ELSEVIER

Technical Communication

Influence of air electrode electrocatalysts on performance of air-MH cells

M.V. Ananth[a,*], K. Manimaran[a], I. Arul Raj[b], N. Sureka[c]

[a]Ni-MH Section, Electrochemical Energy Sources Division, Central Electrochemical Research Institute, Karaikudi 630 006, India
[b]Fuel Cells Section, Electrochemical Energy Sources Division, Central Electrochemical Research Institute, Karaikudi 630 006, India
[c]Department of Chemistry, P.S.G.R. Krishnammal College for Women, Coimbatore 641 004, India

Abstract

Ni-MH battery system has been in limelight recently because of its inherent advantages like high-energy density, eco-friendly nature, devoid of memory effect, etc. Replacement of the heavy nickel oxide electrode with lighter air electrode is expected to improve its energy density further by 20% and also to bring down the cost. Hence some studies have appeared in literature on the development of air-MH system. But the main problem is to have an adequate bifunctional electrode with suitable electrocatalyst. Several materials are available for use in air electrodes. A detailed study is required to identify the best catalytic material and optimize the battery activity. Hence, air-MH cells using different oxides like Ag_2O, $LaMnO_3$ and $La_{0.65}Sr_{0.30}MnO_3$ as catalysts for air electrode have been investigated in the present study with $MmNi_{3.5}Co_{0.8}Mn_{0.4}Al_{0.3}$ metal hydride negative electrode. Life cycling along with charge and discharge characteristics was studied in detail. The air-MH cells assembled with Ag_2O and $LaMnO_3$ as catalysts in the air electrode gave encouraging performance. $LaMnO_3$ when incorporated as electrocatalyst delivered stable cycle life whereas incorporation of Sr resulted in inferior performance in the studied composition range.
© 2007 International Association for Hydrogen Energy. Published by Elsevier Ltd. All rights reserved.

Keywords: Air-MH batteries; Hydrogen storage alloys; Bifunctional air electrodes; Electrocatalysts and cycle life

1. Introduction

Hydrogen, the third most abundant chemical element on earth, is of enormous importance as a feedstock in chemical industry with a worldwide annual production of over 25 million tonnes currently and an assumed potential for accelerated growth. In recent years, air-metal hydride (MH) system has attracted substantial attention. A significant increase of the energy density per unit weight of typically 15–20% can be achieved by replacing the heavy Ni-electrode by a lightweight air electrode. Therefore, despite the lower cell voltage of the air-MH system, the energy density per unit weight is higher in comparison to the Ni-MH system. Using an air electrode capable of oxygen reduction and evolution, a rechargeable battery can be obtained. The end of the battery life is determined by the cycle life of the air electrode. The plateau potentials of the metal hydride and of the air electrode depend on the cycle number though in different ways.

The use of bifunctional air electrodes that are less sensitive to corrosion is therefore demanded for a necessary increase of the cycle lifetime. The materials used as the bifunctional catalyst and the carbon support material greatly influence the lifetime of the air electrode. At the present stage, employing $La_{0.6}Ca_{0.4}CoO_3$ perovskite material as the catalyst and graphite-like carbon material as the support have been reported to give a maximum discharge power density of $34.8\,mW\,cm^{-2}$ for air and $51.0\,mW\,cm^{-2}$ for oxygen, respectively [1].

The key problem in the development of air-MH batteries is the oxygen-diffusion electrode. Usually, it is a porous, carbon-based oxygen-diffusion electrode consisting of a mixture of catalysts and carbon. Various types of electrocatalysts, e.g. Pt and Pt–Ru alloys have been investigated as a key component of the electrodes, but they are expensive. Significant progress has been made in recent years in the development of less expensive electrocatalysts such as perovskite (e.g. $La_{1-x}Ca_xCoO_3$), spinels (e.g. Co_3O_4, $NiCo_2O_4$), pyrochlores (e.g. $Pb_2Ru_2Pb_{1-x}O_{1-y}$, $Pb_2Ru_2O_{6.5}$), other oxides (e.g. $Na_{0.8}Pt_3O_4$), and pyrolyzed macrocycles with Co additives.

* Corresponding author. Fax: +91 4565 227713.
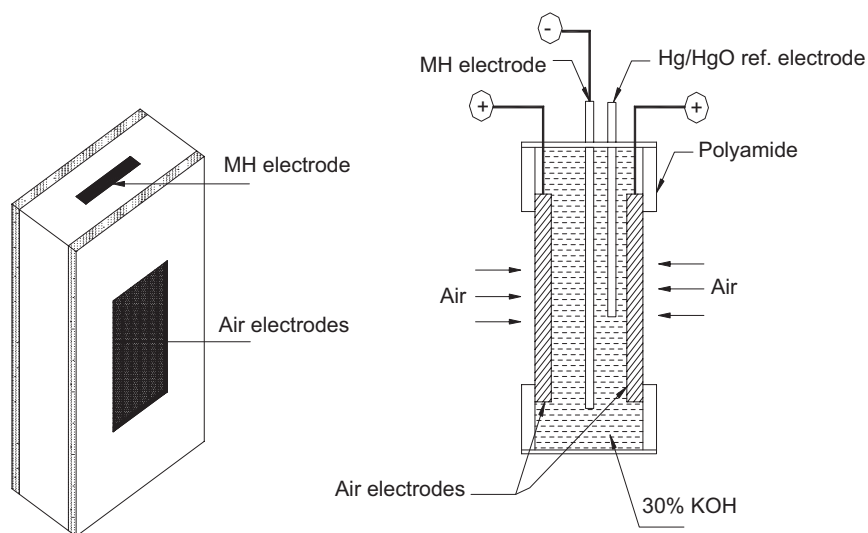 *E-mail address:* mvananth@rediffmail.com (M.V. Ananth).

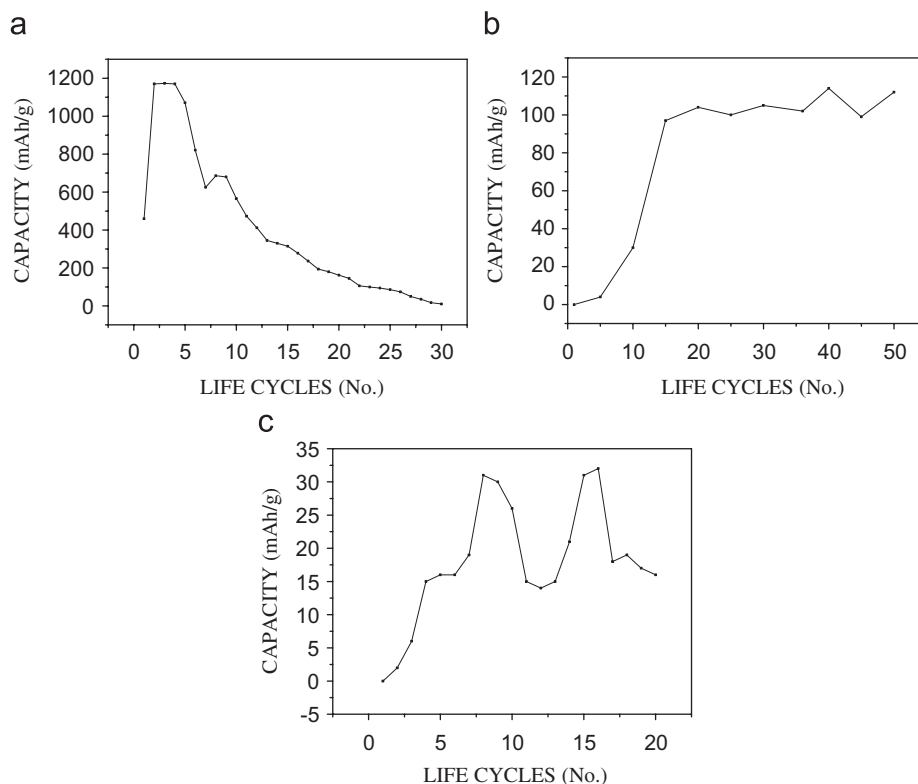Fig. 1. Schematic illustration of the air-MH cell.

Fig. 2. (a) Life cycling of air-MH cell with Ag_2O as electrocatalyst in air electrode; (b) life cycling of air-MH cell with $LaMnO_3$ as electrocatalyst in air electrode; (c) life cycling of air-MH cell with $La_{0.65}Sr_{0.30}MnO_3$ as electrocatalyst in air electrode.

Also a series of complex oxides $REMn_2O_5$ (RE = Dy, Ho, Er, Tm, Yb, and Lu) and $Er_{0.76}Zr_{0.11}Ca_{0.13}Mn_2O_5$ with large specific areas and nanoscale grain sizes prepared by an improved amorphous citric precursor method have been tried for such uses. Among the alternatives for platinum catalysts, MnO_2 shows some promise of success due to its low cost and its high catalytic activity for the oxygen reduction. However, the recommended technical parameters associated with the fabrication of MnO_2 catalyzed air electrodes varies

from one report to another. Trygve Burchardt has evaluated the electrocatalytic activity and stability for air electrodes [2]. AB_5-type hydrogen-storage alloys, such as $LaNi_5$ [3], $MmNi_{3.6}Co_{0.7}Al_{0.6}Mn_{0.1}$ [4,5], $La_{0.8}Ce_{0.2}Ni_{4.25}Co_{0.5}Sn_{0.25}$ [6] $SrTiO_3$–$LaNi_{3.76}Al_{1.24}H_n$ [7], $MmNi_{3.6}Co_{0.7}Mn_{0.4}Al_{0.3}$ [8] and $MmNi_{3.5}Co_{0.7}Al_{0.7}Mn_{0.1}$ [9], have been reported as negative electrode (anode) for metal-hydride-air (MH-air) systems. Mohamad et al. have used mechanically alloyed Mg_2Ni alloys for assembling MH–air secondary battery [10].
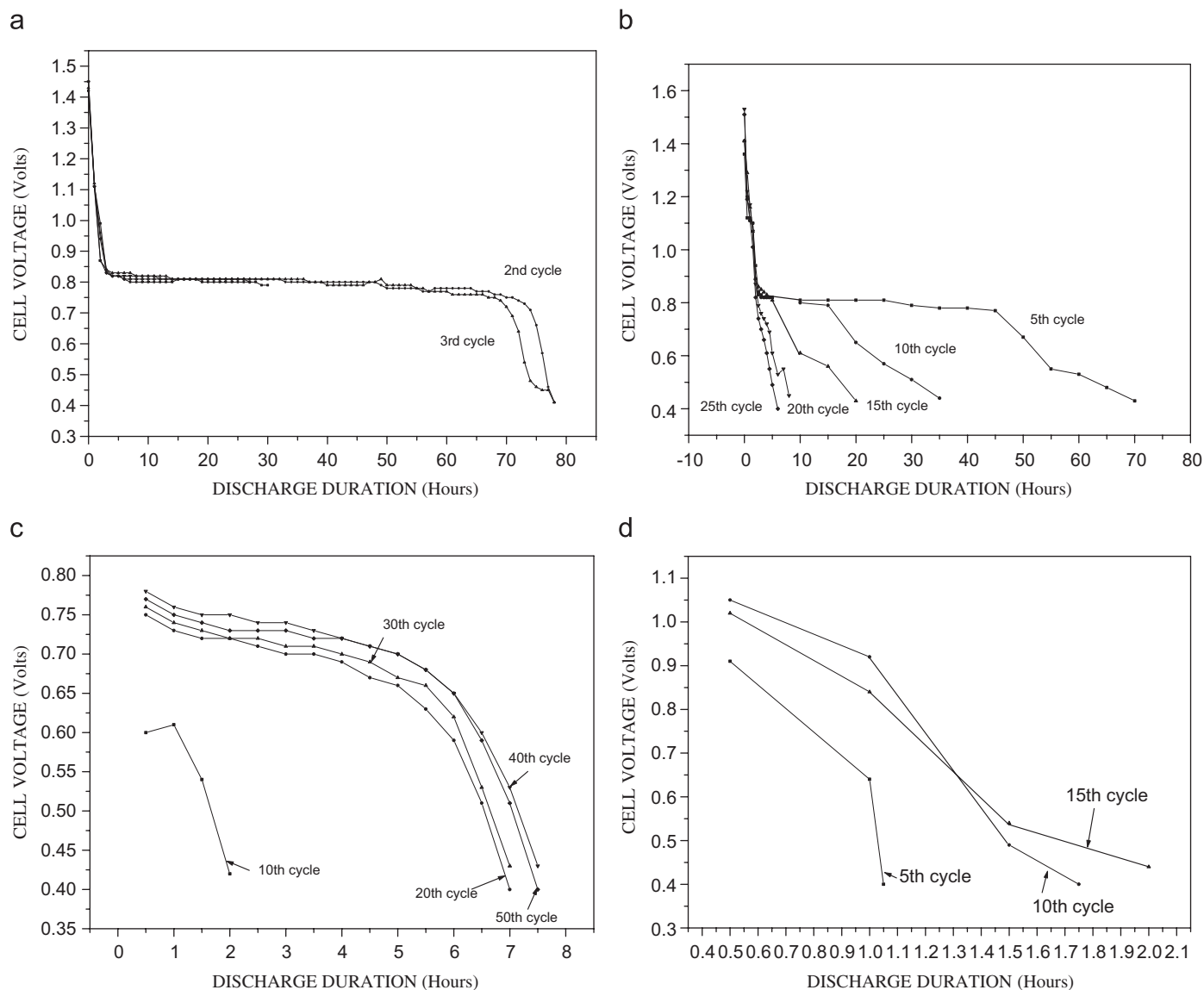
Fig. 3. (a) Discharge patterns of air-MH cell with Ag_2O as electrocatalyst in air electrode in initial stages of cycle life; (b) discharge patterns of air-MH cell with Ag_2O as electrocatalyst in air electrode during life cycling; (c) discharge patterns of air-MH cell with $LaMnO_3$ as electrocatalyst in air electrode; (d) discharge patterns of air-MH cell with $La_{0.65}Sr_{0.30}MnO_3$ as electrocatalyst in air electrode.

Some studies have appeared in literature on the development of air-MH system. But the main problem is to have an adequate bifunctional electrode with suitable electrocatalyst. Several materials are available for use in air electrodes. A detailed study is required to identify the best catalytic material and optimize the battery activity. Hence in the present study three such potential materials—Ag_2O, $LaMnO_3$ and $La_{0.65}Sr_{0.30}MnO_3$—have been explored for use in bifunctional air electrodes.

2. Experimental

The composition of the alloy investigated was $Mm\,Ni_{3.5}Co_{0.8}Mn_{0.4}Al_{0.3}$ with a La/Ce ratio of 11.65 in Mm (mish metal). The alloy was produced at DMRL, Hyderabad in collaboration with CECRI, Karaikudi. It was prepared by arc melting

followed by necessary treatments. The purity of all elements was above 99 wt%. The annealed alloys were crushed mechanically into powder ($< 75\,\mu m$). MH alloy of 8 g was mixed with 20% KS44 Graphite powder, 10% carbonyl nickel and 10% silver oxide. PTFE was used as binder and the active material paste was applied over the foam substrate. Subsequently, compaction was done at $5 \times 10^3\,kg\,cm^{-2}$ for 3 min to obtain the metal-hydride electrode followed by heat treatment at $120\,°C$ for 1 h under normal conditions. The geometric area of the negative electrode was $2 \times 2.5 \times 2.5\,cm^2$ and the thickness was 1.5 mm.

Air electrodes were produced in two layers: the catalyst layer on the electrolyte side and a hydrophobic diffusion layer on the gas side. The active layer contained a catalyst (typically 40 wt%), KS44 graphite powder (45 wt%) and PTFE (15 wt%). In this part we used three different types of oxide catalysts
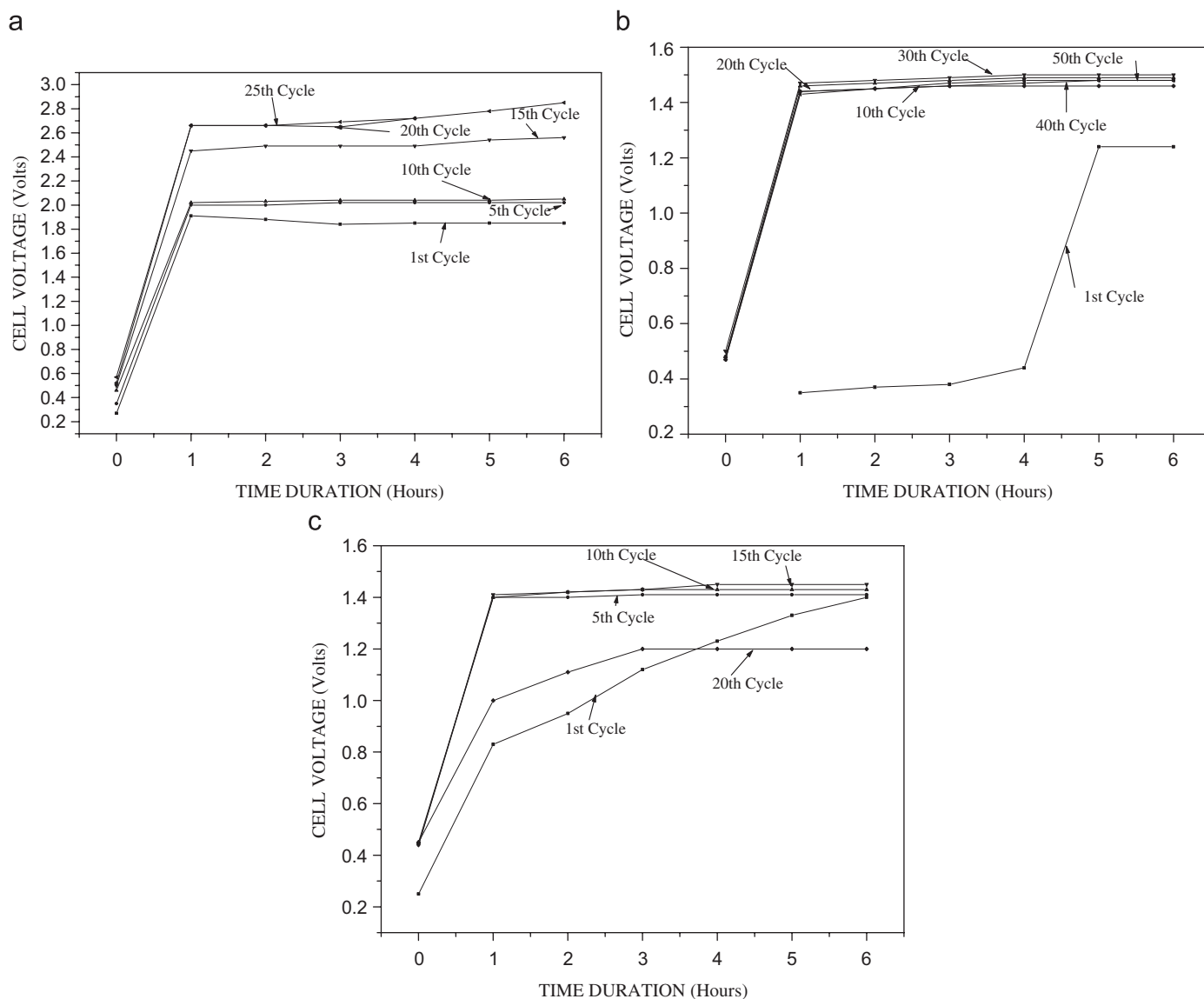
a

b

c

Fig. 4. (a) Charging behaviour of air-MH cell with Ag_2O as electrocatalyst in air electrode; (b) Charging behaviour of air-MH cell with $LaMnO_3$ as electrocatalyst in air electrode; (c) Charging behaviour of air-MH cell with $La_{0.65}Sr_{0.30}MnO_3$ as electrocatalyst in air electrode.

namely Ag_2O, $LaMnO_3$ and $La_{0.65}Sr_{0.30}MnO_3$. The first one was a commercial AR grade variety and the rest were the samples synthesized by Pechini method. The graphite powder and the binder were ground and mixed together using isopropyl alcohol as dispersing agent and dough was obtained by adding PTFE. This dough was coated on one of the sides and similarly another dough was prepared containing graphite and the active material, were ground and mixed together using isopropyl alcohol and a dough was obtained by adding PTFE and this was coated on the other side. Then the electrode was compacted at a pressure of $5 \times 10^3 \, kg \, cm^{-2}$ for 3 min followed by heat treatment at $120 \, °C$ for 1 h under normal conditions. The geometric area of the negative electrode was $2 \times 2.5 \times 2.5 \, cm^2$.

The air electrode (cathode) and the metal-hydride electrode (anode) were assembled and sealed in a prismatic container

as depicted in Fig. 1. Subsequently, the cell was subjected to formation cycles after soaking in 30% KOH solution. After the completion of formation cycles, the cells were charged at 500 mA for 6 h and discharged at 15 mA after a rest for 10 min in the case of engaging Ag_2O as electrocatalyst. In other cases, the cells were charged at 25 mA for 6 h and discharged at 15 mA after a rest for 10 min. The life cycling of the cells were studied using a 'Bitrode' LCN Battery Testing System at room temperature.

3. Results and discussions

3.1. Cycle life experiments

The results of the cycle life experiments are shown in Fig. 2(a–c). Reasonably good performances are seen in cases

of Ag_2O and $LaMnO_3$ as electrocatalysts. Because of high charge inputs a maximum discharge output of about 1200 mAh is obtained with Ag_2O. Though with $LaMnO_3$ a maximum capacity of only about 110 mAh was obtained because of comparatively lower charge inputs, a stable and steadily improving cycle life pattern is seen. It is found that the used $La_{0.65}Sr_{0.30}MnO_3$ is not useful, as the cycle life is inferior with a dismal capacity output. Gradual degradation in performance is noticed with Ag_2O after reaching the maximum capacity. With $La_{0.65}Sr_{0.30}MnO_3$ after reaching a maximum capacity of about 30 mAh within 15 cycles, virtually there is no battery activity after 20 cycles thereby rendering the compound unsuitable for the intended applications.

3.2. Discharge behaviour

The discharge pattern with Ag_2O does not change much with cycling in initial stages (Fig. 3a). After an initial steep drop within 2 h the discharge voltages remain stable for a significant period followed by a steep drop in the concluding stages. There is about 0.65 V drop on discharge (almost half of the voltage at zero time) that probably signals high internal resistance of the battery with silver oxide catalyst. The discharge patterns, however, change with cycling (Fig. 3b). The discharge pattern in case of $LaMnO_3$ gets stabilized with cycling. The voltage fall is gradual in later stages of life cycling. The discharge voltage patterns in $La_{0.65}Sr_{0.30}MnO_3$ indicate regular steep fall especially in initial stages.

3.3. Charging behaviour

The charging behaviours of three types of studied air-MH cells are shown in Fig. 4(a–c). With Ag_2O a two-step pattern charging can be seen. Within an hour of charging the flat plateau is reached. The maximum voltage, however, increases with cycling thereby indicating the development of the high internal resistance of the battery with silver oxide catalyst. Similar pattern is seen with $LaMnO_3$ except in initial stages. Except in initial and concluding stages the charging patterns for $La_{0.65}Sr_{0.30}MnO_3$ are similar to those of $LaMnO_3$. The maximum charging voltages achieved are, however, lower in $LaMnO_3$ and $La_{0.65}Sr_{0.30}MnO_3$ (with low over voltage during charge) than Ag_2O thereby revealing their superior charging characteristics.

4. Conclusions

Amongst the investigated electrocatlysts for air electrode, $LaMnO_3$ appears to be the best one due to stable cycle life and superior charging characteristics with low over voltage during charging. However, incorporation of Sr in $LaMnO_3$ resulted in inferior performance in the studied composition range. Good discharge performance is obtained with Ag_2O as electrocatalyst with better discharge profiles but moderate cycle life and inferior charging characteristics with high over voltages during charging renders it unattractive for air-MH cell applications. Detailed investigations with proper substitutions in $LaMnO_3$ are expected to result in identification of better electrocatlysts for use in air-MH cells.

References

[1] Chartouni D, Kuriyama N, Kiyobayashi T, Chen J. Metal hydride fuel cell with intrinsic capacity. Int J Hydrogen Energy 2002;27(9):945–52.

[2] Burchardt T. An evaluation of electrocatalytic activity and stability for air electrodes. J Power Sources 2004;135(1–2):192–7.

[3] Sarradin J, Bronoel G, Guegan AP, Achard JC. In: Thompson J, editor. Power sources, vol. 7. New York: Academic Press; 1979. p. 345–51.

[4] Sakai T, Iwaki T, Ye Z, Noreus D, Lindstrom O. In: P.D. Bennett, T. Sakai, editors. Proceedings of the electrochemical society on hydrogen and metal hydride batteries, vol. 94-27, Pennington, NJ, 1994. p. 393–402.

[5] Sakai T, Iwaki T, Ye Z, Noreus D, Lindstrom O. Air-metal hydride battery construction and evaluation. J Electrochem Soc 1995;142(12):4040–5.

[6] Gamburzev S, Zhang W, Velev OA, Srinivasan S, Appleby AJ, Visintin A. Development of a novel metal hydride-air secondary battery. J Appl Electrochem 1998;28(5):545–9.

[7] Akuto K, Sakurai Y. A photorechargeable metal hydride/air battery. J Electrochem Soc 2001;148(2):A121–5.

[8] Hu W, Ye Z, Noreus D. Influence of MH electrode thickness and packing density on the electrochemical performance of air-MH batteries. J Power Sources 2001;102(1–2):35–40.

[9] Chartouni D, Kuriyama K, Kiyobayashi T, Chen J. Air-metal hydride secondary battery with long cycle life. J Alloys Compds 2002;330–332:766–70.

[10] Mohamad AA, Mohamed NS, Alias Y, Arof AK. Mechanically alloyed Mg_2Ni for metal-hydride-air secondary battery. J Power Sources 2003;115(1):161–6.