In situ formation of high performance Ni-phytate on Ni-foam for efficient electrochemical water oxidation

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Abstract:

Electrochemical water splitting in an alkaline electrolyte for large-scale hydrogen production is currently a hot research topic. However, developing high-performance and durable oxygen-evolving electrocatalysts is an ongoing challenge. In this work we prepared Ni-phytate thin films with a bubble-like structure on Ni-foam through an in situ growth process. The resulting material can be used as an oxygen-evolving electrode in basic media without requiring the use of a conductive binder. The Ni-phytate electrode has high catalytic activity ($\eta_{j=10 \text{ mA cm}^{-2}} = 280 \text{ mV}$) and good stability (the current activity remained 95% after 5h) towards OER. This is an effective approach to simplifying the large-scale preparation of catalysts for water-splitting applications.

Keywords: Oxygen evolution reaction; In situ formation; Ni-phytate; Sodium Phytate; Water oxidation

1. Introduction

The increasing energy needs of the future challenge us to develop efficient technologies producing renewable energy [1, 2]. Hydrogen plays a major role as an energy carrier in a future hydrogen economy [3, 4]. Electrochemical water splitting offers a simple way to produce hydrogen and store the electricity, but is limited by the large anodic overpotential associated with the oxygen evolution reaction (OER). IrO₂ and RuO₂ are commonly used as OER catalysts due to their high electrocatalytic activity. However, they are not appropriate for large-scale applications owing to their high cost and the relative scarcity of Ir and Ru [5].

Researchers have therefore been searching for more cost-efficient transition-metal-based (eg Co, Ni) catalysts [6,7,8], especially Ni-based materials, which have good catalytic activity [6,7,9,10]. However, most of oxygen-evolving catalysts must be effectively coated onto current collectors via polymer binders which

generally increase the series resistance [11] and may also block active sites and inhibit diffusion leading to reduced catalytic activity [12]. Fortunately, such problems can be avoided by directly growing active materials on current collectors. Electrochemical treatments of inorganic metal salt solutions aimed at preparing active oxygen-evolving electrodes have been reported [7, 13, 14]. Phytic acid and its salts, known as organic food additives, exist naturally in all plant seeds, many roots and tubers [15, 16]. They are able to chelate numerous different metal ions to form metal-phytate compounds with unique structures owing to the six phosphate groups linked to the inositol ring. However, little attention [8, 17, 18] has been paid to the possibility of using phytate salts as OER electrocatalysts.

In this work, we propose a strategy for the in situ formation of Ni-phytate thin films on a Ni-foam substrate. The binder-free 3D Ni-phytate has a bubble-like structure, which increases the electrochemically active area and exposes more electro-active sites. This material is used directly as an oxygen-evolving anode and exhibits excellent catalytic activity with low overpotential and good stability. This approach thus provides a facile, cost-effective and scalable method of fabricating efficient catalysts for water oxidation.

2. Experimental

2.1 Preparation of electrodes

Firstly, Ni-foams (NFs) (Changsha Liyuan Advanced Material Co., Ltd (China)) were sonicated three times in distilled water and once in alcohol (Aladdin Ltd. (Shanghai, China)). The NFs were then dried in an oven overnight. The in situ formation process was carried out in a three-electrode cell using NF as the working electrode, a parallel-positioned graphite plate as the counter electrode and Hg/HgO as the reference electrode in 0.3 M phytate sodium ($\text{C}_6\text{H}_6\text{O}_{24}\text{P}_6\text{Na}_{12}$: 85-90%, Chengdu Eastern Enterprises (Sichuan, China), treated by spray drying). The electrochemical procedure used to produce Ni-phytate electrodes involves cycling the potential from -1.93 to 2.07 V vs. RHE at a potential sweep rate of 20 mV s^{-1} . This was done for 1, 2, 3, 4 and 5 cycles, to check which electrochemical treatment produced the best electrocatalytic activity. The as-prepared electrodes were rinsed with water and dried in an oven overnight at 80°C .

For comparison, we conducted electrochemical measurements on RuO_2 (Alfa Aesar (U.K)) loaded on a bare NF. The mixed solution containing 5.8 mg of RuO_2 powder, 10 μL Nafion solution (5% wt, Dupont, USA), 375 μL distilled water and 125 μL isopropyl alcohol (Aladdin Ltd. (Shanghai, China)) was dispersed to prepare the catalyst inks for electrochemical testing. Then, 200 μL of the catalyst inks were drop-cast onto NF and dried naturally at room temperature. The loading mass is about 2.3 mg cm^{-2} which is the same as that of the best Ni-phytate electrode.

2.2 Characterization

X-ray diffraction (XRD) studies were carried out on a Fangyuan DX-1000 powder X-ray diffractometer (China) with $\text{Cu K}\alpha$ radiation. The scanning electron microscopy

(SEM) measurements were conducted using a field emission Hitachi S4800 microscope (Japan). Transmission electron microscopy (TEM) was carried out with a FEI Tecnai G2 F20 S (USA). The X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos AXIS ULTRADLD Photoelectron Spectroscopy (UK) with Mg K α radiation. Raman spectroscopy was carried out on a LabRAM HR Raman microscope (Horiba, France) with a laser excitation wavelength of 532 nm. A NICOLET 6700 FTIR spectrophotometer (Thermo Fisher U.S.A.) was used to obtain the attenuated total reflection infrared spectrum (ATR-IR).

2.3 Electrochemical measurements

The electrochemical measurements were performed with an Autolab electrochemical station PGSTAT 128 N potentiostat/galvanostat (Metrohm, Switzerland). All electrochemical measurements were obtained using the three-electrode system described earlier. All the potentials reported in this work were vs. RHE (reversible hydrogen electrode). $E_{(RHE)} = E_{(Hg/HgO)} + 0.059 \times pH + 0.098$, $\eta = E_{(RHE)} - 1.23$ V. Tafel plots were obtained to confirm the onset potential and iR compensation from EIS measurements was applied to all the electrochemical measurements.

3. Results and discussion

The preparation process and chelating mechanism are shown schematically in Fig. 1. Firstly, the NF surface is oxidized to Ni²⁺ at about 0.02 V and the Ni²⁺ ions are immediately captured by the surrounding phytate anions (which have strong chelation properties) to form a thin layer of Ni-phytate. The Ni substrate can then be further oxidized and the Ni ions and phytate anions crosslink to form Ni-phytate complexes resembling metal-organic frameworks [18].

Fig. 1 (a) The in situ growth process and (b) the Ni-phytate chelating mechanism.

As shown in the SEM image (Fig. 2a), the Ni-phytate film is grown in situ on the NF (indicated by the dashed circle). A bubble-like structure can be clearly observed in the formed film - this is generated as a result of H₂ and O₂ evolution when the potential sweeps from -1.93 to 2.07 V. This structure has the advantage of increasing the active area and exposing more electro-active sites. The cross section (Fig. 2b) reveals that the film consists of grains and is up to seven hundred nanometers thick.

Fig. 2 (a, b) SEM images, (c) TEM, SAED (inset of (c)), (d) XRD, (e) ATR-IR, (f) Raman and (g) XPS spectra of Ni-phytate sample.

The TEM image in Fig. 2c further confirms its grainy nature. The selected area electron diffraction (SAED) pattern suggests that the product is in a non-crystalline state. The XRD pattern shown in Fig. 2d exhibits the three diffraction peaks corresponding to the NF and no other peaks, further confirming that the Ni-phytate is amorphous. The chemical and electronic states of Ni-phytate were determined by XPS analysis (see Fig. 2g), indicating the presence of Ni, P, O and C. As shown by the images inset in Fig. 2g, the Ni 2p_{3/2} peak is mainly composed of Ni (0) and Ni (II) [18, 20] derived from the Ni substrate and divalent Ni chelated with the phytate anion, respectively. The successful chelation of phytate anions was confirmed by the peaks corresponding to C 1s [21] and P 2p [11] in the XPS spectrum.

Figure 2e shows Raman peaks at about 815 and 1520 cm⁻¹ which correspond to P-O-C rock stretching [22] and ring C-H bending [22-24], respectively. The peaks at 972, 983 and 1679 cm⁻¹ are attributed to the -C-H out-of-plane deformation [25], C-C-H bending, O-P-O stretching [16] and asymmetrical stretching modes [24]. Compared with the original sodium phytate [26, 16], the ATR-IR (Fig. 2f) [27-33] and Raman spectra show shifts which further demonstrate the growth of metal-phytate compounds on the electrode surface.

Fig. 3 (a) Polarization curves for Ni-phytate (before and after iR corrected), blank Ni-foam and RuO₂ at a scan rate of 10 mV s⁻¹ and corresponding Tafel plots. (b) The relationship between the current density and sweep cycles of the catalyst. (c) The EIS and fitted curves of Ni-foam, Ni-phytate electrode before and after stability test at 1.57 V; the corresponding equivalent circuit diagram and the values of R_{ct} and R_s. (d) The electrical double-layer capacitance measurements of the obtained Ni-phytate and NF at a series of scan rates; the linear fitting curves of the charged currents at 1.1 V for these two electrodes. (e) The stability of Ni-phytate at 1.57 V and the corresponding XPS spectra. (f) Faradaic efficiency testing of the Ni-phytate at 1.55 V.

The Ni-phytate was used directly as an independent electrode to perform electrochemical measurements in 1 M KOH. As shown in Fig. 3a and Table 1, Ni-phytate exhibits current densities of 10 and 100 mA cm⁻² at low overpotentials (η) of 280 and 330 mV, respectively, which is superior to RuO₂ and most other electrodes. However, a lower current signal is observed from the bare NF substrate, demonstrating that there is little background contribution from the substrate to the OER performance of Ni-phytate. We also find from the curve without iR correction that this catalyst is able to perform well in industrial alkaline electrolyzers. The corresponding Tafel plots were obtained from the Tafel equation: $\eta = b \log j + a$, where b is the Tafel slope and j is the current density [34]. The Tafel slope of the

Ni-phytate is significantly smaller than that of NF and RuO₂ (inset of Fig. 3a), implying more favorable kinetics and superior catalytic activity. Fig. 3b shows that NF treated with 4 scan cycles results in the best electrocatalytic activity. The charge transfer resistances (*R*_{ct}) and the corresponding equivalent circuit diagram of the electrodes are shown in Fig. 3c. It is observed that the structure formed in situ shows a decrease in *R*_{ct} which corresponds to the semicircular diameter in the high frequency region, demonstrating the highly improved electron-transfer efficiency of Ni-phytate for OER. In addition, the low resistance after the stability test implies that the catalyst still provides efficient electron transfer for OER in a long-term electrochemical process. However, the slight increase in the resistance compared with the as-prepared electrode might be caused by the formation of NiO_x species on the surface of the electrode. The electrochemically active surface areas (ECSA) of the blank NF and Ni-phytate electrode were determined through measurement of the electrical double-layer capacitance (*C*_{dl}) with a well-polished glassy carbon electrode (GCE) as reference [8]. The corresponding linear fitted graphs of the charged current densities at different scan rates (*v*) are shown in Fig. 3d. It can be seen that the Ni-phytate electrode exhibits much higher *C*_{dl} than bare NF, showing that the electrode has more electro-active sites and a larger ECSA (NF: 3.4 cm², Ni-phytate:12.56 cm²) (*C*_{dl} ∝ *v* × ECSA) [35].

As shown in Fig. 3e, the steady current curve reveals the good stability of the new catalyst with only a slight loss (5%) of current density (>5 h). The XPS spectra, inset in Fig. 3e, show a decreased peak intensity for C and P and a shifted peak for Ni, which may be due to the in situ formation of NiO_x species on the surface of the Ni-phytate. Unlike other Ni-based active centers [36], NiO_x species with high valence states are considered to be electrochemically active sites for OER [18]. Figure 3f shows the actual O₂ production obtained via a PASCO oxygen sensor (USA) based on Henry's law. Compared with the theoretical O₂ yield based on the current, the current efficiency of oxygen production is close to 100%, which suggests a high-efficiency current-to-oxygen conversion.

Table 1

Comparison of performances for the electrode in this work and several other reported catalysts in 1 M KOH.

4. Conclusions

In summary, a 3D Ni-phytate structure was grown directly on a Ni-foam surface using an electrochemical method. The introduction of the phytate units increases the material's electrocatalytic activity towards OER because the crosslinked structure improves the electron transfer efficiency and exposes more active sites. Offering outstanding catalytic activity, stability and a scalable fabrication process, this method represents a simple approach for the construction of novel electrodes for efficient

energy exploitation.

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d. Figure 1

d. Figure 2

d. Figure 3

e. Table 1

Catalyst	Substance	Tafel slope (mV dec ⁻¹)	η at 10 mA cm ⁻² (mV)	Ref
Ni-phytate	NF	40	280	This work
Ni-P nanoparticles	NF	59	290	[37]
NiO _x	Au-coated QCM	40	360	[38]
NiFe/NF	NF	28	215	[7]
Ni _{2.3} %-CoS ₂ /CC	carbon cloth	119	270	[39]
NiCo ₂ O ₄	FTO	292	565	[40]
Co-P film	Cu foil	47	345	[41]
Co ₃ V ₂ O ₈	GC	80	411	[42]
V-Co-Fe-343	GC	36	307	[43]
Co ₃ O ₄	ITO	161	500	[44]