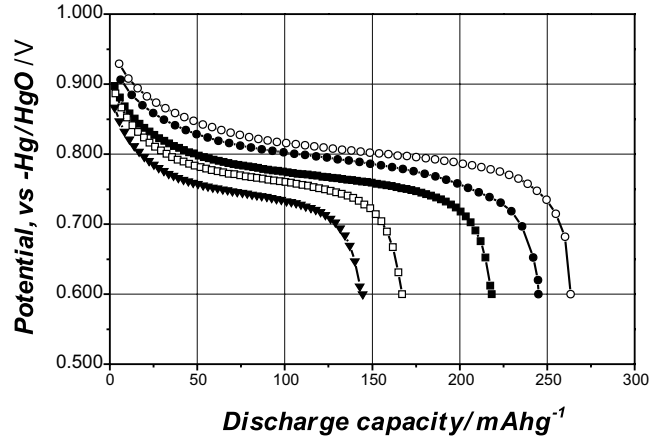


Fig. 7. Rate-capacity change of a sintered MH alloy electrode (2 mm thick) containing the bilayer current collector of perforated copper foil for different discharge currents. Key: (○) 300, (●) 600, (■) 1000, (□) 1200 and (▼) 1500 mA cm^{-2} .

3.3. Electrochemical properties of thick MH electrode employing bilayer current collector

Figure 7 shows the rate-capacity change of a thick sintered MH alloy electrode (2 mm in thickness) containing the bilayer current collector of perforated copper foil at discharge current density of 300, 600, 1200, 1500 and 1800 mA cm^{-2} after three cycles.

In Figure 7, the discharge potentials of thick sintered MH electrodes varied gradually at end-of-discharge state for the higher discharge rate. Increasing the discharge rate the rate of charge-transfer reaction increases, but there are sufficient charges (hydrogen) left in the electrode even at the end-of-discharge state because the diffusion rate of atomic hydrogen from the bulk to the surface of the MH particles is slower than the charge transfer reaction on the surface of the particle. Therefore the potential varied gradually. For the lower discharge rate, at the end-of-discharge (cut-off voltage of -0.5 V) the hydrogen concentration within the electrode and on the electrode/electrolyte interface almost reaches a value close to zero because atomic hydrogen has enough time to diffuse, which causes the electrode potential to be changed rapidly to more positive values [16]. As a consequence, the use of perforated copper foil as substrate material for a sintered MH electrode increased its specific power density.

3.4. Electrochemical properties of thicker composite MH electrode employing trilayer current collector

Figure 8 shows the rate-capacity change of a thicker sintered MH composite electrode (5mm in thickness) containing the trilayer current collector of perforated copper foil at discharge current density of 300 and 600, 1000, 1200 and 1500 mA cm^{-2} after three activation cycles.

The discharge capacity of the folded electrode exhibits the better rate-capacity from 300 to 1500 mA cm^{-2} . This

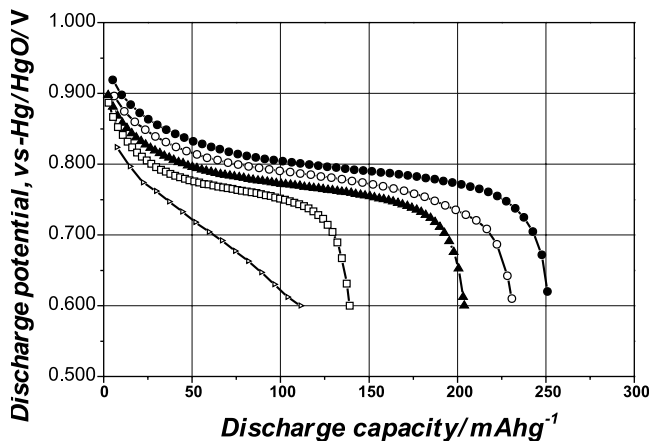


Fig. 8. Rate-capacity change of sintered MH composite electrode (5 mm thick) with the trilayer current collector of perforated copper foil for various discharge currents. Key: (●) 300, (○) 600, (▲) 1000, (□) 1200 and (△) 1500 mA cm⁻².

may be explained by the better heat dissipation of thicker composite MH electrodes. The main advantage of copper lies in its high thermal conductivity.

Using a copper substrate can easily eliminate excess heat generated during charge and discharge of the system and reduce the thermal runaway. The fold-type structure electrode has a better temperature distribution than other structures because of the current collectors, which are formed at each end of the electrode in stack structure. This advantage is suitable for large scale fuel cells or batteries. Further, the cell design on heat evolution using thermal simulation and experimental tests is needed much consideration [16–18]. A fundamental study of the heat transfer phenomena and electrochemical process is still under investigation.

4. Conclusions

The electrochemical properties of sintered hydrogen storage alloy electrodes were investigated. In this work, the following experimental results have been obtained:

- (i) For sintering of a AGA hydrogen storage alloy powdered-electrode, optimum sintering conditions are at 700–800 °C for 10–20 min.
- (ii) The activation and high-rate dischargeability of a sintered hydride electrode is improved compared to that obtained with the conventional pasting process.
- (iii) Using copper as porous metal substrate of negative electrode decreases the resistance of the negative electrode and thereby provides a MH electrode with increased output power. Copper

substrate malleability also allows the substrate to more reliably hold the active hydrogen storage material that is pressed onto the substrate surface.

- (iv) Fold-type structure electrodes have a better temperature distribution than other structures because of their current collectors, which are formed at each end of the electrode in a stack structure. This design is suitable for large scale fuel cells/batteries without accumulating heat in charge-discharge processes.

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