Efficient Water Electrolysis Using Ni\textsubscript{2}P as a Bifunctional Catalyst: Unveiling the Oxygen Evolution Catalytic Properties of Ni\textsubscript{2}P

Lucas-Alexandre Stern\textsuperscript{§} and Xile Hu\textsuperscript{*}

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Abstract: The excellent bifunctional catalytic activity of nickel phosphide (Ni\textsubscript{2}P) for water splitting is reported. Ni\textsubscript{2}P, an active hydrogen evolving catalyst, is shown to be highly active for oxygen evolution. Only 290 mV of overpotential is required to generate a current density of 10 mA cm\textsuperscript{-2} in 1 M KOH. Under oxygen evolving conditions, Ni\textsubscript{2}P undergoes structural modification to form a Ni\textsubscript{2}P/NiO\textsubscript{x} core-shell assembly, the catalytic active species. Ni\textsubscript{2}P is applied on both electrodes of an alkaline electrolyser and a current density of 10 mA cm\textsuperscript{-2} is generated at 1.63 V.

Keywords: Electrochemistry · Janus catalyst · Ni\textsubscript{2}P · Oxygen evolution · Water splitting

1. Introduction

Global scale exploitation of renewable energy resources, such as wind and solar energy, demands efficient energy storage techniques. Electrochemical water splitting is one of the most attractive method for energy storage.\textsuperscript{[1]} Water splitting is subdivided in two half-reactions, namely, the hydrogen evolution reaction (HER, Eqn. (1)) and the oxygen evolution reaction (OER, Eqn. (2)).

\begin{align*}
2 \text{H}^+ + 2 \text{e}^- &\rightarrow \text{H}_2 \\
2 \text{H}_2\text{O} &\rightarrow 4 \text{H}^+ + 4 \text{e}^- + \text{O}_2
\end{align*}

Both reactions require electrocatalysts to proceed efficiently. State-of-the-art catalysts rely on the use of scarce and expensive noble metals, e.g. platinum.\textsuperscript{[2]} While promising Earth-abundant water-splitting catalysts have been developed, only few materials are able to catalyse both HER and OER in the same media. Bifunctional catalysts made from Earth-abundant metals would facilitate production and implementation of electrolyser devices. The reported bifunctional systems include Co,\textsuperscript{[2]} Ni,\textsuperscript{[3]} Cu,\textsuperscript{[4]} NiFe LDH,\textsuperscript{[5]} NiFeO\textsubscript{x},\textsuperscript{[6]} NiCo\textsubscript{S}_x,\textsuperscript{[7]} Ni\textsubscript{2}P,\textsuperscript{[8]} CoO\textsubscript{x},\textsuperscript{[9]} CoP,\textsuperscript{[10]} FeP.\textsuperscript{[11]}

In this article, we show that Ni\textsubscript{2}P, an active HER catalyst, is efficient for the oxygen evolution reaction in alkaline medium. Under OER conditions, the material forms a Ni\textsubscript{2}P/NiO\textsubscript{x} core-shell heterostructure. This assembly generates a current density of 10 mA cm\textsuperscript{-2} at an overpotential of only 290 mV.\textsuperscript{[12]} The Janus behaviour of the material permits the fabrication of an efficient alkaline electrolyser using Ni\textsubscript{2}P as catalyst for both the cathode and the anode.

2. Oxygen Evolution Activity of Ni\textsubscript{2}P

The Ni\textsubscript{2}P nanoparticles were prepared via a solid-state thermal reaction previously reported by our group.\textsuperscript{[13]} Briefly, a phosphorus source, NaH\textsubscript{2}PO\textsubscript{4} (0.66 g, for analysis, Acros), and a nickel salt, NiCl\textsubscript{2}.6H\textsubscript{2}O (0.3 g, ReagentPlus\textsuperscript{®}, Aldrich), were ground together at ambient atmosphere and then placed in a quartz boat. This was then transferred into a tubular furnace and heated at 250 °C under a constant flow of nitrogen. The obtained powder was further ground and the impurities were washed off from the product using copious amount of distilled water. The product was then dried in an oven at 50 °C for a few hours. X-ray diffraction of the obtained powder is shown in Fig. 1b. The diffraction signal was compared

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{a) TEM image of polycrystalline Ni\textsubscript{2}P, b) Powder X-ray diffraction pattern of the Ni\textsubscript{2}P nanoparticles. Adapted by permission of The Royal Society of Chemistry from ref. [12].}
\end{figure}
to the reference diffraction pattern obtained from the International Center of Diffraction Data. The overlapping signals indicated the successful synthesis of pure phase Ni$_2$P. The transmission electron microscopy (TEM) image shows that the Ni$_2$P nanoparticles have an averaged size of 50 nm and are coated with a thin amorphous layer (Fig. 1a).

To evaluate the catalytic activity of Ni$_2$P for the oxygen evolution reaction, linear sweep voltammetry scans were performed in 1 M KOH. The catalytic activity of nickel phosphide was measured and compared to various nanomaterials including IrO$_2$, Ni, NiO$_2$, and an electrodeposited Ni(OH)$_2$ film (Fig. 2a). IrO$_2$ (99.9% Ir, abcr) and NiO$_2$ (99.8% trace metals basis, Aldrich) were used as received, while Ni nanoparticles and Ni(OH)$_2$ film preparation has been reported previously.$^{[14]}$ The loading of IrO$_2$, Ni, NiO$_2$ applied on the glassy carbon electrode was identical to Ni$_2$P loading. Fig. 2a shows that Ni$_2$P nanoparticles catalytic activity is superior to that of the different catalysts evaluated. The overpotential to generate a current density of 10 mA cm$^{-2}$ is only 290 mV for Ni$_2$P. To reach similar current density, IrO$_2$ and Ni(OH)$_2$ requires an additional 40 mV of overpotential compared to Ni$_2$P. Ni and NiO$_2$ drive a current density of 10 mA cm$^{-2}$ at 365 mV of overpotential.

The electrochemical surface area (ESCA) of the materials was assessed and compared. For this purpose, the double-layer capacitance of the materials was calculated. Fig. 2b shows the ESCA of the nickel-based catalysts. The ESCA for the different materials were expressed in terms of surface averaged double layer capacitance. Ni$_2$P have higher surface area for similar loading than other nickel materials: 176.9 µF cm$^{-2}$, followed by Ni(OH)$_2$ 137.2 µF cm$^{-2}$. NiO$_2$ and Ni nanoparticles have smaller ESCA values 68 and 37 µF cm$^{-2}$ respectively. The correlation determined between the ESCA of Ni, NiO$_2$, Ni(OH)$_2$, and their respective catalytic activity at the fixed overpotential of 325 mV cannot be applied to Ni$_2$P. This indicates that high surface area is not the sole reason for the superior catalytic activity of nickel phosphide.

The stability of the nickel phosphide nanoparticles was probed by galvanostatic experiment. Fig. 2c shows that the overpotential to generate 10 mA cm$^{-2}$ increased only of 10 mV over the course of 10 hours indicating high stability of the catalyst. The nickel phosphide oxygen evolution activity was also compared to several state-of-the-art materials (Table 1). It can be seen that Ni$_2$P is more active than many Ni and Co-based oxides, and even IrO$_2$ in base.

3. Ni$_2$P/NiO$_2$ Core-shell Structure: The OER Catalytic Active Species

To identify the nature of the chemical modifications undergone by nickel phosphide during water oxidation, the Ni$_2$P nanoparticles were characterized prior and after catalysis by high-resolution TEM, energy-dispersive X-ray element mapping and X-ray photoelectron spectroscopy (XPS) (Fig. 3). The data indicate that prior to catalysis crystalline

![Table 1. Comparison of the OER catalytic activity of state-of-the-art catalysts. Adapted by permission of The Royal Society of Chemistry from ref. [12].](image_url)

<table>
<thead>
<tr>
<th>Material</th>
<th>Loading (mg cm$^{-2}$)</th>
<th>$\eta$ @ 10 mA cm$^{-2}$ [mV]</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>0.14</td>
<td>377</td>
<td>This work</td>
</tr>
<tr>
<td>NiO$_x$</td>
<td>0.14</td>
<td>364</td>
<td>This work</td>
</tr>
<tr>
<td>Ni(OH)$_2$</td>
<td>0.14</td>
<td>331</td>
<td>This work</td>
</tr>
<tr>
<td>NiP</td>
<td>0.14</td>
<td>290</td>
<td>This work</td>
</tr>
<tr>
<td>NiO$_x$</td>
<td>0.02</td>
<td>360</td>
<td>[15c]</td>
</tr>
<tr>
<td>$\alpha$-Ni(OH)$_2$</td>
<td>0.20</td>
<td>331</td>
<td>[15d]</td>
</tr>
<tr>
<td>$\beta$-Ni(OH)$_2$</td>
<td>0.20</td>
<td>444</td>
<td>[15d]</td>
</tr>
<tr>
<td>NiCo$_2$O$_4$</td>
<td>0.53</td>
<td>565</td>
<td>[15c]</td>
</tr>
<tr>
<td>NiFe-LDH</td>
<td>0.20</td>
<td>320</td>
<td>[16]</td>
</tr>
<tr>
<td>CoO$_2$@CN</td>
<td>0.42</td>
<td>410</td>
<td>[9]</td>
</tr>
<tr>
<td>BSCF82</td>
<td>0.25</td>
<td>320</td>
<td>[17]</td>
</tr>
<tr>
<td>IrO$_2$</td>
<td>-</td>
<td>320</td>
<td>[15b]</td>
</tr>
<tr>
<td>IrO$_2^{+}$</td>
<td>0.35</td>
<td>275</td>
<td>[18]</td>
</tr>
</tbody>
</table>

* Catalytic activity measured in acidic conditions
nanoparticles of Ni,P are embedded in an amorphous matrix, which is oxygen-rich, contains phosphorus, and is free of any metallic content (Fig. 3a–e). This layer likely consists of residual P₂O₅ as a side product of the catalyst synthesis. Important structural change can be observed on the catalytic material after oxygen evolution for 1 h. The HRTEM image (Fig. 3g) shows that after OER, the layer surrounding the nanoparticles is composed of ultrafine particles of about 2–3 nm diameter. Closer inspection of the particles in the layer revealed the presence of lattice registry indicative of crystalline materials. Fast Fourier transform (FFT) (Fig. 3g inset) allowed measurement of the crystal lattice spacing of the fine particles. The distance between two crystal planes is characteristic of NiO₂ material. A crystal lattice spacing of the material’s core was also determined and it is characteristic of the (100) facet of Ni,P. Elemental mapping images of the catalyst after OER (Fig. 3h–k) clearly show the Ni,P/NiO₂ core-shell heterostructure that the material adopts under oxidative conditions. Nickel is present in both layers of the material. Oxygen coats homogeneously the particle surface.

Phosphorus is present only in the core. The structure of the material was further corroborated by XPS measurements (Fig. 3l). Electrochemical measurements also validate the formation of a Ni,P/NiO₂ core-shell heterostructure during OER. The oxidation peak observed is indicative of the NiO₂/Ni⁺ oxidation in many nickel oxide hydroxide and bimetallic NiFeOₓ OER catalysts [13,15a,15d,20]. The pre-activation of the catalyst is, thus, hypothesized to allow the in situ formation of a stable Ni,P/NiO₂ core-shell heterostructure with improved OER catalytic properties.

The enhanced catalytic activity of the Ni,P/NiO₂ core-shell structure compared to other NiO₂ catalysts for OER has two possible origins. On one hand the unique assembly provides significant improvement in electron conduction. On the other hand, Ni,P allows the in situ formation of ultrafine nanoparticles of NiO₂, which allows higher active site exposure. Synergistic effects, which warrant further investigation, may play a role as well.

4. Efficient and Inexpensive Alkaline Electrolyser Fabricated Using Ni,P as Catalyst

The hydrogen evolving capabilities of Ni,P have been reported recently [13,22]. Given the presented OER catalytic activity, an alkaline electrolyser using Ni,P as both cathode and anode catalyst was fabricated. The catalyst support used for this device was nickel foam. The loading of catalyst applied on the two Ni foam was 10 mg cm⁻². Fig. 4 shows the measured catalytic activity of the alkaline electrolyser in 1 M KOH. The activity is compared with bare Ni foams as reference. To generate a current density of 10 mA cm⁻² the alkaline electrolyser employing Ni,P as catalyst only requires 400 mV of overpotential while bare Ni foams demands 560 mV of overpotential to reach the same value of current density [12]. During water electrolysis, the cathode and the anode were separated using a glass frit membrane to avoid any undesirable reactions. The stability of the alkaline electrolyser was tested via galvanostatic measurement. A constant current density of 10 mA cm⁻² was applied for 10 h. Fig. 4 inset shows that the overpotential hardly increases during the course of the experiment and indicates high stability of the fabricated electrolyser. To confirm that all the current generated results from water splitting, the total pressure increase due to hydrogen and oxygen evolution was recorded using a pressure sensor during the electrolysis. The pressure sensor data allows the amount of gas evolved to be calculated over the course of the water electrolysis. The
the Faradaic efficiency of the alkaline electrolyser. Fig. 5 illustrates that the experimental and theoretical amount of gas evolved overlaps indicative of a quantitative Faraday efficiency for the device. Ni,P is thus an active and stable bifunctional catalyst for water splitting in alkaline media.

5. Conclusion

In summary, Ni,P is an active catalyst for OER in alkaline conditions. The catalyst is prepared via a simple solid-state reaction from abundant and cheap reagents. The catalytic active species is a Ni,P/ NiO core-shell heterostructure that is formed in situ under OER conditions. The catalytic activity is superior to several state-of-the-art catalysts. The Janus behaviour of the catalyst allows the fabrication of an efficient alkaline electrolyser which generates 10 mA cm$^{-2}$ at an overpotential of only 400 mV. Ni,P shows promise of potential applications for future devices and highlights the potential of Earth-abundant catalysts as viable electrocatalysts for energy conversion devices and fuel cell applications.

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