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# A comparative study of electrocatalytic performance of metal molybdates for the water oxidation

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## ABSTRACT

Binary mixed oxides of molybdenum and a metal of the first-row transition metals with compositional formulae,  $\text{MMoO}_4$  (where  $M = \text{Cr, Fe, Mn, Co, Ni, Cu}$  or  $\text{Zn}$ ), were prepared by a microwave-assisted co-precipitation method and their electrocatalytic activities have been investigated for oxygen evolution reaction (OER) in 1 M KOH. Materials were characterized for structural and electrocatalytic surface properties using FT-IR, XRD, TEM, BET, XPS, cyclic voltammetry (CV) and anodic Tafel polarization techniques. The crystallite size of oxides ranged between ~17 and ~41 nm. For electrochemical studies, oxides obtained in powders form were produced in the thin-film form on the pretreated glassy carbon (GC) support. It has been observed that among electrocatalysts investigated, the  $\text{CoMoO}_4/\text{GC}$  electrode was the greatest OER active while that the  $\text{MnMoO}_4/\text{GC}$  electrode was the least active. The OER produced low Tafel slopes, ~36, ~43 and ~46 mV respectively on  $\text{FeMoO}_4$ ,  $\text{CoMoO}_4$  and  $\text{CuMoO}_4$  while it showed the higher Tafel slopes on  $\text{CrMoO}_4$  (~57 mV),  $\text{NiMoO}_4$  (~71 mV) and  $\text{MnMoO}_4$  (~89 mV).

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## Introduction

The electrochemical splitting of water is the simplest and an attractive process for converting electrical energy into a clean and renewable hydrogen fuel [1,2]. The water electrolysis is comprised of two half-cell reactions,  $\text{H}_2$  evolution (HER) and  $\text{O}_2$  evolution (OER). The water oxidation reaction is energetically more challenging, as it involves  $4e^-$  to produce a single  $\text{O}_2$  molecule.  $\text{RuO}_2$  and  $\text{IrO}_2$  [3,4] are presently considered as the best water oxidation catalysts, however, these oxide catalysts are scarce and pretty costly which restrict their large-scale

applications. It is, therefore, desired to develop efficient, robust and low-cost catalysts for OER from water [5–8]. Efforts are already continued in this direction and out of researches carried out, transition metal mixed oxides of spinel (mainly Co-based [9–22]) and perovskite (mainly  $\text{LaNiO}_3$  [23–26],  $\text{LaCoO}_3$  [27] and their substituted derivatives [28,29]) families are considered as promising electrode materials for OER in alkaline solutions and have been studied in detail [30–33]. Some new active electrode materials containing Co were also recently discovered, such as  $\text{Co}_3\text{O}_4$  nano-clusters [34], Ni–Co–S nano-sheets [35], a robust molecular catalyst based on cobalt-cored

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polyoxometalate [36] and perovskite oxide ( $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ ) [37]. The latter has one order of magnitude higher intrinsic activity than  $\text{IrO}_2$  in alkaline solutions.

Recently, a novel series of transition metal complex oxides with nominal compositional formulae,  $\text{MMoO}_4$  (where  $M = \text{Mn, Fe, Co or Ni}$ ) [38,39] and their substituted products [39–42] have been reported as active electrocatalysts for OER in alkaline solutions. These novel metal oxides have OER activities similar to those of active Co-based spinel oxides [9–20,43]. In these studies, oxide catalysts were deposited on the nickel support. The latter is known to influence the electrocatalytic properties of the catalyst over layer [38]. Further, the catalyst loadings on Ni were not similar and no effort has been made to determine their intrinsic catalytic activities also. Under these conditions, it is not possible to know the comparative activities of metal molybdates towards the OER.

We have, therefore, synthesized binary oxides of molybdenum with a metal of the first transition metal series, i.e. Cr, Mn, Fe, Co, Ni, Cu or Zn, using a microwave-assisted co-precipitation. To avoid any significant influence of the metal support on the catalyst overlayer, the glassy carbon (GC) has been used as the support material. The catalyst loading ( $\Gamma$ ) was kept constant and low ( $0.2 \text{ mg cm}^{-2}$ ) so as to make almost all the catalyst sites available for the OER. Detailed results of the investigation are described in this paper.

## Experimental section

### Oxide catalysts preparation

Binary oxides of molybdenum and a metal belonging to the first-transition metal series having molecular formulae,  $\text{MMoO}_4$  (where  $M = \text{Cr, Mn, Fe, Co, Ni, Cu or Zn}$ ) were prepared by a microwave-assisted co-precipitation method. The precursors used were  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (AR, BDH),  $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  (Merck, India),  $\text{Fe}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$  (Merck, India),  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Merck, India),  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Merck, India),  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (AR, CDH),  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  (AR, CDH) and  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  (Merck, India). All precursors were used as such without further purification. In a particular synthesis of 100 mg of  $\text{CrMoO}_4$ , 188.81 mg of  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and 83.30 mg of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  were dissolved in double distilled water separately and both the solutions were then mixed together to form a homogeneous mixture. pH of the solution maintained between 7 and 8 with the aid of ammonia solution [44] and it was then exposed to microwave radiation for 5 min at 800 Watt power with a pause of 15 s after every 30 s. The precipitate, so obtained, was left overnight, centrifuged [45], repeatedly washed with hot double distilled water and then dried in a vacuum oven at 393 K overnight. Finally, the residue was crushed, heat treated at 773 K for 8 h, as mentioned previously [42]. Similarly, other oxides of the investigation were also synthesized. For simplicity, chromium molybdate, manganese molybdate, iron molybdate, cobalt molybdate, nickel molybdate, copper molybdate and zinc molybdate have been represented as CrMo, MnMo, FeMo, CoMo, NiMo, CuMo and ZnMo, respectively.

### Oxide electrodes preparation

Oxide electrodes were obtained on the pretreated glassy carbon (GC) support by ink-suspension coatings as described elsewhere [46]. After coatings, the oxide electrodes (oxide/GC) were first dried in air for 2 h and electrical contact was then made for use in the electrochemical study as mentioned previously [28]. In contrast to loadings of similar oxide films on Ni already studied [38,39,44,47], a considerably low loading of the oxide catalyst on GC (i.e.,  $0.2 \text{ mg cm}^{-2}$ ) was kept and maintained constant.  $0.5 \text{ cm}^2$  of a geometrical area of the oxide electrode was used in each investigation.

### Material characterization

Structural characterization of materials was carried out by FT-IR (Varian FT-IR spectrometer, model 3100), X-ray diffraction (BRUKER D8 ADVANCE ECO), transmission electron microscopy (TEM TECNAI 20G<sup>2</sup>), and X-ray photoelectron spectroscopy (PHI 5000 Versa Prob II, FEI Inc.). The Cu-K $\alpha$  radiation source ( $\lambda = 1.54184 \text{ \AA}$ ) was used in the XRD study. The XPS study of the catalyst samples was performed using the Al K $\alpha$  source and a pass energy of 23.5 eV. All binding energy values were charge corrected to the C 1s signal (284.6 eV). The BET surface area of samples was determined by a surface area analyzer (Micrometrics, USA, ASAP 2020 model).

### Electrochemical characterization

Electrochemical studies, namely cyclic voltammetry (CV), anodic Tafel polarization have been performed in a conventional three-electrode-single compartment Pyrex glass cell. Pure Pt-foil and Hg/HgO in 1 M KOH ( $E^\circ = 0.098 \text{ V vs. SHE}$ ) were used as the counter and the reference electrodes, respectively. Instruments and software employed in the study were the same as already stated in Refs. [40,41]. The OER activity of oxide electrode was determined by recording IR-compensated 'E vs. log j' curves at  $0.2 \text{ mV s}^{-1}$  in the potential region from 0.50 to 0.90 V in 1 M KOH and at 298 K. Prior to record the Tafel curve, the electrode was first cycled between 0.0 and 0.65 V at  $50 \text{ mV s}^{-1}$  for ten runs in 1 M KOH. The catalyst electrodes became stabilized in 3–4 cycles. To determine the resistance of the catalyst electrode (including the solution resistance), the electrochemical impedance (EIS) study of the catalyst electrode in 1 M KOH has also been carried. For the purpose, impedance measurements were performed over the frequency range, 100 kHz - 10 Hz with an ac amplitude voltage of 10 mV.

## Results and discussion

### Structural and surface characterization

#### FT-IR analysis

Fourier transform infrared (FT-IR) spectra of samples were recorded in the frequency range between 4000 and  $400 \text{ cm}^{-1}$ . As molybdate of metals exhibit characteristic stretching vibrational absorption bands in the frequency region, 1200– $400 \text{ cm}^{-1}$ , only the spectral data in the latter frequency region

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