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Insights into electrodeposition process of nickel from ammonium chloride media with speciation analysis and in situ synchrotron radiation X-ray imaging

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ABSTRACT

The electrodeposition processes of nickel in ammonium chloride media were studied in combination of speciation analysis and *in situ* synchrotron radiation X-ray imaging. The X-ray absorption spectra indicated that the nickel(II) species present an octahedral configuration independent on aqueous pH. The UV–vis spectra and fraction-pH diagram showed that the dominant species is $Ni(H_2O)_6^{2+}$, $Ni(NH_3)_m(H_2O)_{6-m}^{2+}$ (m = 2, 3 and 4) and $Ni(NH_3)_6^{2+}$ in the electrolytes of pH 3, 7.5 and 10, respectively, and chloride ions are not bonded to the inner coordination sphere of nickel species. The electrochemical behaviors and nucleation mechanism of nickel(II) species are dependent on the solution pH and species. The deposited nickel morphology and bubble evolution at the interface of electrode/electrolyte were clearly elucidated by the X-ray real-time images. The results indicate that the inner coordination sphere of nickel species can induce the morphology, growth and adherence processes of the deposited nickel. The competition process between nickel reduction and hydrogen evolution has also been discussed at the different applied potentials. The mixed coordination species and the higher applied potentials are beneficial for the formation of the well-adhered and dense nickel deposits.

1. Introduction

The electrodeposited nickel films have been widely applied in the fields of surface engineering or materials application because of their excellent electrocatalytic, corrosion-resistance and magnetic properties [1–3]. It is known that the electrodeposition of nickel from various electrolytes is a highly inhibited process [4], where several conditional parameters are involved, such as composition of solutions, pH, temperature and substrate types [5–7]. Especially, the coordination chemistry of reduced species in the electrolytes has an important impact on the morphology, structure and property of the electrodeposited metal [8]. The electrochemical reduction of Ni(II) from ammonium chloride bath has attracted much attention. Due to the coordination characteristic of ammonia or chloride ions, the diverse nickel species could present the remarkably different electrodeposition behaviors, like copper and zinc in previous studies [9,10]. These coordination components can also act as additives to modify the properties of the generated deposits. It has been reported that the ammonia coordination sphere can change kinetic parameters of Ag deposition in the ammoniacal electrolytes [11]. Furthermore, the combined utilization of chloride and ammonia species can improve metallic corrosion resistance and brightness [12]. Nam et al. proposed that copper ammonia complexes benefit for the crystal growth along the favorable orientation [13]. Yu et al. thought that the concentration of ammonium ions can control the generation of porous nickel films with high surface area [14]. Thus, it is motivated to study the effect of inner sphere coordination on the electrodeposition of nickel species from the ammonium chloride electrolytes.

Generally, the electrodeposition process on the substrate/solution interface contains two simultaneous processes, namely, nucleation and growth processes [15]. The former is the formation stage of new phase, and the nucleation process kinetically influences the structure of deposits [16]. Meanwhile, the interfacial growth process of deposits continues to receive much attention [17,18]. Some conventional *ex situ* methods, such as atomic force microscope (AFM) [19], scanning electron microscope (SEM) and transmission electron microscope (TEM) [20,21], have been used to visualize the morphological formation and evolution of deposits

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on the substrate. However, the "stop-and-go" observations limit the facts on the dynamic growth process; particularly, it is difficult to observe the amorphous morphologies. The *in situ* technologies are preferred to capture the fast evolution process of deposits and analyze the detailed microstructures. The *in situ* optical observation is a conventional method, but it has the drawback of low resolution [22]. Although the *in situ* TEM and SEM technologies can be used to observe the atomic resolution images in a high vacuum environment, the common aqueous electrolytes are limited due to the high vapor pressure [23,24]. Due to the sufficient time and spatial resolution, the synchrotron radiation X-ray imaging has been applied to monitor the interfacial processes of metal electrodeposition in the real time environment. W.L. Tsai et al. obtained the *in situ* images on the microstructure evolution of zinc dendrites via dynamic X-ray imaging [25], and found that zinc deposits were directly formed on the bubble surface [26]. David observed the 3D dynamic microstructures of electrodeposited lithium in the lithium batteries with the synchrotron radiation X-ray phase contrast imaging [27].

As aforementioned, the goal of the present work is to *in situ* investigate the effect of inner sphere coordination on the interfacial growth of nickel in NH_4Cl solutions via the synchrotron radiation X-ray real-time imaging technology. Therefore, the speciation and structure of nickel(II) in NH_4Cl media were studied by X-ray absorption spectroscopy, UV–vis spectroscopy and fraction-pH diagram. Then, the reduction process and nucleation mechanism of nickel(II) species at different pH were analyzed with cyclic voltammetry and chronoamperometry. Moreover, resorted to the *in situ* X-ray imaging, the real-time nickel morphologies and bubble evolution during nickel deposition process were evaluated at the different pH of electrolytes and applied potentials.

2. Experimental

All electrochemical tests and speciation analyses were carried out in the aqueous solution of $0.05\,\text{mol}\,\text{L}^{-1}$ $NiCl_2$ and $2\,\text{mol}\,\text{L}^{-1}$ NH_4Cl. Ultrapure water (Millipore, $18.2\,\text{M}\Omega\,\text{cm}^{-1}$) was used throughout the experiments. All chemicals including $NiCl_2{\cdot}6H_2O$ and NH_4Cl were of analytical grade reagents. The pH of electrolytes was adjusted by the diluted NaOH or HCl solution.

A conventional three-electrode system was employed to perform the electrochemical experiment. The disk glassy carbon with a diameter of 3 mm was used as the working electrode. The platinum wire (diameter 0.5 mm) and Ag/AgCl electrode were used as counter electrode and reference electrode, respectively. All the potentials were referred to the Ag/AgCl electrode. Prior to each electrochemical measurement, the glassy carbon electrode was polished to a mirror finish with alumina power of different grades (1.0, 0.3 and 0.05 μm) and cleaned ultrasonically with deionized water and ethanol, and then dried. All electrochemical studies were performed at the room temperature. Before the electrochemical tests, the electrolytes were deaerated by bubbling the purified nitrogen for 15 min. The cyclic voltammetry and potential step techniques were monitored using an electrochemical workstation (Chenhua CHI660e).

The dependence of nickel speciation on pH of electrolytes was built with the free Medusa software (Puigdomenech 2004, Sweden). The UV–vis spectrophotometer (a Shimadzu model UV-1601) was utilized to analyze the absorption spectra of Ni(II) species by using quartz cell (path length of 1 cm). The Ni K-edge X-ray absorption spectra (XAS) of electrolytes were collected at the BL14W1 Beamline at Shanghai Synchrotron Radiation Facility (SSRF), China. All XAS were measured with a transmission mode at room temperature. A Si(111) double crystal monochromator was used for energy selection. The photon energy was calibrated against the first inflection point of the K-edge of nickel foil to 8333 eV. The storage ring was operated at an energy of 3.5 GeV with a current between 150 and 210 mA.

The synchrotron radiation *in situ* X-ray imaging studies were carried out at BL13W1 beamline of SSRF. A polystyrene cell (1 cm thickness) was used and the incident X-ray light was vertically focused on the working electrode/electrolyte interface. Nickel electrodeposition was performed with the potential step technique on the remote electrochemical workstation due to the hazardous high-energy irradiation. The real-time images with a resolution of 2.25 μm/pixel were collected by X-ray charged couple device (CCD) camera at a frequency of one frame per second. Scanning electron microscopy (SEM, JSM-6360LV) was used to obtain the surface morphologies of final deposits. The crystalline phases of nickel deposits were studied by X-ray diffraction (XRD, Shimadzu XRD-7000S).

3. Results and discussion

3.1. Structure and speciation of nickel(II) in electrolytes

When the solid $NiCl_2{\cdot}6H_2O$ dissolves into aqueous solutions of ammonium chloride, the colors of Ni(II) solutions change from light green to dark blue with increasing the pH from 3 to 10, indicating the transformation of nickel speciation. The structural information of nickel species as a function of the bulk pH in the Ni(II)-NH_4Cl electrolytes was identified by the X-ray absorption spectroscopy. The normalized Ni K-edge XANES spectra were shown in Fig. 1. The similar spectral features indicate that there is an identical geometric configuration of nickel components at different pH. All XANES spectra show a weak pre-edge peak at 8346 eV and a strong white-line peak at 8362 eV, which can be attributed to $1s \rightarrow 3d$ and $1s \rightarrow 4p_{x\text{-}y}$ electronic transition of nickel (II) species, respectively. Meanwhile, there is no pre-edge peak of $1s \rightarrow 4p_{z2}$ electronic transition, thus clearly indicating that the structure of nickel(II) speciation should be an octahedral configuration [28]. In essence, it is almost impossible from the XANES spectra to distinguish ligands (H_2O, NH_3) in the inner coordination sphere of nickel(II) due to the similar amplitude and phase functions between oxygen and nitrogen atoms.

The fraction-pH diagram was built to evaluate the predominant nickel species in the ammonium chloride media at different pH conditions. As shown in Fig. 2, at the acidic pH range ($pH < 6$), the predominant species seems to be $NiCl_2$. However, Lagarde thought that chloride ions are difficultly coordinated with hydrated Ni(II) [29]. According to the XANES results, the octahedral nickel species

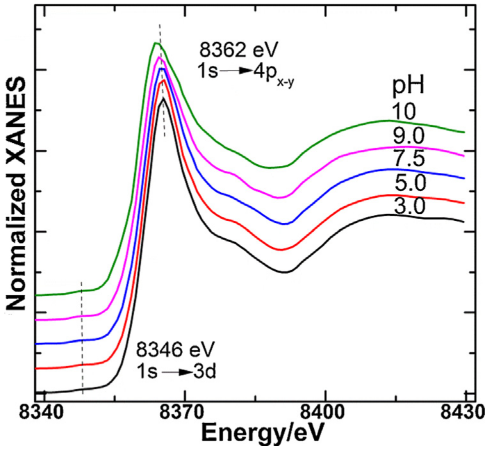

Fig. 1. Normalized Ni K edge XANES spectra at different pH. Conditions: $0.05\,\text{mol}\,\text{L}^{-1}$ $NiCl_2$, $2\,\text{mol}\,\text{L}^{-1}$ NH_4Cl.