

High entropy materials dispersed on carbon substrates as water electrolysis catalysts

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Introduction

The hydrogen and the oxygen evolution reactions (HER and OER, respectively) in acid media are particularly challenging and of special interest, this due to being the reactions taking place in proton exchange water electrolyzers (PEMWE).[1] At present Pt and Ir are employed as electrocatalysts for the HER and the OER, respectively, which in turn limits the wide implementation of PEMWE technology (key technology for the production of green hydrogen) because of the limited natural reserves of noble metals.[2]

Hence there is the pressing need to seek for catalysts formulations with the lowest concentration of Pt or Ir, or ultimately noble metal free formulations. In this regard, HEMs have gained attention for challenging electrochemical reactions such as the HER and the OER. High entropy materials (HEMs) are made of at least five metal components distributed homogeneously within a single phase. Due to the variety of atomic sizes and the concomitant high lattice strain in HEMs the atomic diffusion is restricted, which results in robust structural stability. Moreover, the multielement nature of HEMs results in a diverse absorption sites leading to synergy effects.

Several works suggest that HEMs are more stable and active than their simpler counterparts for both HER and OER in alkaline media, however, there is not enough evidence to suggest that this is also true in acid media.[3] Hence, the aim of this study is to elucidate the corrosion of C-supported and unsupported HEMs during OER at different pH conditions.

Experimental

MnNiCoFeCu high entropy oxides (HEO) were prepared from the co-precipitation of the corresponding metal chlorides in aqueous alkaline solution (this solution containing carbon black vulcan XC 72R for supported catalysts with a 10wt.% total metal content). After co-precipitation, HEMs were recovered by centrifuge and washed with deionised water. Finally, materials were recovered by freeze-drying, and annealed in N₂ (550 °C, 5 C min⁻¹, 3 h). Prior to electrochemical characterisation, catalyst ink (2 mg_{cat}, 740 μL_{H₂O}, 250 μL_{isop}, 10 μL_{nat}) were drop casted onto an area of 1 x 1 cm² of Toray carbon paper, to obtain a catalyst loading of 100 μg_{cat} cm⁻². HEMs were assessed towards the OER in different electrolytes: namely 1.0, 0.1, 0.01 M KOH and 0.01, 0.05 and 0.1 M HClO₄ and H₂SO₄. Metal dissolution in the electrolyte was determined by ICP after 12 h chronopotentiometry at 10 mA cm⁻². Whilst catalyst characterisation (XRD, XPS, SEM) was performed before and after OER.

Results and discussion

As prepared HEMs were amorphous as indicated by X-ray diffraction (XRD), and a small-crystallite size spinel structure (PDF ref 01-071-6336) evolved after annealing in air and N₂ at 550 °C (Figure 1a). However, according to XRD characterisation heat treatment at 850 °C resulted in CuO (PDF ref. 01-080-1916) segregation from the HEM phase.

As an example of electrochemical characterisation towards OER, activity and stability of HEO-550C-air in 1.0 M KOH are shown in figure 1b and 1c, respectively. As a general trend, for all HEMs activation is observed by linear sweep voltammetry (LSV) after cycling voltammetry (CV, 1-1.6 V_{RHE}, 25 cycles). Based on chronopotentiometry (CP), as well on LSV performed after the CP stress test, no degradation was observed in KOH electrolyte after 12 h at 10 mA cm⁻². On the contrary, as-synthesised samples suffer from fast dissolution in acid electrolyte, even without reaction. Nevertheless, after annealing at 550 °C the stability against corrosion improved considerably.

Conclusions

HEMs present improved stability towards OER and HER in alkaline media compared to their mono and bi-metallic counterparts. However, based on our work there are no conclusive evidence yet to state that HEMs are more stable in acid media. Supporting HEMs in carbon materials (e.g., Carbon black, graphene) is an efficient route to reduce the metal loading on the electrode without compromising activity nor stability.

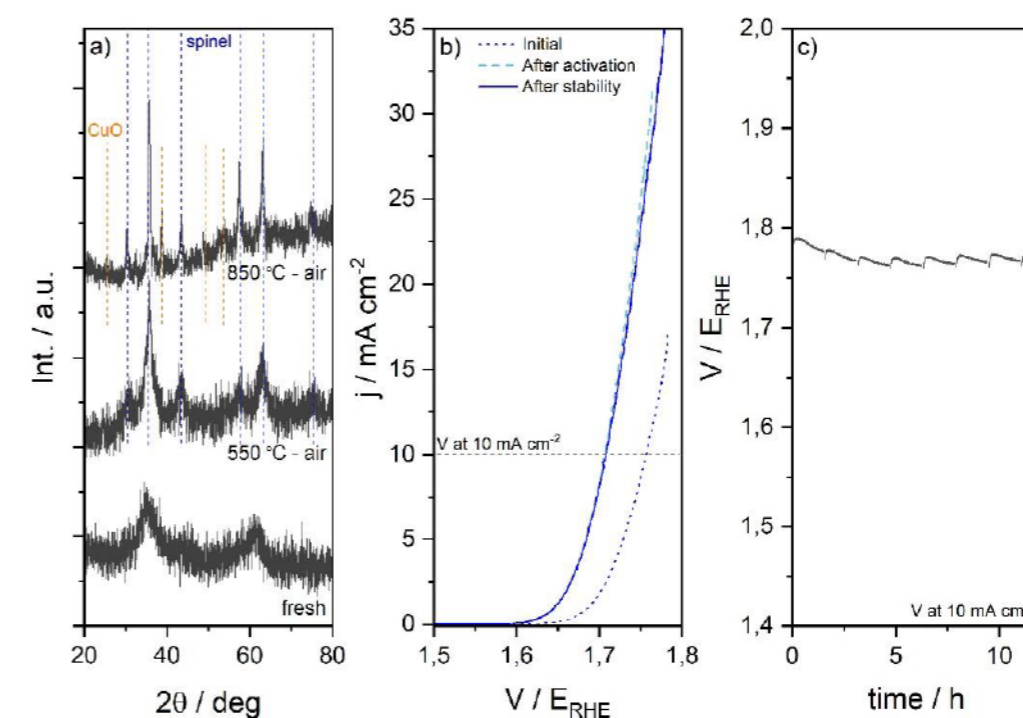


Figure 1. a) XRD patterns for MnNiFeCoCu HEO as prepared, annealed in air at 550 and at 850 °C, b) activity towards OER determined by linear sweep voltammetry in 1.0 M KOH for HEO-550C-air and c) stability by chronopotentiometry at 10 mA cm⁻² for 12 h.

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