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Article

Ag_{2-x}O with highly exposed {111} crystal facets for efficient electrochemical oxygen evolution: Activity and mechanism

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ABSTRACT

A series of Ag_{2-x}O/FTO-*i* electrodes (where *i* denotes the current density during the electrodeposition, and *i* = 0.5, 1, 2, 3, 4, or 7) was fabricated in 0.1 M K₂B₄O₇ electrolyte containing Ag⁺ ions by galvanostatic electrocrystallization. The electrode composition and morphology were characterized using X-ray powder diffraction, scanning electron microscopy, and X-ray photoelectron spectroscopy. The results reveal that the electrode films consist of Ag₂O, but some of the Ag⁺ ions on the {111} crystal facets are oxidized into Ag²⁺ ions. Furthermore, the Ag_{2-x}O/FTO-1 electrode shows a triangular slice shape of a parallel matrix with a larger exposed area of {111} crystal facets than other Ag_{2-x}O/FTO-*i* (*i* = 0.5, 2, 3, 4, or 7) electrodes. Electrocatalytic experiments prove that the Ag_{2-x}O/FTO-1 electrode produces the highest oxidative current density, has an overpotential of 417 mV at 10 mA cm⁻², and has a Tafel slope of 47 mV dec⁻¹ in 0.1 M K₂B₄O₇. Electrochemical impedance spectra indicate that Ag_{2-x}O/FTO-1 electrodes have the best ability for charge transfer. In addition, in the *I*-*t* test over 10 h, the current density decreased 4%. Fortunately, both O–O and Ag²⁺ species were detected after electrocatalysis and a possible mechanism for the oxygen evolution reaction is proposed in which the formation of Ag²⁺ and O–O species on {111} facets plays a critical role.

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1. Introduction

The oxygen evolution reaction (OER) is a bottleneck to water splitting to evolve H₂ and to comprehensive utilization of CO₂ at industrial scale [1]. It is mechanistically complicated, involving the transfer of four electrons and four protons coupled with the formation of an O–O bond [2,3]. Photosystem II in nature exhibits very high catalytic efficiency with TOFs in the range of 100–400 s⁻¹ [4], which provides an example to motivate researchers to develop efficient, robust, and economical oxygen evolution catalysts (OECs) [5]. In a steady stream, exciting research results have been reported in past decades

[6–16]. To date, Ru and Ir-based oxides and carbides have been widely acknowledged as excellent electrocatalysts. At a current density of 10 mA cm⁻², their overpotentials are 0.28–0.36 V in 1 M NaOH and 0.34–0.44 V in 1 M H₂SO₄ [17,18]. However, the scarcity and high cost of such noble metals, as well as their stability, hampers their widespread usage [17–21]. Therefore, inexpensive and earth-abundant transition-metal (TM = Fe, Co, Ni, Mn, Mo, V, W, etc.) alternatives such as oxides [22–25], hydroxides [26–29], sulfides [30–32], selenides [33], phosphides [34,35], nitrides [36], and borides [37] have been explored in connection with promising advances in recent years.

The economy and abundance of Ag-based catalysts have at-

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tracted deep interest because both Ag and Ru are in the fifth period so that they have similar properties. Moreover, both have higher electron density and more adjustable coordination numbers than those of the 3d transition metals. In addition, Ag can exist in three oxidation states (I, II, and III). This makes it advantageous to employ catalysts based on Ag as OECs. In fact, it has been reported that both simple Ag^+ ions and the coordination compound $[\text{H}_3\text{Ag}(\text{H}_2\text{O})\text{PW}_{11}\text{O}_{39}]^{3-}$, as homogeneous OECs, exhibit high catalytic activity in acidic aqueous solutions [38–41]. Li's group [42–45] has fabricated Ag_2O - AgO /ITO electrodes by in situ electrochemical deposition in $\text{K}_2\text{B}_4\text{O}_7$ and NaHCO_3 electrolytes, and the electrodes have higher overpotentials than the corresponding Co and Ni-based electrodes do at room temperature. However, the overpotential decrease to 132 mV at 1 mA cm^{-2} (when the OER takes place) occurs at 70°C .

In recent years, crystal facet engineering has emerged as an important strategy in designing efficient electrocatalysts for water splitting [46]. A semiconductor with selective exposure of facets exhibits different electrochemistry of charge transfer, adsorption-to-reaction of reactants, and catalytic performance due to differences in atomic coordination and configuration of different facets. For example, the different preferentially exposed crystal facets of Co_3O_4 exhibit different activities for electrochemical water oxidation, of which the order is $\{111\} > \{112\} > \{110\} > \{001\}$ [47,48]. It is reported that Ag_2O can be fabricated to have many morphologies, including cubes, great rhombicuboctahedra, cuboctahedra, corner-truncated octahedra, octahedra, nanocubes, rhombic dodecahedra, edge and corner-truncated cubes, small rhombicuboctahedra, and edge-truncated octahedral [49]. Different morphologies mean differences in the exposed crystal facets, which exhibit distinctive properties. For instance, the cubic Ag_2O particles enclosed by the $\{100\}$ facets adsorb bacteria more easily [50]. Ag_2O octahedra and hexapods bounded by positively charged $\{111\}$ facets respond repulsively when dispersed in a solution of positively charged methylene blue solution, but can be suspended in a solution containing negatively charged methyl orange [51]. The cubic $\text{Ag@Ag}_2\text{O}$ photocatalyst with exposed $\{100\}$ facets show the greatest activity for the degradation of methyl orange (MO) under visible light irradiation [52]. For the exposed crystal facets, the order of stability against chemical etching or dissolution in NH_3 - NaOH solution is $\{111\} > \{110\} > \{100\}$ [53].

Recently, Zhao et al. [54] reported that AgO crystals with mainly $\{111\}$ exposed crystal facets yield superior catalytic activity for the OER over those facets with mainly $\{202\}$ exposed crystal facets. It (an exposed $\{111\}$ facet) has a modest overpotential of 418 mV at 1 mA cm^{-2} and a Faradaic efficiency of 93%. It is of interest to study the relationship of crystal facets in relation to the activity of Ag_2O . Therefore, in this work a series of Ag_{2-x}O electrodes was fabricated by galvanostatic electrocrystallization in $0.1 \text{ M K}_2\text{B}_4\text{O}_7$ electrolyte. It was found that the Ag_{2-x}O crystals with preferentially exposed $\{111\}$ facets show higher electrochemical water oxidation activity. In addition, the mechanism of electrocatalytic water oxidation on the Ag_{2-x}O electrode was also studied.

2. Experimental

2.1. Materials and chemicals

All reagents including AgNO_3 (99.8%), $\text{K}_2\text{B}_4\text{O}_7$ (99.5%), and H_2O_2 (30.0%) employed were commercially available and used as supplied without further purification. Ultrapure water with a resistivity of $\sim 18 \text{ M}\Omega \text{ cm}^{-1}$ was used to prepare all solutions. F-doped SnO_2 -coated (FTO) glass slides ($15 \Omega \text{ }\gamma^{-1}$, Sheet Glass) were purchased from Dalian Heptachroma Solar Tech Co., Ltd. The FTO glass slides were washed ultrasonically in acetone and then rinsed with ultrapure water before being used.

2.2. Fabrication of the Ag_{2-x}O /FTO-i electrodes

Anodic electrolysis deposition was performed by galvanostatic electrocrystallization according to reported methods [42,55], using a LANHE CT2001A electrochemical workstation at current density 0.50, 1.00, 2.00, 3.00, 4.00, and 7.00 mA cm^{-2} at room temperature in an H-type divided cell separated by a G2 glass filter. As shown in Fig. S1, the anode compartment of the H-type cell contained an aqueous solution of 1.00 mM AgNO_3 - $0.10 \text{ M K}_2\text{B}_4\text{O}_7$ and the cathode compartment contained an aqueous $0.10 \text{ M K}_2\text{B}_4\text{O}_7$ solution. An FTO glass slide was used as a positive electrode and the electrodeposition area was controlled to remain at 1.00 cm^2 . The reference electrode was a saturated $\text{Hg}/\text{Hg}_2\text{Cl}_2$ electrode (SCE) and the counter electrode was a platinum sheet. Electrochemical deposition was carried out until the charge reached 5.0 C. After deposition, the Ag_{2-x}O /FTO-i electrode was rinsed with ultrapure water, dried in the air, and then stored for subsequent experiments. Based on the current density in the electrodeposition process, they were marked as Ag_{2-x}O /FTO-0.5, Ag_{2-x}O /FTO-1, Ag_{2-x}O /FTO-2, Ag_{2-x}O /FTO-3, Ag_{2-x}O /FTO-4, and Ag_{2-x}O /FTO-7, respectively.

2.3. Characterization

X-ray powder diffraction (XRD) patterns were recorded on an Advance diffractometer (Empyrean) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) in the 2θ range of 20° to 70° with operating potential of 30 kV. SEM images were obtained using a scanning electron microscope (ZXM636-LV). HRTEM images were recorded on a JEM 2100F field emission microscope operating at 200 kV. Raman spectra were collected using a 532 nm diode-pumped solid-state laser, commercial Raman spectrometer (Invia). XPS patterns were recorded on a spectrograph (VG ESCALABMKII) with $\text{Al K}\alpha$ radiation (1253.6 eV). A vacuum pressure of $6.2 \times 10^{-6} \text{ Pa}$ was maintained during the testing process.

2.4. Electrochemical measurements

All electrochemical experiments were performed on a CHI660E electrochemical workstation (Shanghai Chenhua Instrument Corp., China) with a three-electrode system and collected in $0.10 \text{ M K}_2\text{B}_4\text{O}_7$ electrolyte at pH 9.2 with a scan rate of 100 mV s^{-1} . A platinum sheet and an SCE electrode were used as the counter and reference electrodes, respectively. The working electrodes were of Ag_{2-x}O /FTO-i. Electrode potentials were converted relative to a reversible hydrogen electrode

Fig. 1. XRD patterns of FTO, $\text{Ag}_{2-x}\text{O}/\text{FTO}-0.5$, $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$, $\text{Ag}_{2-x}\text{O}/\text{FTO}-2$, $\text{Ag}_{2-x}\text{O}/\text{FTO}-3$, $\text{Ag}_{2-x}\text{O}/\text{FTO}-4$, and $\text{Ag}_{2-x}\text{O}/\text{FTO}-7$ electrodes.

(RHE) scale, using the formula $E_{\text{RHE}} = E_{\text{SCE}} + 0.244 + 0.059 \times \text{pH}$. CVs were obtained in the potential range of 1.4–2.0 and 1.4–1.7 V vs. RHE. Linear sweep voltammetry (LSV) was performed in the potential range of 0.8–2.4 V vs. RHE. EIS was measured at a bias potential of -0.5 V in the frequency range of 10^{-2} to 10^5 Hz. The I - t curve was recorded at 1.20 V.

3. Results and discussion

3.1. Fabrication and characterization of $\text{Ag}_{2-x}\text{O}/\text{FTO}-i$ electrodes

The $\text{Ag}_{2-x}\text{O}/\text{FTO}-i$ electrodes were formed at the current density of 0.50, 1.00, 2.00, 3.00, 4.00, and 7.00 mA cm^{-2} in 0.10 M $\text{K}_2\text{B}_4\text{O}_7$ electrolyte by galvanostatic electrocrystallization. When the amount of electric charge reached 5.0 C cm^{-2} , the electrolysis was stopped. The variation of the electrolysis potential with the quantity of electric charge is shown in Fig. S2. It was found that the potential fluctuated slightly when the charge was < 1.0 C cm^{-2} (when the potential remained basically unchanged), but increased with increase in the applied current density. The stable potentials were about 1.00, 1.10, 1.15, 1.20, 1.28, and 1.32 V vs. SCE when the current density was 0.50, 1.00, 2.00, 3.00, 4.00, and 7.00 mA cm^{-2} . A uniform, dark, smooth Ag_{2-x}O film was formed on an FTO glass slide. No sig-

nificant shedding was observed in the experiments.

Fig. 1 shows the normalized XRD patterns of the $\text{Ag}_{2-x}\text{O}/\text{FTO}-i$ ($i = 0.5, 1, 2, 3, 4$, and 7) electrodes. Except for the diffraction peaks of the FTO substrate, the diffraction peaks at 26.6° , 38.0° , and 65.4° correspond to $\{110\}$, $\{200\}$, and $\{311\}$ crystal facets of Ag_2O (JCPDS no. 41-1104). This demonstrates that the electrode films are composed of Ag_2O . However, it was noted that the diffraction peak at 32.8° for the $\{111\}$ crystal facets of standard Ag_2O , obviously shifts to 33.4° with a $\text{Ag}_{2-x}\text{O}/\text{FTO}-0.5$ electrode and to 33.9° for other $\text{Ag}_{2-x}\text{O}/\text{FTO}-i$ ($i = 1, 2, 3, 4$, and 7) electrodes. The shift of the diffraction peak of the $\{111\}$ crystal facet indicates that Ag^+ ions on the $\{111\}$ crystal facet are partially oxidized into Ag^{2+} ions during the electrodeposition process. Therefore, it was determined that a more accurate description of the component of the electrode films should be Ag_{2-x}O . This result is similar to that of an earlier reference [45], but the shifts are larger because more Ag^{2+} ions were generated in our work. Furthermore, by close inspection of the XRD patterns of the $\text{Ag}_{2-x}\text{O}/\text{FTO}$ samples, it was noted that the diffraction peak intensity ratios of $\{111\}$ and $\{200\}$ crystal facets (Table S1) are approximately 1.59 for the $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ electrode and 0.4, 0.48, 0.39, 0.32, and 0.36 for the other $\text{Ag}_{2-x}\text{O}/\text{FTO}-i$ electrodes ($i = 0.5, 2, 3, 4$, and 7, respectively). This result indicates that a $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ electrode exhibits a larger exposed $\{111\}$ facet, and more noteworthy, that some of the Ag^+ ions on the $\{111\}$ facet are oxidized to Ag^{2+} ions. This could affect the OER.

Fig. 2a shows the XPS survey spectrum of the $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ electrode. The C 1s hydrocarbon peak was fixed at the binding energy of 284.6 eV to subtract the surface charging effect. This shows that the electrode film consists of O and Ag elements and that no other elements exist. Fig. 2b is the Ag 3d XPS spectrum of the $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ electrode. The two broad peaks appearing at 368.02 and 374.03 eV were assigned to the binding energy of Ag $3d_{5/2}$ and $3d_{3/2}$, respectively. The peak at ~ 377.5 eV was assigned to a weak satellite signal. According to the fitting results, the two peaks at 368.21 and 374.10 eV could be attributed to Ag^+ ions [56], while the other two peaks at 367.81 and 373.89 eV were derived from Ag^{2+} ions. The ratio of the peak areas belonging to Ag^+ and Ag^{2+} was approximately 1.46. This indicates that some Ag^{2+} ions exist on the $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ electrode, which is in good accord with the XRD results. The higher valence state Ag^{2+} ions may be advantageous for the OER

Fig. 2. (a) XPS survey spectrum and (b) Ag 3d XPS spectrum for the $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ electrode before the LSV measurement.

Fig. 3. SEM images of $\text{Ag}_{2-x}\text{O}/\text{FTO}-i$ electrodes with i equal to (a) 0.5, (b) 1, (c) 2, (d) 3, (e) 4, and (f) 7; (g) HRTEM image of $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ electrode with $\{111\}$ plane.

[57–63].

Fig. 3 shows the SEM and HRTEM images of $\text{Ag}_{2-x}\text{O}/\text{FTO}-i$ electrodes. The SEM images show that $\text{Ag}_{2-x}\text{O}/\text{FTO}-i$ ($i = 0.5, 1, 4$, and 7) electrodes display relatively dense Ag_{2-x}O film while $\text{Ag}_{2-x}\text{O}/\text{FTO}-i$ ($i = 2$ and 3) electrodes are composed of sparse Ag_{2-x}O particles with poor density. The morphologies of Ag_{2-x}O particles can be observed at magnification of 10000 times in the insets of Fig. 3a–3f. It is shown that $\text{Ag}_{2-x}\text{O}/\text{FTO}-0.5$ and $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ exhibit a triangular slice of the vertical matrix and parallel matrix, respectively, whereas $\text{Ag}_{2-x}\text{O}/\text{FTO}-i$ ($i = 2, 3, 4$, and 7) electrodes show wheat-ear shapes with a parallel

Fig. 4. LSV curves of $\text{Ag}_{2-x}\text{O}/\text{FTO}-i$ ($i = 0.5, 1, 2, 3, 4$, and 7) electrodes in $0.10 \text{ M K}_2\text{B}_4\text{O}_7$ aqueous solution with potential windows from 0.8 to 2.4 V vs. RHE , and no compensation for iR drop.

matrix. The triangular surface morphology of the $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ electrode corresponds to the preferred growth orientation of $\{111\}$ crystal facets of Ag_{2-x}O [53]. The HRTEM image of Ag_{2-x}O was examined (Fig. 3g) and showed that Ag_{2-x}O has a crystal-line structure with lattice spacing of 0.267 nm , which was attributed to the d-spacing for the $\{111\}$ plane of Ag_{2-x}O [54]. It is known that many more terminal Ag ions are exposed on the $\{111\}$ crystal facet (than on other facets), which might lead to higher activity for electrocatalytic water oxidation there.

3.2. Electrocatalytic water oxidation of $\text{Ag}_{2-x}\text{O}/\text{FTO}-i$ electrodes

The electrocatalytic water oxidation performance of the $\text{Ag}_{2-x}\text{O}/\text{FTO}-i$ electrodes was studied by linear sweep voltammetry (LSV) in $0.10 \text{ M K}_2\text{B}_4\text{O}_7$ solution at pH 9.2. As shown in Fig. 4, the anode currents of $\text{Ag}_{2-x}\text{O}/\text{FTO}-i$ electrodes start and continue until the applied potential increases to $\sim 1.76 \text{ V vs. RHE}$ without compensation for an iR drop. Additionally, it is noted that $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ electrodes show obviously higher oxidative current density than the other $\text{Ag}_{2-x}\text{O}/\text{FTO}-i$ ($i = 0.5, 2, 3, 4$, and 7) electrodes do. For instance, at 2.39 V vs. RHE , the current density was 10.00 mA cm^{-2} for the $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ electrode, but was $5.18, 4.22, 4.43, 5.86$, and 5.44 mA cm^{-2} for $\text{Ag}_{2-x}\text{O}/\text{FTO}-i$ ($i = 0.5, 2, 3, 4$, and 7 , respectively), and only 0.55 mA cm^{-2} for a bare FTO electrode. That is, the $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ electrode has oxidative current density nearly 2 times higher than that of the other $\text{Ag}_{2-x}\text{O}/\text{FTO}-i$ ($i = 0.5, 2, 3, 4$, and 7) electrodes and 18 times higher than that of the FTO electrode. The Tafel plots (Fig. S3) and Tafel equations can be obtained by

Table 1

Tafel formula, Tafel slope, overpotential and onset potential for $\text{Ag}_{2-x}\text{O}/\text{FTO}-i$ electrodes at current density of 10 mA cm^{-2} (the overpotentials were corrected for the iR drop of the solution).

$\text{Ag}_{2-x}\text{O}/\text{FTO}-i$ electrode	Tafel formula	Tafel slope (mV dec^{-1})	Overpotential (mV)	Onset potential (V vs. RHE)
0.5	$\eta = 0.37 + 0.063 \log j $	63	433	1.74
1	$\eta = 0.37 + 0.047 \log j $	47	417	1.76
2	$\eta = 0.44 + 0.059 \log j $	59	439	1.77
3	$\eta = 0.42 + 0.088 \log j $	88	438	1.77
4	$\eta = 0.37 + 0.068 \log j $	68	428	1.76
7	$\eta = 0.39 + 0.061 \log j $	61	431	1.75

analyzing the data in Fig. 4. As listed in Table 1, the onset potentials of the $\text{Ag}_{2-x}\text{O}/\text{FTO}-i$ electrodes are all similar (1.74–1.77 V vs. RHE). The overpotentials ($\eta = V_{\text{RHE}} - iR - 1.23$ V, where V_{RHE} is the applied potential vs. RHE) are 433, 417, 439, 438, 428, and 431 mV at 10.00 mA cm^{-2} and the Tafel slopes are 63, 47, 59, 88, 68, and 61 mV dec^{-1} for $\text{Ag}_{2-x}\text{O}/\text{FTO}-i$ ($i = 0.5, 1, 2, 3, 4$, and 7 , respectively). As a consequence, $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ electrodes have the lowest overpotential and the smallest Tafel slope, which are ascribed to their larger exposed {111} crystal facets and to the existence there of high valence Ag^{2+} ions. The above results prove clearly that Ag_{2-x}O is an efficient OEC under alkaline conditions and that the {111} crystal facets are more active. Compared to a AgO/FTO electrode [54], a $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ electrode shows lower overpotential. The OER catalytic performances of partial Ag-based catalysts and of Ir/C, IrO_2 or RuO_2 catalysts, are listed in Table S2 for comparison.

Electrochemical impedance spectra (EIS) of $\text{Ag}_{2-x}\text{O}/\text{FTO}-i$ electrodes were measured at a bias potential of -0.50 V vs. SCE, and the Nyquist curves are shown in Fig. 5. To interpret these plots, an equivalent circuit (inset) is presented that shows electrochemical pseudocapacitance (CPE1) and charge transfer resistance (R_{ct}) [64,65]. A variety of impedance parameters can be obtained by fitting the Nyquist curve. The R_{ct} values are 2.63×10^4 , 2.02×10^3 , 3.45×10^4 , 2.81×10^4 , 1.71×10^4 , and $2.21 \times 10^4 \Omega$ for $\text{Ag}_{2-x}\text{O}/\text{FTO}-i$ ($i = 0.5, 1, 2, 3, 4$, and 7) electrodes, respectively. The $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ electrode shows the lowest R_{ct} value, which suggests that $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ electrodes have the preferred capacity to transfer electrons at the electrode and electrolyte interface. This result explains why the $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ electrode has better catalytic activity for the OER.

Moreover, the electrocatalytic durability of catalysts is a vital indicator for their commercial viability. Therefore, we determined the OER stability of a $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ electrode using an $I-t$ test at 1.2 V vs. SCE in $0.1 \text{ M K}_2\text{B}_4\text{O}_7$ electrolyte at pH 9.2. As shown in Fig. 6, electrolysis begins with electrochemical pseudocapacitance, which is ascribed to the oxidation of Ag^+ to Ag^{2+} . After 1 h, the current density gradually rises to 2.84 mA cm^{-2}

Fig. 6. Time course of current density for the $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ electrode. The conditions included $0.10 \text{ M K}_2\text{B}_4\text{O}_7$ electrolyte (at pH 9.2), applied voltage of 1.2 V vs. SCE, and no compensation for iR drop.

cm^{-2} and then decreases slightly to 2.72 mA cm^{-2} in 10 h. In this case, the OER current became predominant. Even more encouraging, the $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ electrode remained stable during 10 h of electrochemical testing.

3.3. Mechanism of electrocatalytic water oxidation for oxygen evolution using Ag_{2-x}O

Fig. 7 shows the CV curves of $\text{Ag}_{2-x}\text{O}/\text{FTO}-i$ electrodes with potential in the range 0.2 – 2.0 V vs. RHE with a scanning rate of 100 mV s^{-1} . It is clear that the $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ electrode has a better electrochemical property. It shows oxidative current density 3 times higher than that of other $\text{Ag}_{2-x}\text{O}/\text{FTO}-i$ ($i = 0.5, 2, 3, 4$, and 7) electrodes and 16 times higher than that of a bare FTO electrode at 2.0 V vs. RHE. This further proves that the $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ electrode, which has larger {111} well-exposed crystal facets, has superior catalytic activity for the electrochemical OER. Furthermore, the CV curve of $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ clearly shows a strong oxidation peak (I) at 1.4 V vs. RHE and two reduction peaks (II and III) at 0.82 and 1.33 V vs. RHE. This

Fig. 5. Electrochemical impedance spectra of the $\text{Ag}_{2-x}\text{O}/\text{FTO}-i$ electrodes in $0.10 \text{ M K}_2\text{B}_4\text{O}_7$ at -0.50 V vs. SCE. The frequency range was 0.01 to 10^5 Hz , with the ac amplitude perturbed at 5 mV . In an equivalent circuit that exhibits one-time constant models, R_{ct} is the charge transfer resistance, and CPE1 represents the constant phase elements.

Fig. 7. CV curves of $\text{Ag}_{2-x}\text{O}/\text{FTO}-i$ and FTO electrodes in $0.10 \text{ M K}_2\text{B}_4\text{O}_7$ aqueous solution with electrical potential held at 0.2 – 2.0 V vs. RHE, and no compensation for iR drop.

Fig. 8. CV curves of $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ in 0.10 M $\text{K}_2\text{B}_4\text{O}_7$ aqueous solution with a scan rate of 100 mV s^{-1} . (a) Scanning potential in the range of 0.2–2.0 V vs. RHE, (b) Scanning potential in the range of 0.2–1.7 V vs. RHE, and (c) Scanning potential in the range of 0.2–1.7 V vs. RHE in 0.10 M $\text{K}_2\text{B}_4\text{O}_7$ aqueous solution containing 0.05 mM H_2O_2 , and no compensation for iR drop.

implies that it may offer a convenient opportunity to study the electrochemical and electrocatalytic performance of heterogeneous Ag^+ -based catalysts.

In earlier work, the oxidation peak (I) and reduction peak (II) were assigned to the redox of Ag^0 and Ag^+ [66]. The reduction peak (III) may be due to the reduction of Ag^{2+} or O_2^{2-} , which ions were produced in the water oxidation process at high potential. Accordingly, the CV curves b and c (Fig. 8) were

recorded carefully by design. From Fig. 8b, it can be seen that the reduction peak (III) disappears when the scanning potential is from 0.2 to 1.7 V vs RHE; meanwhile, Fig. 8c shows that the reduction peak (III) appears as 0.5 mM H_2O_2 is added to the electrolyte at 0.2 V and 1.7 V vs RHE. This phenomenon indicates that the reduction peak (III) does not originate from the reduction of Ag^{2+} on the $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ electrode, but instead from the reduction of residual O_2^{2-} generated on the surface of Ag_{2-x}O at 0.2–2.0 V vs. RHE.

To determine further the chemical status of the O and Ag elements in $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ during electrocatalysis, XPS spectra were recorded after the LSV measurement and are shown in Fig. 9. As shown in Fig. 9b and 9d, in contrast to the single peak of O 1s at 531.70 eV for the freshly prepared $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$, two XPS peaks at 531.70 and 533.10 eV of O 1s emerge for the $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ electrode after the LSV measurement at 0.8–2.4 V vs. RHE. In this case, the peak at 531.70 eV belongs to O^{2-} ions, and the other at 533.10 eV is assigned to O_2^{2-} on the surface of $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ [67]. This result further confirms the previous speculation from the CV curves. Fig. 9c shows the Ag 3d XPS spectrum of the $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ electrode before and after the LSV measurement from 0.8 to 2.4 V vs. RHE. Compared to the Ag 3d XPS spectrum of freshly prepared $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$, it is found that the binding energies of Ag 3d_{5/2} and Ag 3d_{3/2} undergo a slight shift to lower energies, which is attributed to increases in Ag^{2+} . The peak area ratio of Ag^+ and Ag^{2+} decreases from 1.46 to 0.65, from which it was inferred that there was a noticeable increase in the content of Ag^{2+} after the LSV at 0.8–2.4 V vs. RHE. It was deduced that the Ag^{2+} and O_2^{2-} ions coexist in equilibrium.

Fig. 9. (a) XPS survey spectrum, (b) O 1s XPS after the LSV measurement in the range 0.8–2.4 V vs. RHE, (c) Ag 3d XPS spectra of $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ electrode before and after the LSV measurement in the range 0.8–2.4 V vs. RHE, and (d) O 1s XPS spectrum of $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ before the LSV measurement.

Fig. 10. Raman spectra of (a) freshly prepared $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ electrode, (b) $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ electrode after the CV test at 0.2–1.7 V vs. RHE, and (c) $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ electrode after the LSV test at 0.8–2.4 V vs. RHE in 0.1 M $\text{K}_2\text{B}_4\text{O}_7$.

The visible-Raman spectrum was employed to investigate the O_2^{2-} species on the surface of $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ electrode. As shown in Fig. 10a and 10b, only two peaks at 430 and 470 cm^{-1} appear for both the freshly prepared $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ electrode and that after the CV measurement at 0.2–1.7 V vs. RHE, which are associated with the Ag–O stretching vibration [68]. In contrast, additional peaks at 980, 1053, and 1300 cm^{-1} appear for the $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ electrode after the LSV at 0.8–2.4 V vs. RHE, which corresponds to the Ag– O_2^{2-} species [69].

Based on the above results, a possible mechanism of water oxidation for oxygen evolution is proposed. As shown in Scheme 1, when more Ag^+ ions are oxidized to Ag^{2+} ions at higher potential, OH^- and H_2O adsorb to the surface of Ag_{2-x}O , then the electron-transfer from OH^- to Ag^{2+} takes place at the adjacent Ag^{2+} –OH species. It can be seen that the active electrons on adjacent oxygen atoms tend to transfer to Ag^{2+} to form Ag^+ , and simultaneously the O–O bond is formed by the departure of two H^+ . Furthermore, O_2 molecules are generated when the Ag^+ ions connecting the O–O bonds are oxidized to Ag^{2+} or Ag^{3+} . Because Ag_{2-x}O crystals with a larger {111} crystal facet area expose more Ag ions that can preferably combine with

Scheme 1. Mechanism sketch of electrochemical OER for an $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ electrode.

OH^- ions and H_2O molecules [53], these facets are remarkably well suited to catalyze water oxidation and generate oxygen evolution on $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ electrodes.

4. Conclusions

In this work, a series of $\text{Ag}_{2-x}\text{O}/\text{FTO}-i$ electrodes were fabricated by galvanostatic electrocrystallization. Among them, the $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ electrode exhibits larger {111} well-exposed crystal facets, and its intensity ratio of diffraction peaks of {111} and {200} crystal facets is 3 times higher than the other $\text{Ag}_{2-x}\text{O}/\text{FTO}-i$ ($i = 0.5, 2, 3, 4$, and 7) electrodes. Furthermore, it was found that some of the Ag^+ ions on {111} crystal facets were oxidized to Ag^{2+} ions. The $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ electrode has an overpotential of 417 mV at 10.00 mA cm^{-2} and a Tafel slope of 47 mV dec^{-1} during electrocatalytic water oxidation in 0.1 M $\text{K}_2\text{B}_4\text{O}_7$ at pH 9.2. The $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ electrode exhibits obviously better electrocatalytic OER performance than the other $\text{Ag}_{2-x}\text{O}/\text{FTO}-i$ electrodes, which result is ascribed to the larger exposed {111} crystal facet area and to more $\text{Ag}^+/\text{Ag}^{2+}$ ions being exposed in $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$. In addition, Ag^{2+} ions and O_2^{2-} species were fortunately observed in the CV, XPS, and Raman spectra during electrocatalysis, based on which a possible mechanism of electrocatalytic water oxidation on $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ electrodes is proposed.

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Graphical Abstract

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Ag_{2-x}O with highly exposed {111} crystal facets for efficient electrochemical oxygen evolution: Activity and mechanismXiao-Feng Zhang, Jian-Sheng Li *, Wan-Sheng You *, Zai-Ming Zhu
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A series of Ag_{2-x}O/FTO-*i* (*i* = 0.5, 1, 2, 3, 4, 7) electrodes were fabricated. The results from studies on the activity and mechanism of one electrode (Ag_{2-x}O/FTO-1) with unusually large and well-exposed {111} crystal facets and production of Ag²⁺ showed more efficient electrochemical oxygen evolution.

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高暴露{111}晶面 Ag_{2-x}O 用于高效电催化析氧反应及其活性和机理

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摘要: 析氧反应(OER)是工业上制约水裂解制氢和 CO_2 综合利用的瓶颈, 涉及四电子、四质子耦合以及O—O键的形成, 是一个复杂的、高活化能(高过电位)的动力学过程。模拟自然界光系统PS II, 发展高效、稳定、经济的析氧催化剂(OEC)是一个具有挑战性的研究课题。 Ag 基催化剂因具有以下优势而成为候选: (1) Ag 与 Ru 同属第五周期性质相近, 且有经济性且储量丰富; (2) Ag 比第三周期过渡金属具有更高的电子密度和更多可调节配位数; (3) Ag 存在I, II, III多种氧化态。本课题组前期工作证明, Ag 基配合物 $[\text{H}_3\text{Ag}^{\text{I}}(\text{H}_2\text{O})\text{PW}_{11}\text{O}_{39}]^{3-}$ 在酸性水溶液体系中能够形成高氧化态 Ag^{II} 和 Ag^{III} 配合物, 用于OER时展现出高活性和稳定性。受此启发, 我们选择简单银基氧化物用于研究电催化OER活性并探究其催化机理。

本文通过恒电流沉积法在含有 Ag^+ 离子的0.1 M $\text{K}_2\text{B}_4\text{O}_7$ 电解质溶液中设计合成了系列 $\text{Ag}_{2-x}\text{O}/\text{FTO}-i$ ($i = 0.5, 1, 2, 3, 4, 7$ mA cm^{-2})电极, 并通过XRD, SEM和TEM方法对其组成和形貌进行了表征。XRD结果表明, 电极膜由 Ag_2O 组成, 随着沉积电流密度增加, 其{111}晶面衍射峰向高角度移动, 推测是由部分 Ag^+ 离子氧化成 Ag^{2+} 离子所致。SEM显示, $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ 电极膜上 Ag_{2-x}O 主体呈现三角薄片状, 拥有比其它电极 $\text{Ag}_{2-x}\text{O}/\text{FTO}-i$ ($i = 0.5, 2, 3, 4, 7$)暴露更多的{111}晶面。同时, 高倍TEM显示晶面间距为0.267 nm, 进一步证明存在较多暴露{111}晶面。线性扫描伏安曲线(LSV)显示, $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ 电极具有最高的OER电流密度, 通过对Tafel区域进行拟合, 得到Tafel方程 $\eta = 0.37 + 0.047 \log |j|$, 计算得出在10 mA cm^{-2} 电流密度下 $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ 电极具有较低的Tafel斜率47 mV dec^{-1} 和过电位417 mV vs. RHE, 可用作高效的OEC。电化学阻抗谱(EIS)表明, 相比其它电极, $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ 具有最佳的电荷转移能力。电流-时间($I-t$)曲线显示10 h内其电流密度仅下降4%, 表明电极稳定性良好。通过XPS和拉曼光谱发现, $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ 经过循环伏安(CV)测试后存在O—O键, 说明 Ag_{2-x}O 电催化OER过程中形成了过氧物种。XPS进一步显示催化反应前后 Ag^+ 和 Ag^{2+} 峰面积比由1.46降至0.65, 说明反应后 Ag^{2+} 含量显著增加。通过对 $\text{Ag}_{2-x}\text{O}/\text{FTO}-1$ 电极电催化OER机理的研究, 我们推测其具有优异活性的原因是 Ag_{2-x}O 表面更高暴露{111}晶面有利于 $\text{Ag}^+/\text{Ag}^{2+}$ 吸附 OH^- 和 H_2O , 相邻的吸附氧原子在脱去 H^+ 的同时, 氧原子上活性电子易于转移给 Ag^{2+} 形成O—O键和 Ag^+ 。电极上 Ag^+ 进一步被氧化生成 Ag^{2+} , Ag^{2+} 将过氧物种氧化, 放出 O_2 , 完成催化剂的循环再利用。

关键词: 氧化银; 晶面; 二价银离子; 电催化; 水氧化; 析氧反应

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