

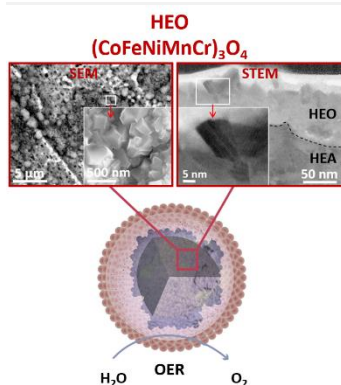
(CoFeNiMnCr)₃O₄ High Entropy Oxide: Innovative Synthesis Route and Application in Electrocatalysis

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The electrochemical water splitting is a promising green technology for the production of hydrogen. However, one of the bottlenecks is the oxygen evolution half-reaction (OER), which could be overcome with the development of a suitable electrocatalyst. Therefore, this study focused on the formulation of a nanostructured spinel type (CoFeNiMnCr)₃O₄ high entropy oxide (HEO) thin film on a CoFeNiMnCr high entropy alloy (HEA) with the innovative synthesis strategy of facile electrochemical and thermal treatment method. The prepared (CoFeNiMnCr)₃O₄ HEO electrocatalyst exhibited a superior overpotential of 341 mV at 10 mA·cm⁻² and a Tafel slope of 50 mV·dec⁻¹ along with remarkable long-term stability for OER in alkaline media. The outstanding catalytic activity and stability could serve as a promising catalytic platform for the practical utilization of (CoFeNiMnCr)₃O₄ HEO for the alkaline OER process.

Introduction

Global energy consumption is constantly increasing to satisfy the demands of the human population [1]. The dominant source of energy is still based on fossil fuels, which are associated with environmental pollution and climate change. Therefore, the development and utilization of green energy technologies are of great importance to achieve a renewable energy landscape. The electrochemical water splitting is considered a promising approach to address this problem [2]. The water splitting process consists of hydrogen and oxygen evolution reactions (HER and OER), whereby the OER represents the bottleneck of the overall water splitting process due to the intrinsically sluggish reaction kinetics [3]. Therefore, substantial efforts are being put into developing effective, stable, available, and affordable electrocatalysts. Recently, high-entropy oxides (HEO), were suggested as a new catalytic platform for efficient electrocatalysts, as the high-entropy effect enables the incorporation of five or more elements in (near)equimolar ratios, offering more opportunities to tune the catalytic properties than conventional electrocatalysts [4]. However, the synthesis strategies to obtain HEO electrocatalysts can be very complex. Therefore, it is necessary to simplify and refine the synthesis methods. In line with all mentioned, this study aimed to synthesize a (CoFeNiMnCr)₃O₄ HEO thin film on a conductive CoFeNiMnCr HEA support using simple and efficient electrochemical and subsequent thermal treatment methods, followed by evaluating the performance of the resulting (CoFeNiMnCr)₃O₄ HEO electrocatalyst for the alkaline OER.

Material and Methods

Synthesis of CoFeNiMnCr and (CoFeNiMnCr)₃O₄:

Firstly, pristine CoFeNiMnCr HEA was prepared with vacuum melting in a tube furnace at 1550 °C for 1 hour (Ar atm.), further annealed at 1000 °C for 25 hours (Ar atm.), then cooled to 800 °C and finished with quenching in H₂O. Then, the (CoFeNiMnCr)₃O₄ HEO thin film on pristine CoFeNiMnCr HEA was prepared in two steps. First, the surface of pristine HEA was electrochemically treated in a two-electrode system [5] at 50 V for 30 min in an ethylene glycol electrolyte containing 0.45 M H₂O and 0.1 M NH₄F. The electrochemically treated HEA was in the second step thermally treated in a muffle furnace under air atm. at 650 °C for 1 h.

Electrochemical characterization: The prepared (CoFeNiMnCr)₃O₄ HEO electrocatalyst was tested for the OER in 1 M KOH in a three-electrode cell system with a platinum mesh and reversible hydrogen electrode (RHE) as counter and reference electrodes, respectively. The electrochemical experiments included linear-sweep voltammetry (LSV) in 1.2–1.7 V at 20 mV·s⁻¹, cyclic voltammetry (CV) in 1.12–1.17 V at 2–20 mV·s⁻¹, electrochemical impedance spectroscopy (EIS) at 1.6 V and 0.01 V over 0.1–10⁵ Hz and chrono-amperometry stability test at 1.6 V for 10 h.

Chemical and physical characterization: In each step of the study, the chemical and physical structure of all materials were characterized by different advanced analyzing techniques (SEM, S/TEM, XRD, XPS, and Raman). The water contact angle was also determined and the surface free energy was calculated with the Neumann Equation of State.

Results and Discussion

Pristine CoFeNiMnCr HEA solidified into a few 100 μm large grains with a primary matrix phase and secondary phase particles in the shape of rods and blocks located within grains and grain boundaries. The matrix phase consisted of equal atomic portions of all 5 metals, while the secondary particles corresponded to M_{23}C_6 -type carbides and Mn_2O_3 oxides. The pristine CoFeNiMnCr HEA surface was further electrochemically treated, which resulted in the formation of a microporous structure with nanopits and incorporated fluoride species into the solid solution matrix derived from the electrolyte. The breakdown of the natural passivity and removal of carbide and oxide particles contributed to the creation of a suitable surface more susceptible to oxidation during thermal treatment causing the formation of $(\text{CoFeNiMnCr})_3\text{O}_4$ HEO. The newly formed $(\text{CoFeNiMnCr})_3\text{O}_4$ HEO surface on CoFeNiMnCr HEA support had a discontinuous ribbon- and ball-type oxide morphology consisting of nanocrystals different in size up to 500 nm. The $(\text{CoFeNiMnCr})_3\text{O}_4$ HEO thin film with a thickness of around 100 nm consisted of mostly oxygen anion (O^{2-}) and near equal atomic portions of all 5 metal cations in mixed valence states ($\text{Co}^{2+} / \text{Co}^{3+}$, $\text{Fe}^{2+} / \text{Fe}^{3+}$, $\text{Ni}^{2+} / \text{Ni}^{3+}$, $\text{Mn}^{2+} / \text{Mn}^{3+} / \text{Mn}^{4+}$, $\text{Cr}^{3+} / \text{Cr}^{6+}$), which is the characteristic binding configuration in cubic spinel $(\text{CoFeNiMnCr})_3\text{O}_4$ HEO. The prepared electrocatalyst was further tested for catalytic activity toward OER. The LSV curve showed an onset

potential of 1.571 V and an overpotential of 341 mV at a current density of $10 \text{ mA}\cdot\text{cm}^{-2}$. The Tafel plot acquired from the LSV curve gave a Tafel slope of $50 \text{ mV}\cdot\text{dec}^{-1}$. Furthermore, the Nyquist plot constructed from EIS data was elucidated with a simple Randle equivalent circuit, which consisted of electrolyte resistance, charge transfer resistance (R_{ct}) over the electrolyte-electrode interface, and constant-phase element (CPE), whereby the R_{ct} was fitted with a value of 18Ω . The double-layer capacitance (C_{dl}) and electrochemically active surface area (EASA) values obtained from CV measurements were $99.22 \mu\text{F}$ and 2.48 cm^2 , respectively. Altogether, a small Tafel slope, low R_{ct} , high C_{dl} , and high EASA indicated a rapid electron transfer at the electrode-electrolyte interface and the presence of many catalytically active sites to boost the OER performance [6]. Moreover, the water contact angle and approximated surface free energy were $73.2 \pm 1.3^\circ$ and $39.7 \pm 0.8 \text{ mJ}\cdot\text{m}^{-2}$, respectively. Since the electrocatalyst showed a hydrophilic surface (contact angle $< 90^\circ$) and a high surface free energy, high catalytic activity toward OER was somehow expected. Nevertheless, the electrocatalyst maintained a current density of approx. $18\text{--}19 \text{ mA}\cdot\text{cm}^{-2}$ under 1.6 V for 10 h. After the stability test, no major overall changes in (electro)chemical and physical properties were observed indicating very good stability. High catalytic activity and stability of the electrocatalyst are believed to be induced by the characteristic core effects of HEO materials.

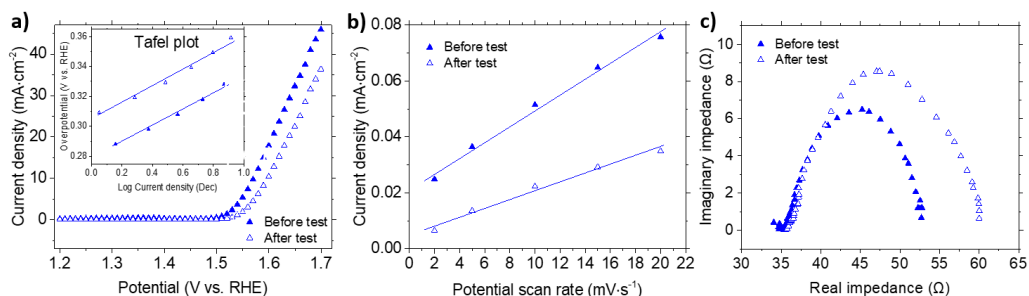


Figure 1. a) LSV curve with inset of Tafel plot, b) CV plot with C_{dl} , and c) Nyquist plot of $(\text{CoFeNiMnCr})_3\text{O}_4$ HEO for OER process.

Conclusions

This study showed a state-of-the-art and facile synthesis approach for the development of a spinel $(\text{CoFeNiMnCr})_3\text{O}_4$ HEO thin film electrocatalyst on an immediately available, conductive CoFeNiMnCr HEA support with excellent activity and stability with respect to the OER process.

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