Electrolytic Manganese Dioxide from Secondary Sources for Energy Storage

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A novel approach has been made to synthesize γ-electrolytic manganese dioxide (EMD) from a range of secondary sources, such as manganese cake (EMD_{Cake}), manganese leach residue (EMD_{LR}) and cobalt manganese bromide spent catalyst sludge (EMD_{CMBS}). Microscopy analysis suggests the presence of needle like grains within the range of 20-40 nm. Galvanostatic charge-discharge technique revealed that the discharge capacity of EMD_{Cake}, EMD_{LR} and EMD_{CMBS} were 280, 267 and 240 mA h g^{-1} respectively when tested in 9M KOH electrolyte. The Zn/EMD system found suitable for energy storage battery applications.

1. Introduction

Rapid industrialisation has resulted in the current scenario of energy crisis by depleting the reserves of high grade ores with simultaneous increase in industrial pollution. This demands restricted use of fossil fuels and recommends recycling of industrial wastes and use of lean grade ores. As an eco-friendly energy material, MnO_2 has been choice of interest for energy storage applications over long decades. Development process for the economic recovery of manganese from low grade manganese ores, secondary resources [1] is in need to fulfil the rapidly growing demand of this low cost energy material. In the present work, a comparative study has been carried out among the electrolytic manganese dioxides (EMDs) synthesized from secondary sources [2] such as manganese cake (EMD_{Cake}), manganese leach residue (EMD_{LR}) and cobalt manganese bromide spent catalyst sludge (EMD_{CMBS}) suitable for energy storage applications. Physicochemical and electrochemical properties of these materials suggest that they are suitable for energy storage applications. In the course of diminishing supply of fossil fuels and climate change, this study may be a land mark in fulfilling the escalating demand for energy materials and energy storage devices.

2. Sample preparation

Leaching of Manganese cake, manganese leach residue were carried out at 75± 2 ^{o}C with required amount of sulphuric acid and reductant. Cobalt manganese bromide spent (CMBS) catalyst sludge dissolution was carried out in the required amount of sulphuric acid without any reductant. All the leaching/dissolution experiments were carried out in 1L glass reactor. The details of the leaching conditions have been discussed elsewhere [3, 4]. Then the slurry was treated to remove other impurities to generate purified manganese solution used as electrolyte for EMD synthesis. Manganese dioxide has been electrodeposited from the above mentioned purified manganese sulphate and sulphuric acid in 2:1 ratio at an anodic current density of 200 A m^{-2} in a thermostatic glass cell for 3 h.

X-ray diffraction (XRD) patterns were measured with Siemens D500 X-ray diffractometer 5635 using Cu Kα radiation (λ = 1.54 Å) at 40 kV and 28 mA within the range

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of 10^{o} – 80^{o} with scan speed of 1° per min. The transmission electron microscopy (TEM) imaging were carried out using an electron microscope (FEI, TECNAI G2 20, TWIN) operating at 200 kV, equipped with a GATAN CCD camera. Elemental analyses were carried out with atomic absorption spectrophotometer (Perkin Elmer AA 200).

Charge-discharge measurements were carried out in a two electrode system by using a BITRODE battery tester (LCN1-25-24). The setup comprised of EMD cathode and Zinc anode immersed in potassium hydroxide (9M) solution as the aqueous electrolyte. Pellets were made from uniform mixtures of various EMD samples with graphite powders in the ratios 4:1 in the presence of 2-3 drops of 5% polyvinyl alcohol (PVA) as binder. The mixture was placed in a stainless steel mesh meant for electrical contact and then subjected to a pressure of 12 ton for 3 minutes by means of a pelletiser (KBr press) in a 20 mm die. The applied current density for these experiments were 20 mA g^{-1} with discharging and charging cut-off voltages of 0.9 and 1.75 V, respectively. Cyclic voltammetry (CV) was carried out in a three electrode system using a BioLogic VSP-300 instrument. The working electrode used in this system was EMD and metallic Zn strip as the counter electrode. Mercury–mercuric oxide (Hg/HgO) served as the reference electrode with 9M KOH as the electrolyte.

3. Results and Discussion

3.1 Structural Behaviour

Figure 1 is X-ray diffraction (XRD) patterns of the EMD samples and showed that all the samples comprised of five major peaks at various 2θ values such as 22^{o} (110), 37.2^{o} (021), 42^{o} (121), 56^{o} (221) and 68^{o} (002) without any second phase as an impurity indicating the electrodeposited product is phase-pure MnO_2. These diffraction peaks can be indexed to an orthorhombic phase of γ-type MnO_2 with lattice constants: a = 8.70 Å, b = 2.90 Å and c = 4.41 Å. These cell parameters are in good agreement with the standard values of JCPDS card no. 65–1298 (a = 9.27 Å, b = 2.87 Å, c = 4.53 Å). The observed peak for EMD_{CMBS} showed a little different peak shape for its first peak than the other two EMD samples, which may be attributed due to the presence of cobalt in the EMD making it more crystalline.

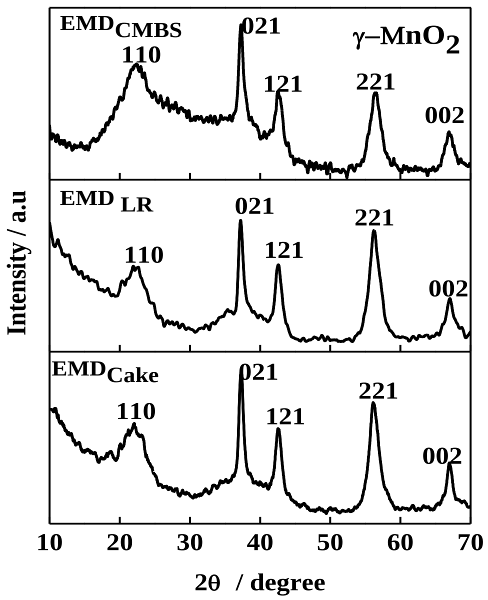

Fig. 1. XRD patterns of EMD samples synthesized from different sources.

Figure 2 shows the TEM images of all the synthesized samples, suggesting that the synthesized EMD material consists of nano sized grain within the range of 20-50 nm. Among the samples studied, EMD_{cake} showed a compact arrangement. This nanostructured material exhibits good electrochemical behaviour. EMD_{CMBS} showed smaller grain size than EMD_{cake} and EMD_{LR} resulting in more accessibility for easy transfer of ions. Hence EMD_{CMBS} showed more structural stability in continuous charge-discharge cycling.

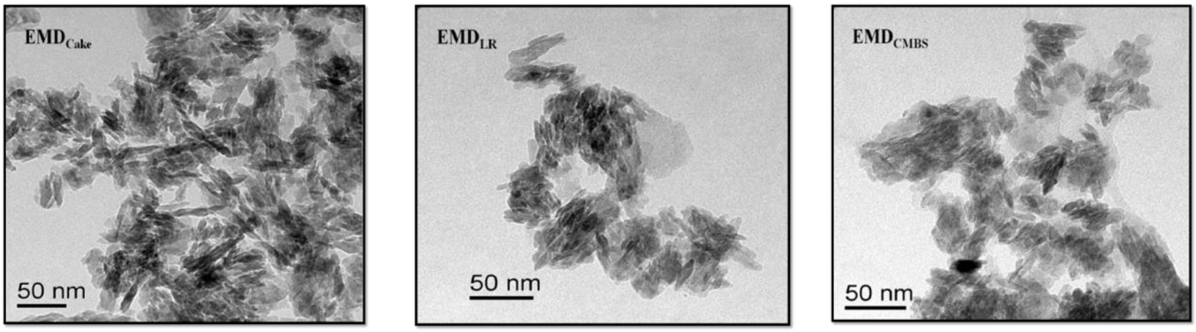

Fig. 2. TEM images of EMD samples synthesized from different sources.

3.2 Electrochemical Behaviour

Galvanostatic (charge-discharge) and potentiostatic (cyclic voltammetry) studies were carried out for all the samples to evaluate their capability in energy storage under identical conditions. For charge-discharge study, the EMD electrodes were subjected to discharge followed by charge in 9M potassium hydroxide solution. The typical discharge-charge profiles for the different EMD samples were compared in Fig. 3 (a). All the cells are found to be reversible with mid-discharge and mid-charge potentials at 1.3 and 1.4 V respectively. The result revealed that EMD_{Cake}, EMD_{LR} and EMD_{CMBS} showed an initial discharge capacity of 280, 267 and 240 mA h g^{-1} respectively.

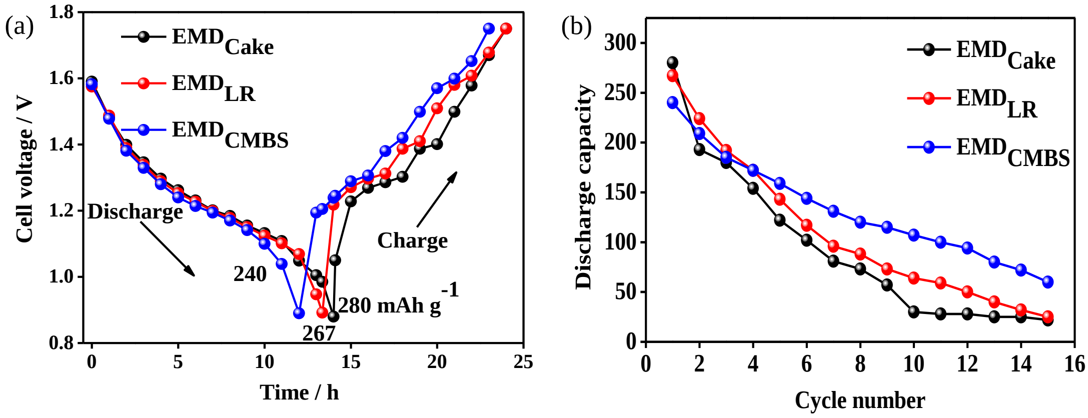

Fig. 3. (a) The first discharge–charge profile and (b) discharge capacity *vs* cycling behaviour of Zn/EMD cells obtained from different sources.

Continuous charging and discharging up to 15 cycles (Fig. 3b) were carried out for all samples. All the synthesised materials are found to be cyclable, however EMD_{CMBS} showed better cyclic stability in comparison to the other two samples. This is attributed to the doping of cobalt in EMD lattice, as some amount of cobalt has been retained in the leach liquor during purification. To understand the role of Cobalt in EMD as it showed the best performance in terms of cyclability, we have carried out cyclic voltammetric experiment. Cyclic voltammetry shown in Fig. 4 represents cycles for continuous cycling. It showed a pair of reduction (C1) and oxidation (A1) peak corresponding to $Mn^{4+/3+}$ [3]. The result suggests that EMD_{CMBS} showed quite excellent cyclability with continuous cycling. From the CV, there is no evidence for the presence of cobalt in the EMD. To confirm the presence of Co, elemental analysis for all the samples have been carried out and the results are tabulated in Table 1. From Table 1, it is clear that the EMD materials produced from three secondary sources are comparable to the available BIS standard [5] and hence they are found to be eligible for battery applications.

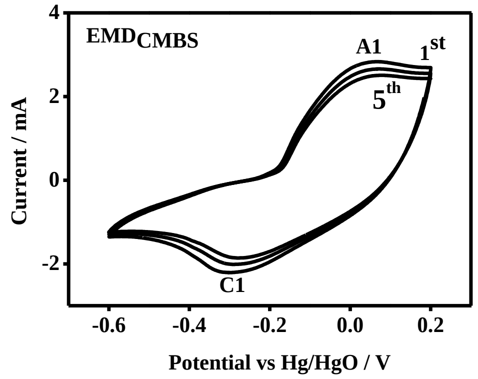

Fig. 4. Cyclic voltammetry plot of EMD_{CMBS} with cycling at a scan rate of 0.2 mV s^{-1}.

Table 1. Chemical analysis of the EMD samples synthesized from different sources.

Element	BIS (IS11153:1996)	EMD_{Cake}	EMD_{LR}	EMD_{CMBS}
MnO_2 (min), %	90	91.50	91.00	91.25
Fe (max), %	0.1	0.03	0.05	0.02
Ni, %	---	0.005	0.004	0.001
Cu, %	0.002	0.002	0.002	0.002
Co, %	---	0.002	0.004	0.05
Moisture (max), %	3	2.4	2.2	2.8

4. Conclusion

All the samples showed characteristics of γ-MnO_2 which is essential for their electrochemical activity. It was observed that all EMD samples have nano-grain like structure with variation in grain size. EMD_{Cake} is found to result in superior discharge capacity of 280 mA h g^{-1} when compared to EMD_{LR} (267 mA h g^{-1}) and EMD_{CMBS} (240 mA h g^{-1}). Synthesized EMD samples matched with the BIS standard and found suitable for battery application. EMD_{CMBS} showed better cyclability than the other due to the presence of cobalt in the EMD lattice.

References

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