

CHAPTER-6

General conclusions and overview

6.1. Summary

In conclusion, a series of self-supported CoFe-PBAs were developed by the metal hydroxide template route. The self-supported PBAs were converted into corresponding Fe-Co(OH)₂-Co(O)OH active catalysts through anodic potential-driven bulk reconstruction.

In chapter 2, we have explored the effect of applied potential and time on the electrochemical bulk reconstruction of CoFe-PBA@CC. Moreover, the effect of applied potential and time on the structure, morphology, and OER activity of the active catalysts have been well established. Interestingly, our study has shown that the active catalysts have similar structure and morphology with varying Fe content.

The effect of the modulation of structure and properties of the PBA precatalysts on the electrochemical bulk reconstruction has been investigated in chapter 3. In addition, the effect of the modulation of the PBA precatalysts on the structure and properties of the active catalysts as well as on their catalytic OER activity has also been demonstrated. The results have established the facile transformation of PBA precatalysts by tuning the structure and properties. Although active catalysts have the same crystal structure and morphology, those have different atomic and electronic structures as well as water oxidation activity. The high catalytic activity and stability of electrochemically

reconstructed nanosheets can be attributed to the tuned atomic and electronic structure, which stabilize the reactive intermediates and lower the free energy barrier to promote the catalytic performance.

In chapter 4, we have demonstrated the cathodic as well as anodic bulk reconstruction of PBA precatalysts to form two different active catalyst structures at the cathode and anode. The effect of Fe-doping in the active catalysts has been investigated to improve the water splitting activity. Interestingly, the active catalysts at cathode and anode have different structures, thickness as well as Fe-content. The coupling of anodic and cathodic active catalysts has been attained to get the overall water splitting activity.

In chapter 5, we have developed a hybrid water electrolyzer cell by replacing the anodic OER with electrocatalytic benzyl alcohol oxidation. We have integrated the benzyl alcohol oxidation with electrochemical HER to produce high-value-added benzoic acid as well as H₂ fuel. Our study has established that the active catalyst can reach the 1 A cm⁻² current density at low potential than the onset of OER. Moreover, ~100% conversion of benzyl alcohol into benzoic acid with improvement in the hydrogen evolution efficiency has also been determined.

In our work, the catalytic OER activity of the active catalysts varied from 220 mV-300 mV to produce a 10 mA cm⁻² current density. The HER overpotential was found to be 155 mV overpotential to reach the same cathodic current density. The overall water splitting was also achieved with the reconstructed catalysts at 1.58 V cell voltage for 20 mA cm⁻² current density. The stability of the active catalysts also varied from 24 h to 50 h for OER. The electrochemically reconstructed active catalysts furnished outstanding performance compared to the noble metal RuO₂ as well as hydrothermally prepared CoHC@CC and CoFe-LDH@CC. Moreover, the superior performance of the

reconstructed catalysts was also demonstrated when compared with literature reported LDH, PBA-derived materials, and self-supported catalysts (Table 6.1).

Table 6.1. Comparison of the OER activity of electrochemically synthesized active catalysts with the literature-reported catalysts.

Active catalysts	Current density (mA cm ⁻²)	Overpotential (mV)	Electrolyte	Reference
AC-1	10 mA cm ⁻²	250 mV	1.0 M KOH	Chapter-2
AC-2	10 mA cm ⁻²	270 mV	1.0 M KOH	Chapter-2
AC-3	10 mA cm ⁻²	300 mV	1.0 M KOH	Chapter-2
AC-4	10 mA cm ⁻²	300 mV	1.0 M KOH	Chapter-2
AC-5	10 mA cm ⁻²	300 mV	1.0 M KOH	Chapter-3
AC-6	10 mA cm ⁻²	249 mV	1.0 M KOH	Chapter-3
AC-7	10 mA cm ⁻²	220 mV	1.0 M KOH	Chapter-4
AC-9	10 mA cm ⁻²	260 mV	1.0 M KOH	Chapter-4
Prussian blue analogue-derived catalysts				
NiCoO _x	10 mA cm ⁻²	380 mV	1.0 M KOH	[290]
Co ₃ O ₄	10 mA cm ⁻²	370 mV	1.0 M KOH	[291]
Ni _x P _y	10 mA cm ⁻²	300 mV	1.0 M KOH	[292]
NiCoFeS	10 mA cm ⁻²	320 mV	1.0 M KOH	[293]
(Ni _{0.62} Fe _{0.38}) ₂ P	10 mA cm ⁻²	290 mV	1.0 M KOH	[294]
NiFeP	10 mA cm ⁻²	271 mV	1.0 M KOH	[295]
(NiCo)Se ₂	10 mA cm ⁻²	320 mV	1.0 M KOH	[296]
FeCoO	10 mA cm ⁻²	310 mV	1.0 M KOH	[297]
CoFeB	10 mA cm ⁻²	261 mV	1.0 M KOH	[298]
O-NiCoP	10 mA cm ⁻²	310 mV	1.0 M KOH	[299]
Carbon cloth-supported catalysts				
Co-P/NC	10 mA cm ⁻²	330 mV	1.0 M KOH	[300]
CoMoO ₄	10 mA cm ⁻²	290 mV	1.0 M KOH	[301]
CoFe ₂ O ₄	10 mA cm ⁻²	378 mV	1.0 M KOH	[302]
NiMoP ₂	10 mA cm ⁻²	330 mV	1.0 M KOH	[303]
CoP	10 mA cm ⁻²	281 mV	1.0 M KOH	[131]
(Ni,Co) _{0.85} Se	10 mA cm ⁻²	300 mV	1.0 M KOH	[304]
Layered double hydroxide catalysts				
Co ₂ Fe-LDH	10 mA cm ⁻²	420 mV	1.0 M KOH	[305]
ZnCo-LDH	10 mA cm ⁻²	340 mV	1.0 M KOH	[306]
NiFe-LDH	10 mA cm ⁻²	259 mV	1.0 M KOH	[307]
CoMn-LDH	10 mA cm ⁻²	350 mV	1.0 M KOH	[308]
NiFe-LDH	10 mA cm ⁻²	290 mV	1.0 M KOH	[309]
CoCr-LDH	10 mA cm ⁻²	400 mV	1.0 M KOH	[310]
NiCo-LDH	10 mA cm ⁻²	367 mV	1.0 M KOH	[311]
CoFe-LDH	10 mA cm ⁻²	280 mV	1.0 M KOH	[312]
NiFeMo-LDH	10 mA cm ⁻²	280 mV	1.0 M KOH	[313]
CoFeV-LDH	10 mA cm ⁻²	318 mV	1.0 M KOH	[314]

6.2. Future scope and perspective

We have established the bulk electrochemical reconstruction of a series of self-supported CoFe-PBAs into ultrathin Fe-Co(OH)₂-Co(O)OH nanosheets. The tuned structural as well as electronic properties of the nanosheets with atomic level thickness results in excellent catalytic activity and stability. The thesis work can be further extended to achieve the following points:

(i) The structure of PBA precatalysts can be modulated by tuning the A sites as well as the B sites of the PBAs. The PBAs with the new structure, morphology, and properties can be designed and utilized as precatalysts for electrochemical reconstruction.

(ii) As the electrochemical cathodic reconstruction of self-supported PBA precatalysts has been demonstrated by us, this method can be applied to various PBA precatalysts and can be further explored to achieve new active catalysts for electrochemical hydrogen evolution reaction. In addition, the PBA-derived active catalysts can be further demonstrated for the overall water splitting at high current density.

(iii) The implementation of electrochemically reconstructed active catalysts for water splitting requires mechanistic insight into the active catalyst structure and reaction mechanism of water splitting. Therefore, theoretical investigations namely density functional theory (DFT) can be employed to correlate the structure and activity of the active catalysts.

(iv) The electrochemically reconstructed PBA-derived active catalysts can be employed for the electrocatalytic organic oxidation reaction replacing the kinetically slow anodic OER. The active catalysts can be utilized for the electrocatalytic oxidation of amine, alcohols, glucose, biomass, and urea.

We have already established the electrocatalytic oxidation reaction of benzyl alcohol, benzylamine, phenol, and 5-hydroxymethyl furfural with PBA-derived catalysts. However, these works are beyond the scope of the thesis.

Overall, the work of this thesis provides a clear idea of precatalyst design, their anodic and cathodic activation, and the application of the active catalysts in electrochemical energy conversion processes. The structure-activity relationship of precatalyst-active catalyst and electrocatalytic activity will also be helpful for the designing of highly efficient catalyst systems.