Comparative Oxygen Evolution Reaction performance of cobalt oxide electrocatalyst in combination with various metal ions MCo$_2$O$_4$ (M= Mn$^{2+}$, Cu$^{2+}$, Co$^{2+}$, Zn$^{2+}$, Fe$^{2+}$, Mg$^{2+}$)

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Abstract. Oxygen evolution reaction (OER) supported by electrocatalyst is very important reaction in electrochemical system e.g. air-battery based energy storage devices, water splitting, and photoelectrochemical cells. Therefore developing inexpensive, non-hazardous, noble metal free, transition metal oxide based electrocatalyst is necessary for energy application and environmental sustainability. MCo$_2$(III)O$_4$ based oxides in combination of various metal ions (Mn$^{2+}$, Cu$^{2+}$, Co$^{2+}$, Zn$^{2+}$, Fe$^{2+}$, Mg$^{2+}$) are studied as OER electrocatalyst in both acidic and basic medium. When deposited on a glassy carbon current collector the comparative LSV polarization plots revealed that in acidic medium FeCo$_2$O$_4$ is the best OER performing electrocatalyst, showing onset potential +1.62 V vs RHE with current 1.66 mA/cm$^2$, while in basic medium it is MnCo$_2$O$_4$ that preforms the best, showing an onset potential +1.53 V vs RHE with OER current density 2.06 mA/cm$^2$. When nickel foam was used as the current collector, the comparative LSV polarization plots revealed that in acidic medium FeCo$_3$O$_4$ shows the best OER performance, with an onset potential 1.508 V vs RHE and OER current 159 mA/cm$^2$ in acidic medium. However in the basic medium the substrate nickel foam outperforms all the oxides combinations with different metal ions due to partially oxidized NiO at nickel foam, showing onset OER potential +1.58 V vs RHE and OER current density 13mA/cm$^2$. No correlation was found between the rates of OER and the bond dissociation energies of the respective metal-oxygen bonds nor the metal-hydroxide bond strength.

1. INTRODUCTION

The oxygen evolution reaction[1] (OER) is very important and critical oxidation reaction for energy storage devices, water splitting[2], photoelectrochemical cells[3-5] and natural photosynthetic process. OER electro catalysts are primarily used as cathodes in metal air battery system as shown in Figure 1 schematic diagram of OER mechanism, where the catalyst are finely and efficiently coated over current collector electrodes (e.g. Ni foam, carbon cloth). The OER electro catalyst contributes in the oxidation of OH$^-$/O$^2-$ ions into O$_2$ during charging of the battery cell, with the generated electrons flowing back to the Li anode through the external circuit. Subsequently Li$^+$ ions are reduced and redeposited at anode as Li metal ions. In battery performance, the difference between energy applied during charging and output voltage energy during discharge should be minimum. Therefore, efficient OER catalyst is deemed necessary for a high performance air battery based energy storage system.
The light mediated photosystem PSII is natural oxygen evolution process followed by water splitting in green leaves that involves complex enzyme, many cofactors, water and light. However, this process is not efficient considering the life of leaves that are replaced each year.

Electrocatalyst supported over desired electrodes (conducting substrates) are required to imitate the natural oxygen evolution process at lab scale for energy storage application and water splitting. The precious metal based OER catalysts are more efficient in terms of its durability and application in metal air batteries during charging process. Because of limited resources of precious metals, its need of hour to focus on inexpensive, non-hazardous transition metal oxide based OER catalysts, stable in acid as well as basic medium, for energy and environmental application.

An efficient OER electrocatalyst [6] needs high electronic conductivity, non-solubility in aqueous acidic or basic medium and optimal porosity for fast diffusion of reactants and products. Although transition metal oxides are promising for OER electro-catalytic applications in energy storage system[7-12]. However these oxide materials shows lower electronic conductivity than the expensive noble metal based electro catalyst. Doping the transition metal oxides with heteroatom centres, such as N, S, and F atoms, has been shown to increase electronic conductivity by causing a favourable redistribution of positive charges in the lattices for efficient electro-catalysis[13-16]. Likewise, transition metal oxides supported on conducting carbon [17] powders show efficient OER electro catalysis due to faster electron transfer kinetics between current collector electrodes and the deposited catalyst.

**Schematic of OER electrocatalyst function during charging in Li –air battery**

![Schematic of OER electrocatalyst function during charging in Li –air battery](image)

Here in we report the use of a MCo₂(III)O₄ oxide in combination with various metal ions (M=Mn²⁺, Cu²⁺, Co²⁺, Zn²⁺, Fe²⁺, Mg²⁺) as OER electrocatalyst [6,18-23] in both acidic and basic medium, while using either glassy carbon (GC) or nickel foam as the current collector electrodes in the context of a metal-air battery. When deposited on a GC electrode, it is found that in acid medium FeCo₂O₄ oxide shows the lower onset potential for OER at 1.62 V vs RHE reaching a current of 1.68 mA/cm², while in basic media MnCo₂O₄ oxide was the best performing OER electrocatalyst with an onset potential of
1.53 V vs. RHE with a current 2.0 mA/cm$^2$. When a Ni foam current collector is used, the mixed MCo$_2$O$_4$ oxides show far higher current density in acidic medium than in basic medium, but this was found to be partly due to a contribution from corrosion of the Ni [24], rather than solely due to OER. Nevertheless, in basic media, where Ni foam is corrosion resistant, the OER current densities for all the combination of MCo$_2$O$_4$ oxides were higher on nickel foam than glassy carbon, due to the former having faster electron transfer across catalyst / current collector electrode interface.

2. EXPERIMENTAL

2.1 Synthesis and characterization
The MCo$_2$(III)O$_4$ (M= Mn$^{2+}$, Cu$^{2+}$, Co$^{2+}$, Zn$^{2+}$, Fe$^{2+}$, Mg$^{2+}$), samples were prepared using urea combustion method. In this method Co(OH)$_2$ (Purity 99%) (dissolved in conc. HNO$_3$), metal nitrates M-(NO$_3$)$_2\times$H$_2$O, Urea (NH$_2$CONH$_2$) and NH$_4$NO$_3$ in a 2:1:3.5:1 stoichiometric ratio are dissolved in distilled water and mixed well by magnetic stirring. All chemical purchased from Aldrich with purity >99%. After 3 hours of stirring slowly evaporated to dryness on the hot plate and finally heated at 600°C for 3h in air to get a desired phase and remove the all organic components. Finally black colour powder was stored in a desiccator and used for further characterization X-Ray diffraction (Cu K$_\alpha$ radiation, Bruker D8), Transmission Microscopy (JOEL JEM-2010F) techniques for structure and morphology evaluation.

2.2 Electrochemical Testing (OER)
Electrodes for OER electrochemical testing of the MCo$_2$(III)O$_4$ (M= Mn$^{2+}$, Cu$^{2+}$, Co$^{2+}$, Zn$^{2+}$, Fe$^{2+}$, Mg$^{2+}$) catalyst samples, the synthesized MCo$_2$(III)O$_4$ catalysts were used to prepare catalyst ink by simply disperse 5 mg catalyst into 1000 µL of (750 µL DI water, 200 µL ethanol and 50 µL nafion by sonication. Later 250 µL was drop casted over glassy carbon electrode (GC) and Ni foam after that both the electrodes were allowed to dry in oven at 60 °C for adhesion. The modified GC electrode and Ni foam were tested using linear sweep voltammetry LSV from 1.3 V to 1.8 V vs RHE at a sweep rate of 10 mV/s$^{-1}$ in 0.5 M H$_2$SO$_4$ and 0.1M KOH solutions after N$_2$ purging by Bio-Logic potentiostat (model) in absence of O$_2$ gas. The recorded linear sweep voltammograms were IR corrected by subtracting the uncompensated resistance multiplied by current with corresponding applied voltage.

3. RESULTS AND DISCUSSION

3.1 Materials Characterization
X-ray diffraction patterns for the various MCo$_2$(III)O$_4$(M= Mn$^{2+}$, Cu$^{2+}$, Co$^{2+}$, Zn$^{2+}$, Fe$^{2+}$, Mg$^{2+}$) samples are shown in Figure 2.

All samples indexed based cubic spinel structure, and all showed the prominent (hkl) planes of (111), (022) (311) (222) (004) (422), which are characteristic of cubic spinel structure. Refined cubic lattice parameter values of MCo$_2$(III)O$_4$ using Topas software and obtained lattice parameter values are in the range, a = 8.057 to 8.125 Å and small differences in the lattice parameter values are noted depending the ionic radius of metal ion [25] and observed lattice parameter values are close to previously reported literature on MCo$_2$(III)O$_4$ M= Co [26], Zn [27], Cu [28], Mn [29], Mg [29] and Fe [30].
Figure 2. X-ray Diffraction patterns of MCo$_2$(III)O$_4$ compounds (A= Co$^{2+}$, Mn$^{2+}$, Mg$^{2+}$, Cu$^{2+}$, Fe$^{2+}$, Zn$^{2+}$).

The morphology of select MCo$_2$(III)O$_4$ samples are shown in Figure 3, TEM images revealing submicron sized particles are in the range 10-80 nm and these values close to average crystallite size (are in the range 15-90 nm) calculated using TOPAS software. Select area electron diffraction pattern of MnCo$_2$O$_4$ characteristic rings of nanocrystalline nature the prepared sample and similar characteristic are noted by other sample, indeed we expect similar morphology since all samples are prepared under identical temperature and time.

3.2 Electrochemical studies (OER)

The oxygen evolution reaction occurs at anode as an oxidation half reaction in electrochemical cell set up. The standard electrochemical potential for OER is 1.23 V vs. RHE, which represents the ideal onset potential for the process. In practice, the OER requires an additional over potential before the current density reaches to a measureable value, so the aim of a good catalyst is to minimize this overpotential, which in turn can be measured by linear sweep voltammetry.

The mechanism for OER reactions [1] are as follows in acidic and basic medium. In acidic solution the OER reaction can be written as:

$$2H_2O(l) \rightarrow 4H^+ + O_2(g) + 4e^-; E^0 = 1.23 \text{ V} \quad (a)$$

The overall reaction occurs over a number of steps as shown in reactions [1](b) to (f):

$$M + H_2O(l) \rightarrow MOH + H^+ + e^- \quad (b)$$

$$MOH + OH^- \rightarrow MO + H_2O(l) + e^- \quad (c)$$

$$2MO \rightarrow 2M + O_2(g) \quad (d)$$

$$MO + H_2O(l) \rightarrow MOOH + H^+ + e^- \quad (e)$$

$$MOOH + H_2O(l) \rightarrow M + O_2(g) + H^+ + e^- \quad (f)$$
In basic solution the OER reaction can be written as:

$$4OH^- \rightarrow 2H_2O(l) + O_2(g) + 4e^- E^0 = -0.40\text{V}$$ \hspace{1cm} (g)

The overall reaction occurs over a number of steps as shown in reactions (h) to (l):

$$M + OH^- \rightarrow MOH \quad \hspace{1cm} (h)$$

$$MOH + OH^- \rightarrow MO + H_2O(l) \quad \hspace{1cm} (i)$$

$$2MO \rightarrow 2M + O_2(g) \quad \hspace{1cm} (j)$$

$$MO + OH^- \rightarrow MOOH + e^- \quad \hspace{1cm} (k)$$

$$MOOH + OH^- \rightarrow M + O_2(g) + H_2O(l) \quad \hspace{1cm} (l)$$

Note that in both acidic and basic media intermediate MO or MOH species are formed, meaning that the overall reaction rate depends on the stabilities of these species, which in turn depend on the nature of M; note that in the present case M is the cubic spinel oxide rather than a metal. This has led previous researchers to suspect that OER rates are dependent on either the M-O or M-OH bond strength [31]. However, Trasatti argued that non-stoichiometry is the main factor governing the electrocatalytic activity of transition metal oxides[32], which should make spinels promising candidates. OER Process was carried out in acidic as well as basic medium using GC RDE and Ni foam current collectors as electrode.

Figure 4 (a) and (b) show LSV polarization curves for the MCo$_2$(III)O$_4$ catalysts deposited on glassy carbon electrode in 0.5M H$_2$SO$_4$ and 1M KOH respectively. In the acidic medium the FeCo$_2$O$_4$ shows the best performance, with the lowest onset potential (+1.62 V vs RHE) and highest OER current density (1.66 mA/cm$^2$), while the poorest performer was the ZnCo$_2$O$_4$, (+1.74 V vs RHE and...
The acidic OER onset potentials become more positive in the order of Fe$^{2+}$, Mg$^{2+}$, Cu$^{2+}$, Co$^{2+}$, Mn$^{2+}$ and Zn$^{2+}$. In 1M KOH, MnCo$_2$O$_4$ shows the best performance, with the least positive onset potential (+1.53 V vs RHE) and highest OER current density (2.06 mA/cm$^2$), while the Co$_2$O$_4$ shows onset potential (+1.64 V vs RHE and 0.43 mA/cm$^2$). In the basic medium OER onset potentials become more positive in the order of Mn$^{2+}$, Mg$^{2+}$, Fe$^{2+}$, Cu$^{2+}$, Zn$^{2+}$ and Co$^{2+}$. However, the reason for these trends is not clear, with neither the acidic or basic ones showing any correlation with either the absolute electronegativity or the absolute hardness of the dopant cations [33]. Nevertheless, the LSV curves do demonstrate that the electro catalytic properties not only depend on materials’ crystalline and amorphous nature but also the nature of the test medium e.g. acid and basic medium. To investigate the influence of the nature of the current collector the substrate was switched from glassy carbon to nickel foam, Figure 4 (c) and (d) shows LSV polarization curves for the MCo$_2$(III)O$_4$ catalysts deposited on Ni foam in 0.5M H$_2$SO$_4$ and 0.1M KOH respectively. All together it can be seen that with a nickel foam current collector there is a significant increase in the OER current densities, compared to the glassy carbon electrode. However, in the acidic medium much of this increased current density likely arises from the corrosion and catalytic property of the nickel substrate due to oxidation of nickel into nickel oxide [34]. The vulnerability of metal based current collector electrodes to corrosion poses a long-term operational challenges in energy storage systems. OER catalytic properties of nickel foam [11] relies on oxidation of nickel into nickel oxides/hydroxides/oxyhydroxides (mainly NiO) on the catalyst surface [35] that leads to higher current density. Moreover, the OER onset potentials for Co$^{2+}$, Mn$^{2+}$, Mg$^{2+}$, Zn$^{2+}$, Cu$^{2+}$ based Co$_2$O$_4$ remain quite close to 1.50V vs RHE with varying current densities, but the highest is for Co$^{2+}$ (159 mA/cm$^2$), due to formation of NiO on the catalyst surfaces in 0.5 M H$_2$SO$_4$.

In the basic medium, the bare nickel foam shows positive onset potential (+1.58 V vs RHE) and OER current density 13mA/cm$^2$ outperforming all the oxides (shown in figure 4d). The Ni foam in basic medium gets partially oxidised into NiO and the resulting NiO/Ni foam shows OER onset potential very consistent with reported OER electro catalyst NiO700/ Nickel foam system (thermally treated Ni foam)$^{34}$. No correlation was found between the rates of OER and the bond dissociation energies of the respective metal-oxygen bonds [36] nor the metal-hydroxide bond strength [32]. Furthermore, in terms of the importance of non-stoichiometry, examination of the performance of Zn and Mg, the two metals expected to always be in the +2 oxidation state, on the GC substrate showed the opposite trends, with in both acidic and basic media ZnCoO$_4$ being a poor catalyst and MgCoO$_4$ a good one. This suggests that non-stoichiometry is not an over-riding factor. The electrolyte medium, its pH and current collector electrode materials are very critical and important for efficient energy storage application during charging in aqueous metal-air or Li air battery. Thus, the catalysts showing less positive onset potential (close to 1.23 V) with higher oxidation current are supposedly better than those of more positive onset potential with lower values oxidation (OER) current.
Figure 4. OER LSV polarization of $\text{MCo}_2(\text{III})\text{O}_4$ catalysts in combination with different metal cations ($\text{M}=\text{Mn}^{2+}, \text{Cu}^{2+}, \text{Co}^{2+}, \text{Zn}^{2+}, \text{Fe}^{2+}, \text{Mg}^{2+}$) using glassy carbon in acidic medium 0.5M $\text{H}_2\text{SO}_4$ (a) and basic medium 0.1M KOH (b), and nickel foam as current collector electrode in acidic medium 0.5M $\text{H}_2\text{SO}_4$ (c) and basic medium 0.1M KOH (d). (Note all the plots are iR corrected).

4. CONCLUSIONS

Oxygen evolution reaction study of cobalt oxide electro catalysts $\text{MCo}_2(\text{III})\text{O}_4$ in combination with various metal ions ($\text{M}=\text{Mn}^{2+}, \text{Cu}^{2+}, \text{Co}^{2+}, \text{Zn}^{2+}, \text{Fe}^{2+}, \text{Mg}^{2+}$) is presented, with the catalyst’s suitability for metal air battery based energy storage system being discussed. When deposited on a glassy carbon current collector the comparative LSV polarization plots revealed that in acidic medium FeCo$_2$O$_4$ is the best OER performing electrocatalyst, showing onset potential +1.62 V vs RHE with current 1.66 mA/cm$^2$, while in basic medium it is MnCo$_2$O$_4$ that preforms the best, showing an onset potential +1.53 V vs RHE with OER current density 2.06 mA/cm$^2$. When nickel foam was used as the current collector, Co$_3$O$_4$ shows the best OER performance, with an onset potential 1.508 V vs RHE and OER current 159 mA/cm$^2$ in acidic medium. However in the basic medium the substrate nickel foam outperforms all the oxides combinations with different metal ions due to partially oxidized NiO at nickel foam, showing onset OER potential +1.58 V vs RHE and OER current density 13mA/cm$^2$. No correlation was found between the rates of OER and the bond dissociation energies of the respective metal-oxygen bonds nor the metal-hydroxide bond strength.
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