In situ X-ray diffraction study of urea electrolysis on nickel catalysts

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In situ X-ray diffraction (XRD) technique combined with electrochemical analysis was used for investigating the structural changes of nickel hydroxide catalysts in alkaline media and to provide a better understanding of the reaction mechanism of urea electro-oxidation for applications in hydrogen production, fuel cells, and sensors. The evolution of XRD patterns reveals Ni(OH)2 is electrochemically oxidized to NiOOH at cell voltages from 1.2 to 1.6 V. The generated NiOOH reacts with urea and thus is reduced back to Ni(OH)2, while urea is concurrently oxidized. The technique can be extended to other electrochemical systems (alkaline rechargeable batteries, supercapacitors, and fuel cells).

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In the past half decade, urea has attracted growing attention as a promising hydrogen carrier for long term sustainable energy supply.1-3 The intrinsic properties of urea, such as non-toxic, non-flammable, and easy storage (solid state at room temperature), facilitate hydrogen storage and transportation compared to other flammable liquids or gas hydrogen carriers.4-6 Urea electrolysis has been demonstrated as an effective technique for directly converting urea to hydrogen and benign nitrogen.7 Moreover, urea electrolysis finds applications in the removal of urea from wastewater produced from industrial synthesis of urea, providing environmental and energy saving advantages.1-3 Nickel catalysts have been developed for catalyzing the process of urea electro-oxidation, which not only alleviates the requirement of expensive noble metal catalysts, but also promote the reaction rate.2,5 Different structured and componential nickel based catalysts have been evaluated for urea electrolysis.6-8 Although NiOOH has been proposed to catalyze urea electro-oxidation through density functional theory (DFT) calculations9 and Ni-O bending and stretching vibrations of NiOOH has been detected by Raman spectroscopy,10 no direct crystal evidence of the structural changes of the nickel hydroxide catalysts in alkaline media proves the reaction mechanism of urea electrolysis.

X-ray diffraction (XRD) is a powerful technique for phase identification of crystalline materials. Combining X-ray diffraction with electrochemical investigations may bring new opportunities for studying the electrochemical reaction pathways and the phase changes of electrode materials.11-13 Within this context, this paper focuses on developing in situ X-ray diffraction measurements coupled with electrochemical analysis to identify the structural changes of the nickel catalysts and to investigate the reaction mechanism of urea electrolysis. Since nickel electrodes have also been widely used in alkaline rechargeable batteries,13 supercapacitors,14 and fuel cells,15 the developed in situ X-ray diffraction technique can be extended to study these electrochemical systems.

Results and Discussion

The cyclic voltammogram of Ni(OH)2/carbon paper electrode in 5M KOH solution is shown in Figure 1a (curve 1). A pair of redox current peaks is observed, which is due to the reversible transformation between Ni(II) to Ni(III).16,17 The carbon paper substrate does not show any redox peaks in the same scan range (Figure 1a curve 3). In the presence of urea, the oxidation current of Ni(OH)2/carbon paper electrode drastically increased (Figure 1a curve 2), which indicates the electro-oxidation of urea in alkaline media.

The electrocatalytic oxidation of urea on Ni(OH)2 was further investigated with potential stair-step experiments in the two-electrode cell. The cell voltage was stepped from 1.2 V to 1.6 V vs. the Pt cathode (Figure 1b curve 3). The cell voltage range was determined by the voltage conversion from three electrode systems (cyclic voltammetry) to the two-electrode cell (Figure 1c). Since urea oxidation starts at a potential ~ 0.35 V vs. Hg/HgO (Figure 1a curve 2), the corresponding cell voltage was stepped from 1.2 V vs. Pt. As shown in Figure 1b, higher current densities were detected at different cell voltages starting from 1.3 V when urea was present in the KOH solution (Figure 1b curve 2), which agrees well with the results of the cyclic voltammograms and suggests that nickel catalysts are active for urea electro-oxidation.

Figure 1d shows the XRD pattern of as-prepared Ni(OH)2/carbon paper electrode. The diffraction peaks can be indexed to nickel hydroxide (JCPDS 00-014-0117), graphite (JCPDS 00-008-0415), and PTFE (JCPDS 00-047-2217) as labeled in Figure 1d. The diffraction peaks of graphite and PTFE are originated from carbon paper substrate and binder, respectively.

Experimental

All of the electrochemical measurements were performed in a 5M KOH solution in the absence and presence of 1M urea. The details of electrode preparation and electrochemical setup were demonstrated in the supplementary information. In a brief, the cyclic voltammetry (CV) measurements were performed between 0 V to 0.7 V in a conventional three-electrode cell. Ni(OH)2 electrode, Hg/HgO electrode, and platinum foil were chosen as the working, reference, and counter electrodes, respectively. Potential stair-step experiments were carried out in a two-electrode cell and platinum foil was used as counter electrode. The cell voltage was stepped from 1.2 V to 1.6 V in 0.1 V increments with 20 minutes step time. The range of the cell voltage was determined by the potential conversion from three-electrode cyclic voltammograms to a two-electrode system.

XRD patterns were obtained on a Rigaku Ultima IV X-Ray Diffractometer. A Rigaku battery cell attachment was modified to perform the in situ XRD study of urea electrolysis on nickel hydroxide catalyst. The in situ XRD setup and the schematic of the cell are shown in Figure S1 a-b. The detailed description of the in situ cell design is given in the supplementary information. The electrochemical cell was mounted on the multipurpose sample stage of the Rigaku diffractometer and connected with a Solartron 1281 potentiostat for supplying the cell voltages from 1.2 V to 1.6 V. In order to avoid X-ray attenuation, the electrolyte was filled in the cell up to the same level of the working electrode, but it did not cover the top surface of the working electrode.

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Figure 1. (a) CVs of Ni(OH)\textsubscript{2}/carbon paper electrode in 5M KOH in the absence (curve 1) and presence (curve 2) of 1M urea. CV of carbon paper substrate in 5M KOH is shown in curve 3. The scan rate was 10 mVs\textsuperscript{-1}; (b) Potential stair-step experiments of Ni(OH)\textsubscript{2}/carbon paper electrode in 5M KOH in the absence (curve 1) and presence (curve 2) of 1M urea. The cell voltage was stepped from 1.2 V to 1.6 V (curve 3); (c) Potential conversion from three electrode systems to two-electrode cell; (d) XRD pattern of as-prepared Ni(OH)\textsubscript{2}/carbon paper electrode.

Figure 2. Evolution of XRD reflections of (a) Ni(OH)\textsubscript{2} (100) and (101), (b) Ni(OH)\textsubscript{2} (102) and Graphite (004), (c) Ni(OH)\textsubscript{2} (110) and (111), and (d) NiOOH (003) for cell voltage stepped from 1.2 V to 1.6 V for Ni(OH)\textsubscript{2} electrode in 5 M KOH.
Figure 3. Evolution of XRD reflections of (a) Ni(OH)$_2$ (100) and (101), (b) Ni(OH)$_2$ (102) and Graphite (004), (c) Ni(OH)$_2$ (110) and (111), and (d) NiOOH (003) for cell voltage stepped from 1.2 V to 1.6 V for Ni(OH)$_2$ electrode in 5M KOH + 1M urea.

The XRD patterns of Ni(OH)$_2$ electrode in 5M KOH at different cell voltages. Since carbon paper is inert to urea oxidation, the Graphite (004) reflection was used as a reference for the in-situ XRD analysis. The intensities of all other diffraction peaks are normalized to Graphite (004) reflection. It can be seen from Figures 2a to 2c that the intensities of the diffraction peaks of Ni(OH)$_2$ decrease with increasing the cell voltage. Concomitantly, a new diffraction peak at $\sim 12.7^\circ$ is generated and its intensity increases with increasing the cell voltage (Figure 2d). The new diffraction peak can be indexed to NiOOH (003) reflection (JCPDS 00–006–0075). The above in-situ XRD results indicate that Ni(OH)$_2$ is electrochemically oxidized to NiOOH in alkaline solution at a cell voltage between 1.2 V to 1.6 V.

Figure 3 shows the in-situ XRD measurements of Ni(OH)$_2$ electrode at different cell voltages when urea was present in the KOH solution. The XRD patterns show that the intensities of all the diffraction peaks of Ni(OH)$_2$ are stable at the same level (Figures 3a-3c) and no new phase (e.g., NiOOH) is formed (Figure 3d). Two possibilities may lead to no change in the XRD patterns of Ni(OH)$_2$: (1) Ni(OH)$_2$ has no chemical reactions during the whole process; (2) both the electrochemical oxidation of Ni(OH)$_2$ and chemical reduction of electrochemically generated NiOOH occur during the whole process, and the chemical reduction step is rapid so that the NiOOH species cannot be detected by XRD. Figure 2 has already proved the conversion of Ni(OH)$_2$ to NiOOH in alkaline solution and the electrochemical analysis (Figure 1a and 1b) indicates Ni(OH)$_2$ catalyzes the electro-oxidation of urea in alkaline solution; therefore, it is to conclude that both the electrochemical oxidation of Ni(OH)$_2$ and chemical reduction NiOOH occur during the whole process, and the lifetime of NiOOH is short due to its chemical reduction by urea and not detectable on the timescale of the XRD scans taking place and thus keeps the XRD patterns without any change. Therefore, the reaction mechanism of urea electrolysis is demonstrated as follows:

**Anode:**

$$6 \text{Ni(OH)}_2(s) + 6\text{OH}^- \rightarrow 6\text{NiOOH}(s) + 6\text{H}_2\text{O}(l) + 6e^- \quad [1]$$

$$6\text{NiOOH}(s) + \text{CO(NH}_2\text{)}_2(aq) + \text{H}_2\text{O}(l) \rightarrow 6\text{Ni(OH)}_2(s) + \text{N}_2(g) + \text{CO}_2(g) \quad [2]$$

**Net anodic reaction:**

$$\text{CO(NH}_2\text{)}_2(aq) + 6\text{OH}^- \rightarrow \text{N}_2(g) + 5\text{H}_2\text{O}(l) + \text{CO}_2(g) + 6e^- \quad [3]$$

**Cathode:**

$$6\text{H}_2\text{O}(l) + 6e^- \rightarrow 3\text{H}_2(g) + 6\text{OH}^- \quad [4]$$

**Overall reaction:**

$$\text{CO(NH}_2\text{)}_2(aq) + \text{H}_2\text{O}(l) \rightarrow \text{N}_2(g) + 3\text{H}_2(g) + \text{CO}_2(g) \quad [5]$$

**Conclusions**

The reaction mechanism of urea electrolysis on nickel hydroxide catalysts and the structural changes of Ni(OH)$_2$ catalysts in alkaline media were studied by electrochemical analysis and in-situ XRD measurements. The in-situ XRD results reveal Ni(OH)$_2$ is electrochemically oxidized to NiOOH when the applied cell voltage varies from 1.2 V to 1.6 V in alkaline solution in a Ni(OH)$_2$ anode and Pt foil cathode. When urea is present in the alkaline solution, the
electrochemically generated NiOOH reacts with urea molecules and thus is reduced back to Ni(OH)$_2$, while urea is oxidized and converted to nitrogen and hydrogen concurrently. The developed in situ X-ray diffraction technique can also be extended to study the reaction mechanisms of other nickel related electrochemical systems, such as alkaline rechargeable batteries, supercapacitors, and fuel cells.

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