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Communication

In situ evolution of surface Co_2CrO_4 to $\text{CoOOH}/\text{CrOOH}$ by electrochemical method: Toward boosting electrocatalytic water oxidation

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ABSTRACT

Developing non-noble-metal electrocatalyst with efficient and durable activity is a urgent task for addressing the sluggish reaction kinetics of electrochemical water oxidation. Structural evolution of the electrocatalyst is an important strategy for achieving enhanced performance. Herein, *in situ* evolution of surface Co_2CrO_4 to $\text{CoOOH}/\text{CrOOH}$ ($\text{CoOOH}/\text{CrOOH}-\text{Co}_2\text{CrO}_4$) by an electrochemical method under alkaline conditions was designed for enhancing the electrocatalytic performance of water oxidation. The experiments demonstrated that the synergy between $\text{CoOOH}/\text{CrOOH}$ and Co_2CrO_4 resulted in a marked increase in the number of active sites and improved the rate of charge transfer, which enhanced the activity for water oxidation. At a geometrical current density of 20 mA cm^{-2} , the overpotential of the oxygen evolution reaction was 244 mV and the turnover frequency was 0.536 s^{-1} in 1.0 M NaOH.

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Water splitting powered by electricity is considered a promising process for generating hydrogen to alleviate public concerns about the escalating energy depletion and environmental pollution [1–6]. The oxidative process of water splitting, that is, the oxygen evolution reaction (OER), is a multielectron transfer process and a bottleneck in hydrogen generation. The OER involves the breakage of O–H bonds and the reconstruction of O=O bonds [7–10]. Accordingly, it requires highly efficient OER catalysts to obtain a large geometrical current density as low as the overpotential. Ru- and Ir-based catalysts have been proven to be the best OER active electrocatalysts, but the

low quantity and high price of the metals make the large-scale application of these catalysts difficult to realize [11,12], pushing researchers to explore and design abundant and inexpensive OER catalysts with efficient and durable activity for water oxidation.

Co-based oxide catalysts have been recognized as important low-price metal catalysts for water oxidation under alkaline conditions [13–25]. It is known that the incorporation of metallic oxides with Cr-based oxides can enhance the catalyst stability [26]. Therefore, the rational synergistic integration of Cr and Co into one united monolith may yield better catalyst perfor-

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mance. Spinel-type oxides (AB_2O_4) have the essential characteristics of a high content of oxygen-deficiencies and flexible oxidation states; these features lead to the formation of redox couples, which are beneficial for improving the electrochemical activity of the catalysts [27–29]. The performance of the OER is primarily related to the efficiency of OH^- absorption on the catalyst surface [6]. Previous studies indicated that transition metal hydroxide catalysts, such as $MOOH$ and MOH , exhibit promising activity in the electrocatalysis field [29]. Based on our previous work, the anodization of spinel-type compounds can induce atomic-scale phase transformation at the surface and generate $MOOH$ as a product [27].

In this communication, we report the preparation of a $CoOOH/CrOOH-Co_2CrO_4$ nanosheet array on Ni foam ($CoOOH/CrOOH-Co_2CrO_4/NF$) by anodizing Co_2CrO_4 nanosheet arrays on Ni foam (Co_2CrO_4/NF) synthesized via a facile chemical liquid deposition strategy (Scheme 1). At a geometrical current density of 20 mA cm^{-2} , the overpotential of the oxygen evolution reaction was 244 mV and the turnover frequency was 0.536 s^{-1} in 1.0 M NaOH , revealing that $CoOOH/CrOOH-Co_2CrO_4/NF$ exhibits promising electrochemical catalytic activity for the OER. The electrochemical catalytic activity can be maintained for a maximum 40 h, and the mechanical integrity of the catalyst remains unchanged.

Figs. S1(a) and Fig. 1(a) show the X-ray diffraction (XRD) patterns of Co_2CrO_4 and $CoOOH/CrOOH-Co_2CrO_4$. For Co_2CrO_4 (Fig. S1(a)), the peak at 36.4° corresponds to the cubic Co_2CrO_4 phase (JCPDS No. 25-1497) [31]. After anodization, broad diffraction peaks appeared at $\sim 20^\circ$, corresponding to the $CoOOH$ phase (JCPDS No. 26-0480) [32] and $CrOOH$ phase (JCPDS No. 09-0331) [33]. The scanning electron microscopy (SEM) images of Co_2CrO_4/NF (Figs. S1(b,c)) demonstrate that the Co_2CrO_4 nanosheet arrays were evenly distributed and interfaced with each other. Following the oxidation process, the nanosheet array structure of $CoOOH/CrOOH-Co_2CrO_4/NF$ was maintained, while some tiny structures were attached to the Co_2CrO_4 nanosheets at the gaps in the nanosheet array (Figs. 1(b,c)); these species are $CoOOH/CrOOH$ produced during electrochemical oxidation. The morphology of the nanosheet was further observed through transmission electron microscopy (TEM) (Fig. S1(d) and Fig. 1(d)). Fig. S1(d) shows that the surface of the Co_2CrO_4 nanosheets was smooth, whereas the surface of the $CoOOH/CrOOH-Co_2CrO_4$ nanosheets (Fig. 1(d)) had a very obvious convoluted morphology. N_2 adsorp-

Scheme 1. Schematic diagram of the fabrication process for Co_2CrO_4/NF and $CoOOH/CrOOH-Co_2CrO_4/NF$.

Fig. 1. (a) XRD pattern of $CoOOH/CrOOH-Co_2CrO_4$; (b,c) SEM images of $CoOOH/CrOOH-Co_2CrO_4/NF$; (d) TEM image of $CoOOH/CrOOH-Co_2CrO_4$; (e) HRTEM image of $CoOOH/CrOOH-Co_2CrO_4$ (inset: SAED images of $CoOOH/CrOOH-Co_2CrO_4$); (f) SEM and corresponding EDX elemental mapping images of $CoOOH/CrOOH-Co_2CrO_4$.

tion-desorption was used to characterize the Brunauer-Emmett-Teller surface area and porosity of the structures (Fig. S2). The surface area of $CoOOH/CrOOH-Co_2CrO_4$ on Ni foam ($13.11 \pm 1.90\text{ m}^2\text{ g}^{-1}$) was larger than that of Co_2CrO_4 ($7.69 \pm 1.07\text{ m}^2\text{ g}^{-1}$). According to previous reports, the electrochemical reaction sites are dispersed on the surface of the catalysts [29]. Therefore, convoluted $CoOOH/CrOOH-Co_2CrO_4$ may provide more electrochemical reaction sites than Co_2CrO_4 . The inset figure in Fig. S1(d) is the high-resolution TEM (HRTEM) image of Co_2CrO_4 , which shows the lattice fringe with an interplanar distance of 0.246 nm , corresponding to the (311) plane of Co_2CrO_4 . The HRTEM image of $CoOOH/CrOOH-Co_2CrO_4$ provides compelling evidence that the oxidation reaction leads to atomic-scale phase transformation and generates another lattice fringe with an interplanar distance of $\sim 0.439\text{ nm}$, corresponding to the $CrOOH$ plane (Fig. 1(e)). In addition, many defects were introduced in the process, where these defects are beneficial for the electrochemical OER. The electron spin resonance (ESR) signal of $CoOOH/CrOOH-Co_2CrO_4/NF$ can also indicate the existence of defects (Fig. S3). The inset in Fig. S1(e), which shows the selected area electron diffraction (SAED) pattern of $CoOOH/CrOOH-Co_2CrO_4$, demonstrates the corresponding rings. SEM and related energy-dispersive X-ray (EDX) elemental mapping images of $CoOOH/CrOOH-Co_2CrO_4/NF$ (Fig. 1(f)) suggest that Co, Cr, and

Fig. 2. (a) XPS survey spectrum of CoOOH/CrOOH-Co₂CrO₄/NF; XPS spectra of CoOOH/CrOOH-Co₂CrO₄/NF in the Co 2p (b), Cr 2p (c), and O 1s (d) core-levels.

O are uniformly distributed throughout the catalyst. The EDX spectrum indicates that the atomic ratio of Co/Cr/O is close to 2.08:1.00:4.08 (Fig. S4).

Fig. 2 presents the X-ray photoelectron spectroscopy (XPS) spectra of CoOOH/CrOOH-Co₂CrO₄/NF, which shows the chemical valence states of the Co, Cr, and O. The survey spectrum of CoOOH/CrOOH-Co₂CrO₄/NF clearly illustrates the presence of Co, Cr, and O signals. The high-resolution XPS spectra of CoOOH/CrOOH-Co₂CrO₄/NF in the Co 2p, Cr 2p, and O 1s core-levels are shown in Figs. 2(b–d), respectively. The Co 2p core-levels can be divided into six peaks, as shown in Fig. 2(b). The peaks at binding energies (BEs) of 779.6 and 781.8 eV with a shakeup satellite (shortened to “Sat.”) at 785.6 eV correspond to Co 2p_{3/2}, and the peaks at BEs of 794.5 and 798.2 eV, respec-

tively, with a Sat. at 802.4 eV are related to Co 2p_{1/2}, confirming the presence of Co^{II} and Co^{III} [11,34,35], respectively. The Cr 2p core-level spectrum (Fig. 2(c)) shows signals at BEs of 586.6 and 576.4 eV with a Sat. at 578.9 eV corresponding to the 2p_{1/2} and 2p_{3/2} states of trivalent Cr [15,26,29], respectively. Three O 1s peaks at 529.6, 530.8, and 532.2 eV were observed for CoOOH/CrOOH-Co₂CrO₄/NF in Fig. 2(d), which correspond to the M–OH bond (M = Co, Cr), MO–H bond, and H–O–H bond in physically adsorbed H₂O, respectively [36]. Overall, the XPS analyses reveal that CoOOH/CrOOH-Co₂CrO₄/NF was successfully synthesized.

The electrochemical measurements were performed with a three-electrode system using 1.0 M NaOH as the electrolyte. All potential values were calculated on the reversible hydrogen electrode (RHE) scale. Linear sweep voltammetry (LSV) at a scan rate of 2 mV s^{−1} was used to evaluate the OER electrocatalytic activity of CoOOH/CrOOH-Co₂CrO₄/NF (loading: ~2.31 mg cm^{−2}). After *iR* correction, the effect of ohmic resistance is removed, and the data show the intrinsic properties of the catalyst [37–39]. For comparison, RuO₂ on NF (RuO₂/NF), Co₂CrO₄/NF (loading: ~2.23 mg cm^{−2}), and bare NF were also evaluated. Fig. 3(a) shows the LSV curves for bare NF, Co₂CrO₄/NF, CoOOH/CrOOH-Co₂CrO₄/NF, and RuO₂/NF. Clearly, the catalytic activity of bare NF for the OER is poor, whereas RuO₂/NF exhibits excellent activity, requiring an overpotential of 237 mV at a geometrical current density of 20 mA cm^{−2}. To achieve the same current density, the overpotential requirements for the OER are 244 mV for CoOOH/CrOOH-Co₂CrO₄/NF and 360 mV for Co₂CrO₄/NF. At a current density of 250 mA cm^{−2}, the overpotential for CoOOH/CrOOH-Co₂CrO₄/NF was 418 mV, which is lower than that of RuO₂/NF (420 mV), revealing that CoOOH/CrOOH-Co₂CrO₄/NF exhibits better OER performance at high current densities. The above results confirm that

Fig. 3. LSV curves (a) and corresponding Tafel plots (b) for RuO₂/NF, CoOOH/CrOOH-Co₂CrO₄/NF, Co₂CrO₄/NF, and bare NF at a scan rate of 2 mV s^{−1}; (c) Multi-current chronopotentiometric curve for CoOOH/CrOOH-Co₂CrO₄/NF. (d) Nyquist plots for CoOOH/CrOOH-Co₂CrO₄/NF and Co₂CrO₄/NF.

CoOOH/CrOOH formed through the anode oxidation process can play a key role in improving the OER activity. During 0–1.5 h, the OER reactivity was positively related to the time of the electrochemical anode reaction. Thereafter, the activity decreased slightly, which may be due to the accumulation of CoOOH/CrOOH, which increases the charge-transfer resistance [30]; however, the catalytic performance was still superior to that of Co₂CrO₄/NF (Fig. S5). The Tafel slopes of Co₂CrO₄/NF, CoOOH/CrOOH-Co₂CrO₄/NF, and RuO₂/NF (Fig. 3(b)) were obtained from the corresponding LSV curves. The Tafel slopes for CoOOH/CrOOH-Co₂CrO₄/NF, RuO₂/NF, and Co₂CrO₄/NF were 96, 97, and 160 mV dec⁻¹, respectively, suggesting that the catalytic kinetics of CoOOH/CrOOH-Co₂CrO₄/NF is similar to that of RuO₂/NF. The current density in the multicurrent chronopotentiometric curve of CoOOH/CrOOH-Co₂CrO₄/NF (Fig. 3(c)) increased from 20 to 130 mA cm⁻² (10 mA cm⁻² per 500 s). The start potential levelled off at 260 mV and remained constant for the remaining 500 s. The next steps also produced similar results, revealing that the CoOOH/CrOOH-Co₂CrO₄/NF electrode exhibits promising conductivity, mass transport properties, and electrochemical stability. Electrochemical impedance spectroscopy can be used to analyze the OER kinetics at the surface of the catalysts. Fig. 3(d) shows the Nyquist plots of CoOOH/CrOOH-Co₂CrO₄/NF and Co₂CrO₄/NF. The charge-transfer resistance (*R*_{ct}) of CoOOH/CrOOH-Co₂CrO₄/NF (~5 ohm) is much smaller than that of Co₂CrO₄/NF (~20 ohm), which shows that the charge-transfer kinetics is much faster at the surface of the CoOOH/CrOOH-Co₂CrO₄/NF electrode.

The turnover frequency (TOF) is the number of transformations per unit time for a single active site, which can be used to further characterize the inherent OER capacity of the catalysts [40]. First, the number of active sites was mathematically calculated from the slope of the oxidation peak vs. scanning rate plots (Fig. S6). At an overpotential of 300 mV, the TOF value of CoOOH/CrOOH-Co₂CrO₄/NF was 0.608 s⁻¹, which is higher than that of Co₂CrO₄/NF (0.434 s⁻¹, η = 300 mV) and those reported for Co₃O₄ nanorods (0.0008 s⁻¹, η = 410 mV) [41] and Co-Pi (0.002 s⁻¹, η = 410 mV) [42].

The electrochemical surface area (ECSA) is an important parameter that affects the activity of a catalyst, and is evaluated from the double-layer capacitance (*C*_{dl}) [31]. Cyclic voltammograms of CoOOH/CrOOH-Co₂CrO₄/NF (Fig. S7(a)) and Co₂CrO₄/NF (Fig. S7(b)) were collected at a series of scanning rates (10–50 mV s⁻¹). The slope of the current density vs. scanning rate plot provides the capacitance. The capacitance of CoOOH/CrOOH-Co₂CrO₄/NF was 209 mF cm⁻² (Fig. S7(c)), which is much larger than that of Co₂CrO₄/NF (9 mF cm⁻²) (Fig. S7(d)). This indicates that the ECSA of CoOOH/CrOOH-Co₂CrO₄/NF is much higher, indicating more exposed active sites.

The electrochemical durability is also a very important concern for OER catalysts. Fig. 4(a) shows the LSV curves before and after 1000-cycle CVs, illustrating no obvious changes, revealing that the catalyst exhibits very steady catalytic performance. Moreover, the long-term electrochemical catalysis of CoOOH/CrOOH-Co₂CrO₄/NF was evaluated at constant potentials of 1.474 V (Fig. 4(b)) and 1.774 V (Fig. S8). The data show

that the catalyst retains a geometrical current density of ~20 and ~500 mA cm⁻² for at least 40 h. From the XRD pattern of CoOOH/CrOOH-Co₂CrO₄/NF after the electrochemical test (Fig. S9), it can be concluded that there is no change in the crystal structure. The diffraction peaks of the CoOOH/CrOOH sample are not shown in the XRD pattern of Co₂CrO₄/NF after the OER stability test (Fig. S10). In addition, the morphology of CoOOH/CrOOH-Co₂CrO₄/NF was still retained (Figs. S11(a,b)). The superior stability of CoOOH/CrOOH-Co₂CrO₄/NF is plausibly derived from the introduction of Cr. To prove this postulate, we synthesized a spinel Co₃O₄ nanosheet array on NF (Co₃O₄/NF). Fig. S12 shows the SEM images of Co₃O₄/NF before and after the 40 h stability test. After 40 h of stability testing, most of the nanosheet structures were destroyed (Figs. S12(c,d)). In contrast, the nanostructure of CoOOH/CrOOH-Co₂CrO₄/NF barely changed (Fig. S11(a)), revealing that the introduction of Cr can improve the catalyst stability. Comparison of the XPS spectra of CoOOH/CrOOH-Co₂CrO₄/NF before and after the OER test (Fig. S13) also indicates that the chemical states of the elements was also stable. The XPS spectra of Co₂CrO₄/NF after the OER stability test are presented in Fig. S14. By comparing the XPS spectra of Co₂CrO₄/NF after the OER stability test with that of CoOOH/CrOOH-Co₂CrO₄/NF (Fig. 2(b)), we found that the Co^{III} content in Co₂CrO₄/NF after the OER stability test is lower than that of CoOOH/CrOOH-Co₂CrO₄/NF. It is suggested that the oxygen evolution reaction generates CoOOH/CrOOH, but the content is less than that generated in the process of cyclic voltammetry.

In conclusion, the anode oxidation process of spinel-type Co₂CrO₄ under ambient conditions is an efficient approach for the *in situ* electrochemical synthesis of CoOOH/CrOOH-Co₂CrO₄/NF nanosheets. For such OER electrocatalysts, the overpotential of the oxygen evolution reaction was 244 mV and the turnover frequency was 0.536 s⁻¹ at a geometrical current density of 20 mA cm⁻² in 1.0 M NaOH, revealing that CoOOH/CrOOH-Co₂CrO₄/NF exhibits promising electrochemical catalytic activity for the OER. The electrochemical catalytic activity can be maintained for as long as 40 h and the mechanical integrity of the catalyst remains unchanged. This study not only provides an interesting non-noble metal catalyst for the OER, but offers a promising approach for the rational design and synthesis of MOOH as an attractive active constituent from spinel-type oxides for advanced electrochemical OER applications.

Fig. 4. (a) LSV curves of CoOOH/CrOOH-Co₂CrO₄/NF before and after 1000-cycle CVs; (b) Time-dependent current density curve at a fixed potential of 1.474 V.

Graphical Abstract

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In situ evolution of surface Co_2CrO_4 to $\text{CoOOH}/\text{CrOOH}$ by electrochemical method: Toward boosting electrocatalytic water oxidation

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$\text{CoOOH}/\text{CrOOH}-\text{Co}_2\text{CrO}_4/\text{NF}$ behaves as an efficient electrochemical catalyst for the oxygen evolution reaction. In 1.0 M NaOH, an overpotential of 244 mV was required to obtain a current density of 20 mA cm⁻², with a turnover frequency of 0.536 s⁻¹ and long-term electrochemical durability.

Electronic supporting information

Supporting information is available in the online version of this article.

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表面 Co_2CrO_4 电化学转化为 $\text{CoOOH}/\text{CrOOH}$ 及其增强电催化析氧中的性能

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摘要: 以清洁能源发电为动力的水分解技术是一种很有应用前景的制氢方法, 可以缓解日益增长的能源消耗和公众高度关注的环境问题。水分解的氧化过程, 即析氧反应(OER), 是一个四电子-质子耦合反应, 其动力学缓慢, 是实现高效电解水的技术难题。以 RuO_2 和 IrO_2 为代表的贵金属氧化物表现出极高的催化活性, 但受限于储量低及价格昂贵, 很难广泛应用。因此, 迫切需要开发出具有高效和持久活性的非贵金属电催化剂以解决动力学迟缓问题。钴元素储量丰富、价格低廉, 同时具有较高的催化活性, 有望替代贵金属催化剂而在工业电解水中大规模应用。尖晶石型氧化物(A_2BO_4)具有氧缺陷含量高, 氧化态灵活, 能形成氧化-还原对的特点, 有利于提高催化剂的电化学活性。因此, Cr和Co合理协同制备 A_2BO_4 型催化剂可获得更好的催化剂性能。研究结果(*Chem. Commun.*, **2018**, 54, 4987–4990)表明, OER性能主要与催化剂表面 OH^- 的吸收效率有关, 过渡金属羟基氧化物(MOOH)是OER反应的主要活性物质。对 A_2BO_4 型催化剂进行阳极化处理, 可以使其表面发生原子级相变, 生成MOOH产物。因此, 对电催化剂进行结构演化是提高其催化活性的一个重要策略。

本文采用电化学阳极化处理, 即在碱性环境下对 Co_2CrO_4 表面进行原位演化生成 $\text{CoOOH}/\text{CrOOH}$, 从而得到 $\text{CoOOH}/\text{CrOOH}-\text{Co}_2\text{CrO}_4$ 。通过X-射线衍射、扫描电子显微镜、透射电子显微镜、X-射线光电子能谱和氮气吸附-脱附等方法对催化剂的结构和形貌进行表征。结果表明, 阳极化处理后, 光滑的 Co_2CrO_4 表面生成了 $\text{CoOOH}/\text{CrOOH}$ 褶皱, $\text{CoOOH}/\text{CrOOH}$ 和 Co_2CrO_4 的协同效应可以暴露出更多活性位点并加快电子的传输, 明显提升析氧反应性能。在1.0 M NaOH中进行 $\text{CoOOH}/\text{CrOOH}-\text{Co}_2\text{CrO}_4$ 电催化性能测试, 循环伏安曲线结果表明, 电流密度达到 20 mA cm^{-2} 时, 仅需过电位244 mV, 转化频率是 0.536 s^{-1} , 说明催化剂催化析氧反应性能优异。多步计时电流曲线以及长时间电流曲线表明催化剂稳定性较高。

关键词: $\text{CoOOH}/\text{CrOOH}-\text{Co}_2\text{CrO}_4$ 纳米片; 阳极演化; 电化学催化; 析氧反应; 转化频率

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