



Realizing High Water Splitting Activity on Co₃O₄ Nanowire Arrays under Neutral Environment



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ABSTRACT

Enhancing catalytic water-splitting activity under mild environments is significant to solve the long-standing cost, safety and stability issues in photoelectrochemical cells. Here, we demonstrate the crucial role of improving surface H transfer in achieving efficient water-splitting catalytic activity of Co₃O₄ nanowire arrays in near-neutral pH working electrolytes. Under weak OH circumstances, the impedance of mass transfer quickly multiplies and the catalytic current declines to a current plateau in the region of 1.7–2.1 V vs. RHE, due to the surface H concentration approaching a threshold value in the range of 10⁻³–10⁻⁴ M. The proper choice of buffering agents to facilitate the mass transfer, with 0.1 M KPi as a prototype, would decrease the overpotential by 500 mV for neutral electrolyte and favors to achieve a catalytic current comparable to that under strong alkali environments (pH > 13). These results also provide a solid guideline for extending the electrocatalytic utility of other transition metal catalysts to near-neutral pH environments.

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1. Introduction

Sunlight is an important renewable energy source to replace fossil fuels and produce clean energy for the rising global energy demand [1,2]. The most attractive approach to solar energy conversion and storage is using photoelectrochemical cell (PEC) to split water into hydrogen and oxygen [3,4]. A series of PECs were constructed with metal oxide electrodes and catalysts to achieve excellent performance under strong alkali environments (pH > 13) [5–26]. For the ultimate goal of PEC to provide “fast food” and personalized energy source, the efficient operation under mild environment and independent of electrolyte is highly required for the long-standing safety and unrestricted use of PEC [17,18]. However, enhancing the water oxidation reaction activity of transition metal oxides at near-neutral pH working electrolytes still meets a great challenge [12,15,18].

Recently, numerous studies have been performed to investigate the relationship between the water oxidation reaction activity of catalysts and the working electrolyte. Nakamura and co-workers have reported that the pH-dependent activity for water oxidation by MnO₂ relied on the active intermediates of Mn³⁺ which

however were unstable as pH value decreased [12,24]. Stahl *et al.* have investigated the electrochemical water oxidation with cobalt ions in fluoride buffering electrolytes and revealed that the cobalt catalyst films (CoO_x^{cf}s) displayed different mechanisms of water oxidation under environments varying from acidic to basic conditions [25]. It is a well-known fact that the violent reaction on the positive electrode could change the electrolyte compositions near the electrode surface and the mass diffusion process would affect the surface reaction speed. However, for the special roles of water as both solvent and reactant, the influences of the mass transfer progress were generally ignored, and the cause of the dependence of working condition on catalytic activity has not been completely understood yet. In fact, several recent researches have indicated that the limitation of mass transfer indeed existed for the water-splitting catalyst [12,26]. Therefore, quantitative analysis of the impact of mass transfer on the catalytic performance is very essential for maintaining and optimizing the water oxidation activity of water oxidation catalyst under mild reaction environment.

In this work, we realize the water splitting activity of Co₃O₄ nanowires under neutral reaction condition, and attempt to reveal the major factors influencing the water splitting activity of Co₃O₄ nanowire arrays under dilute OH environment. It was found that the mass transfer rate of the reaction product H ions from surface is the determinant factor of catalytic water-splitting speed under weak pH working electrolytes. This mass transfer process can be promoted by about 50 times via adding 0.1 M KPi buffering agent

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in the neutral pH working solution, and can enhance the catalytic current to the comparable amplitude of that under strong alkali environments (pH > 13). These findings provide some quantitative information to extend the electrocatalytic utilities of electrocatalysts in various ambient solution environments.

2. Experimental

Co₃O₄ nanowire arrays were grown on Ti foils in an aqueous solution by hydrothermal method reported in the previous work [27]. 4 mmol of Co(NO₃)₂·6H₂O, 18.75 mmol of CO(NH₂)₂, and 7.4 mmol of NH₄F were dissolved in 25 ml of distilled water to form precursor solution. Then the solution was transferred into a Teflon-lined stainless steel autoclave liner before a piece of clean Ti substrate was immersed into the reaction solution. The liner was sealed and kept in an oven at 120 °C for 6 h and then allowed to cool to room temperature. Finally, the precursor was annealed at 350 °C in air for 2 h, making the original pink sample to black film. The morphology of the black films coating at the Ti substrate was characterized using the field-emission scanning electron microscope (FESEM: JEM-2100F, USTC, China) at an accelerating voltage of 5 kV. The crystalline structures of the samples were characterized by X-ray diffraction (XRD).

The electrolyte solutions were prepared using highly pure distilled water and reagent-grade chemicals, and the pH values were adjusted from 13.0 to 10.0 by dropping 0.1 M HNO₃ into the solution of 0.1 M NaOH. No agents for pH buffering were first studied to simplify the issue [28]. The prepared electrolyte solutions were kept at room temperature and were bubbled with argon gas to exhaust oxygen prior to the measurements. Electrochemical measurements were carried out using an electrochemical workstation (Model CHI760D, CH instruments, Inc., Austin, TX) with a three-electrode system, operated with the Co₃O₄ sample as anode, platinum mesh as cathode, and Ag/AgCl as reference electrode. The positions of these electrodes were all fixed via external bracket to ensure the confidence of electrochemical analysis [29,30]. The temperature of solution was kept at 25 °C (±1) for the entire measurement via the adjustment of air condition and heating support, which ensured the variation of diffusion coefficient below 1%. The curves of potential dependence of the current densities were measured using linear sweep voltammograms (LSV) from 0.0 to 1.6 V at a scan rate of 0.002 V s⁻¹. The Tafel studies of the desired pH values were performed without stirring, and the current densities were recorded when the reaction reached a steady state in order to obtain reproducible linear plots. Electrochemical impedance spectroscopy (EIS) measurements were carried out with frequency range of 0.01–1000 kHz at different bias potentials in different pH values and stirring solutions. All potential values in this work are reported with respect to the RHE reference.

3. Results and Discussion

The SEM images of Co₃O₄ in Fig. 1a show regularly arranged one dimensional nanowire arrays structure with an average diameter of 100 nm and length exceeding 3 μm, which offers a large specific surface area for the reaction [31]. XRD characterization exhibits the crystalline spinel structure of Co₃O₄ with no peaks assignable to other crystal phases of cobalt oxides, as shown in Fig. 1b. The water oxidation performances of Co₃O₄ electrocatalyst immersed in alkaline aqueous electrolytes at different pH values are displayed in Fig. 1c. It is notable that the water oxidation catalytic activity of Co₃O₄ nanowire arrays quickly declines with the decrease of pH values. The anodic current for O₂ evolution reaction starts to flow at 1.6 V for pH 13.0 and pH 12.5 with modest overpotential values of about 350–400 mV, which are comparable to those of previously

reported cobalt-based catalysts [8,32]. However, at pH value from 12.0 to 10.0 the catalytic current densities sharply decrease and positively shift by 400–600 mV, leaving remnant current plateaus at the potential region of 1.70–2.10 V. It is worth noting that the evolution of oxygen gas bubbles can still be directly observed for the remnant current plateau, so that the plateau is not a capacitive current. Moreover, the position and height of the plateau only slightly change with different scanning speeds and the current plateau can recover to anodic current similar to the case of pH 13.0 under violent stirring, indicating the origin of the current plateau is a mass transfer process. For the special roles of water as both solvent and reactant, the impact of mass transfer process was seldom analyzed before. The observed catalytic current plateau value is larger at higher pH value, indicating the OH concentration is significant in the mass transfer process. Considering the uncertainty of oxygen evolution reaction path (Eq. (1), Eq. (2)) [12,24,25,33,34],



the mass transfer process may be attributed to the relevant diffusion of H and OH. Two reaction paths can be observed before and after current plateau in Tafel plots with low pH value (as shown in Fig. 1d). At low current densities, the slope of Tafel plots is about 60 mV decade⁻¹, which is a standard for judging a good catalyst. But with the increasing current density, the Tafel slope sharply increases, indicating the bottleneck effect of the diffusion process on the water oxidation in this reaction. Ultimately, the Tafel plots are located at 120–150 mV decade⁻¹, suggesting a change in the reaction path on the cobalt oxide and the recession of water oxidation activity [35]. Because of the rather high overpotential (about 900 mV) required for the second reaction, it is highly improbable to achieve excellent water splitting activity under mild environment along this reaction path. Thus, to improve the reaction rate of the first reaction becomes the key to realize the utility of Co₃O₄ electrode under near neutral electrolyte.

To quantitatively analyze the rate-determining step in electrode reaction, electrochemical impedance spectroscopy (EIS) measurements of Co₃O₄ electrode at pH 11.0–13.0 with different bias potentials were carried out and the Nyquist plots are shown in Fig. 2a–f [36,37]. For all the pH values, there are two clear semicircles and one diagonal line in the impedance spectra at low potential but only two semicircles exist at high bias potential. A full equivalent circuit used to fit the impedance data is shown in Fig. 2a. The equivalent circuit elements include a space charge capacitance of the bulk cobalt oxide, C_{bulk} , a resistance of the electrode, R_{bulk} , a charge transfer resistance from the electrode surface states to solution, R_{ct} , a mass transfer resistance from bulk solution to the interface, R_{D} , a solution resistance, R_{S} , and two constant phase elements (CPE_{I} and CPE_{D}) standing for the capacitances of double layer and diffusion layer. To allow unambiguous fitting of the impedance data, CPE_{D} is removed for the case of lower potential and both CPE_{D} and R_{D} are removed for that of high potential. The fitting results of R_{bulk} , R_{ct} , and R_{D} of Co₃O₄ electrodes in various solutions with step increased potential are listed in Table 1. The total resistances derived from the impedance results and the slope of steady-state current curves have a close variation trend within the experimental error of 2 percent just like reported by Klahr *et al.* [34], presenting strong evidence of the validity of equivalent circuit. The high frequency semicircle, which is generally attributed to the series arrangement of the capacitance and resistance of the bulk electrode, is constant and independent of potential under identical pH solutions. As can be seen from Fig. 3a, the R_{bulk} are 4.4 Ω at pH 13.0, 8.4 Ω at pH 12.5, 10.3 Ω at pH 12.0, 10.6 Ω at 11.5 and 11.3 Ω at pH 11.0, respectively. Obviously, the resistance of the cobalt oxide is smaller at pH 13.0 and quickly increase to a stable value

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