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Manganese molybdate and its Fe-substituted products as new efficient electrocatalysts for oxygen evolution in alkaline solutions

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ABSTRACT

Pure and Fe-substituted manganese molybdates with nominal compositional formula $Fe_xMn_{1-x}MoO_4$ ($x = 0, 0.25, 0.50$ and 0.75) have been prepared by a co-precipitation method at pH $\approx$ 2 and characterized by FT-IR, XRD, XPS, TEM, electrochemical impedance and polarization techniques. The oxygen evolution reaction (OER) study reveals that Fe substitutions from 0.25 to 0.75 mol for Mn increase the apparent electrocatalytic activity of the base oxide showing maximum with 0.5 mol Fe. At $E = 0.60$ V vs. Hg/HgO in 1 M KOH at 298 K, the apparent activity of the base oxide increased $\sim$58 times. It is observed that on Fe addition, the Tafel slope decreases from $\sim$60 to $\sim$35 mV, however, the order of the OER with respect to OH^- concentration as observed $\sim$2 on the base oxide (i.e. $MnMoO_4$) does not change.

1. Introduction

Oxygen evolution reaction (OER) occurs in a wide range of electrochemical processes, for example, water electrolysis, chlorine evolution, electroplating, peroxide production, etc., and thus, has been a subject of considerable research interest for the last three decades or so [1–5]. In particular, the production of hydrogen and oxygen from alkaline water electrolysis is a potential route to produce clean energy sources. However, the OER involves a high overpotential which reduces the energy efficiency of the OER-involved electrochemical processes. It is, therefore, desired to carry out extensive research efforts so as to develop more efficient electrocatalysts to reduce the overpotential for the OER and hence the cost of electrochemically produced hydrogen. Several metals and their pure as well as mixed oxides have been investigated in electrocatalysis of the OER [2–5]. Among catalysts investigated, transition metal complex oxides possessing spinel (mainly Co-based [5–23] and Fe-based [24–27]) and perovskite (mainly $LaNiO_3$ [28–30] and $LaCoO_3$ [31,32] and their derivatives [33–35]) structures are considered as potent electrocatalytic materials for the OER in alkaline solutions and have been studied extensively [5–35].

Recently, Singh and co-workers [36–42] have synthesized metal (Fe, Co or Ni) molybdates and investigated as electrocatalysts for the OER in strongly alkaline medium. These novel oxide materials are observed to be OER active. It is further reported that an introduction of Fe (0.25–0.75 mol) for Co into

CoMoO$_4$ [40], for Ni into NiMoO$_4$ [41] or for Cr into Cr$_2$(MoO$_4$)$_3$ [42] improves the catalytic activity of corresponding base oxides toward the OER greatly. The active electrodes of each series of substituted oxides followed the activity order: Fe$_{0.5}$Cr$_{1.5}$(MoO$_4$)$_3$ > FeNiMoO$_4$ > FeCoMoO$_4$. The electrocatalytic performance of these active ternary oxides were superior to those of active Co-based spinel-type oxides, recently reported in the literature [7,23,43,44]. These results prompted us to extend this study further. We have now prepared MnMoO$_4$ and its Fe-substituted products, namely Mn$_{0.75}$Fe$_{0.25}$MoO$_4$, Mn$_{0.50}$Fe$_{0.50}$MoO$_4$ and Mn$_{0.25}$Fe$_{0.75}$MoO$_4$ and investigated their structural and electrocatalytic properties toward the OER in 1 M KOH. Details of results of the investigation are described in this paper.

2.   Experimental section

2.1.   Preparation of mixed oxide electrodes

Pure and Fe-substituted manganese molybdates with compositional formula Mn$_{1-x}$Fe$_x$MoO$_4$ (x = 0, 0.25, 0.50, 0.75) have been synthesized by co-precipitation of metals from an aqueous solution (pH = 2) containing stoichiometric amounts of precursors; procedural details can be found elsewhere [41,42]. Metal salts, Fe(NO$_3$)$_3$·9H$_2$O (Merck), Mn(NO$_3$)$_2$·4H$_2$O (Hinweise ≥ 98%) and (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O (Sarabhai, Batch no.4E740296) were used as precursors. The precipitate, so obtained, was thoroughly washed with hot distilled water, dried overnight at 393 K, crushed, heat treated at 773 K for 5 h, removed from the furnace and again crushed and heat treated for 3 h at 773 K to obtain the desired catalyst.

As mentioned earlier, the oxide powders were transformed in the film form on pretreated Ni supports by oxide-slurry coatings. The oxide coated Ni supports were dried in air and then heated in an electrical furnace at 673 K for 1.5 h so as to obtain an adherent oxide film. Pretreatment of the Ni supports and electrical contacts with the oxide films were made as described previously [32]. The mass of each catalytic film used in the study was ~2 mg cm^{-2}.

2.2.   Characterization of mixed oxides

The structural characterization of the catalyst was made by FT-IR (Varian FT-IR spectrophotometer, model 3100), X-ray diffraction (XRD), BET surface area, transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). XRD powder pattern of the catalyst was recorded on an X-ray diffractometer (Rigaku DMAX III) using Cu-Kα as radiation source (λ = 1.542 Å). The BET surface area was determined by a surface area analyzer (Micrometrics, USA, ASAP 2020 Model). Morphology of the catalytic films has been studied by a transmission electron microscope (TECNAI G^2 FEI). The oxidation states of Fe, Mn, and Mo metals in mixed oxide samples were determined using AMICUS-X-ray photoelectron spectrometer.

2.3.   Electrochemical measurements

Electrochemical studies, namely electrochemical impedance and anodic polarization techniques have been carried out in a conventional three-electrode-single-compartment Pyrex glass cell containing pure Pt-foil (~8 cm^2) and Hg/HgO/1 M KOH (E° = 0.098 V vs. SHE) as counter and reference electrodes, respectively. Instruments and softwares employed in the study were the same as already mentioned in Ref. [42].

The order of the OER with respect to OH$^-$ concentration (p) has been determined by recording anodic E vs. log j curves on each catalyst at varying KOH concentrations, maintaining the ionic strength of the medium (μ) constant. The scan rate and the potential region employed in the study were 0.2 mV s^{-1} and 0.50–0.85 V, respectively. KNO$_3$ (Merck) was used to maintain (μ) constant. Thereafter, three constant potentials in the first linear region of E vs. log j curves of the same Tafel slope (b) values were chosen and values of the j corresponding to these chosen potentials were then noted so as to obtain j vs. C_{OH^-} data for each catalyst at three different constant potentials. Subsequently, the linear, log j vs. log C_{OH^-}, plots at constant potentials were constructed and thus, the order was determined by measuring the slope of the straight.

3.   Results and discussion

3.1.   FT-IR

Fig. 1 shows the FT-IR spectra of MnMoO$_4$ and its substituted products. The FT-IR spectrum of MnMoO$_4$ shows seven absorption bands at ~945, ~929, ~914, ~865, ~798, ~723 and ~664 cm^{-1}. Of these, four absorption bands at 945, 914, 865 and 798 cm^{-1} clearly reveal that α-MnMoO$_4$ has Mo in tetrahedral coordination with oxygen. The band at 945 cm^{-1} could be assigned to the Mo=O group [45,46]. The absorption band at 945 cm^{-1} indicates symmetric MoO$_4$ stretching while those near 865 and 798 cm^{-1} indicate asymmetric MnO$_6$ stretching [45]. Thus, results substantiate the formation of a single phase α-MnMoO$_4$. Further, the feature of the FT-IR spectrum of MnMoO$_4$ changes with Fe introduction. All the three spectra for Fe-substituted MnMoO$_4$ look very similar to that reported for
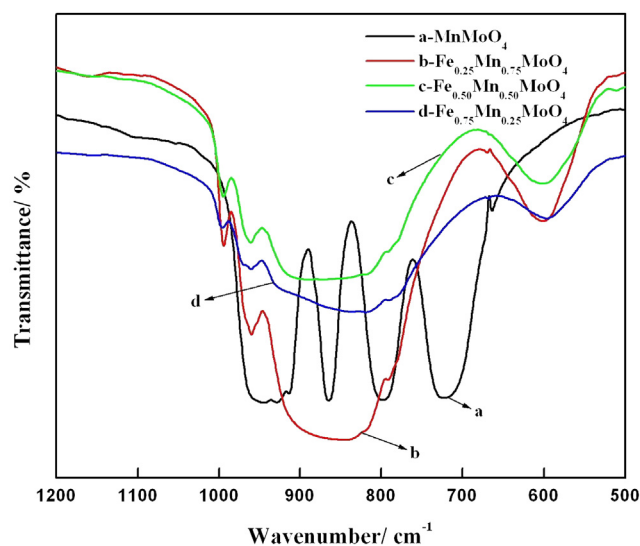

Fig. 1 – FT-IR of Fe$_x$Mn$_{1-x}$MoO$_4$ (x = 0.0, 0.25, 0.50 and 0.75), sintered at 773 K for 8 h.