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Research paper

Co-Cl-C composited films prepared by flash Joule heating system as an efficient electrocatalyst for the oxygen and hydrogen evolution reaction

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ABSTRACT

Co-based compound is a kind of bifunctional electrocatalyst for the half reactions of water splitting. Here we report the catalytic performance of Co-Cl-C composited catalyst prepared by flash Joule heating system in oxygen evolution reaction (OER) and hydrogen evolution reaction (HER). It is found that Co-Cl-C composited film is an efficient electrocatalyst of OER and HER. In addition, the flash Joule heating is a fast, low energy consumption, and environmentally friendly preparation method. It opens up a new idea for the preparation method of composite materials.

1. Introduction

As we all know, energy is an important material basis for human survival and economic development. At present, fossil fuel is main energy supply. However, their non-renewable nature and harm of environmental pollution have been a serious threat to the human living environment and economic development. Hydrogen is a clean and efficient energy carrier due to the advantages of high energy density, high combustion calorific value and clean combustion products, which provide an ideal energy alternative for human beings to fundamentally solve global problems such as energy and environment [1–6]. There are many methods of hydrogen production, including ammonia to hydrogen, methanol to hydrogen, coal and natural gas evaporation to hydrogen and water splitting to hydrogen, etc. Among them, electrochemical water splitting has been much attention due to its simple preparation, low pollution and high efficiency [7]. Water splitting has two half reactions of oxygen evolution reaction (OER) and hydrogen evolution reaction (HER). However, the high theoretical value of 1.23 V in oxygen evolution reaction causes high potential above 1.8 V in water splitting process [8]. Generally, noble metal-base materials such as RuO_2 and IrO_2 for OER [9] and Pt for HER [10] are used as catalysts in half reactions. However, the noble metal-based catalysts are scarce and expensive. To address this problem, ones attempt to make transitional family metal composites replace noble metal-based catalysts.

Electrodeposition [11], hydrothermal synthesis [12] and a combination of the two [13] are the main preparation methods of the noble-metal-free electrocatalysts. For the electrodeposition method, it is easy to operate. And it can regulate the grain size and improve the performance of the samples prepared. But there is a stress among the layers due to the difference between physical properties and growth modes of the various materials. Although the hydrothermal synthesis method is commonly used, the experiment has poor reproducibility. In our work, we prepared the Co-Cl-C composite powder using flash Joule heating system. The ink composited with powder is then dropped on the self-supported substrate to form the film. This preparation method is fast, low energy consumption and environmentally friendly. Tour et al have reported graphene was prepared using carbon-based precursor by flash Joule heating method [14]. Nevertheless, no one reported preparation of metal-based composites using flash Joule heating. The Co-Cl-C composite film has a high catalytic performance in oxygen and hydrogen evolution reaction. Our experiments provide new ideas for the design and preparation of composite materials.

2. Experiment

2.1. Materials

Cobalt chloride hexahydrate ($CoCl_2·6H_2O$), ethanol, acetone and

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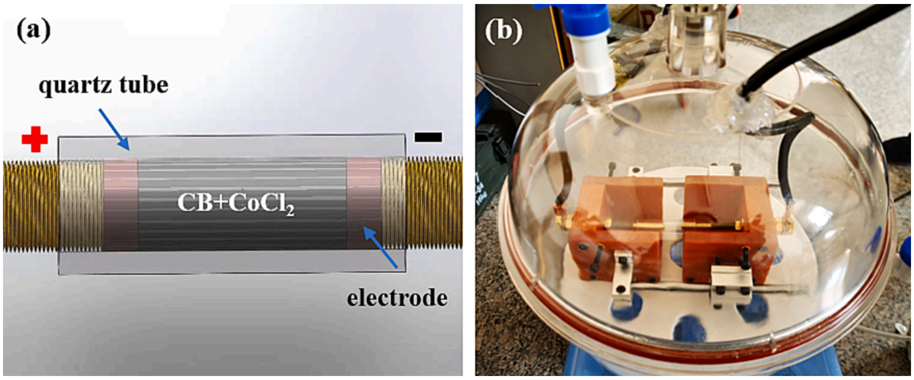

Fig. 1. (a) A schematic drawing of sample cell and (b) the reactor photo.

were purchased from Sinopharm Chemical Reagent Co., Ltd. Carbon black was purchased from Cabot Corporation. Potassium hydroxide (KOH) was purchased from Aladdin Reagents, Inc. Nafion was purchased from Shanghai Hesen Electric Co., Ltd. These materials were not further treatment. Ni foam was purchased from Kunshan Guangjiayuan New Material Co., Ltd. The deionized water was used through an ultra-pure water system made in Beijing Puxi General Instrument Co., Ltd.

2.2. Preparation of the $CoCl_2$-C composited powder

Briefly, 0.3 g carbon black (CB) and 0.9 g $CoCl_2 \cdot 6H_2O$ were mixed in ethanol under centrifugal stirring for 30 min. The above mixture was placed into a drying cabinet and dried at 60 °C for 12 h. Then, the dry powder was enclosed within a quartz tube and pressed between two copper electrodes, a schematic drawing as shown in Fig. 1 (a). Place the sample tube into the home-made flash Joule heating system illustrated in Fig. 1 (b). Co-Cl-C composited powders were prepared by flash Joule heating system with a voltage of 98 V and time of 20 s. In order to avoid oxidation of the sample, the vacuum dryer was replaced using high purity N_2 before flash Joule heating. The specific operation steps are described as follows. First, the vacuum dryer is filled with high purity N_2. Then, the vacuum dryer filled with high purity N_2 is pumped to the limiting vacuum. Repeat this operation several times for reducing oxygen content.

2.3. Electrochemical measurements

All the electrochemical catalytic measurements were performed with a CHI 660E electrochemistry workstation (Chenhua, Shanghai) in a standard three-electrode cell system. 20 mg catalysts were dispersed in a mixture of 200 μl ethanol, 10 μl 5 wt% Nafion and 10 μl deionized water. After that, 70 μl catalyst ink was dropped onto a 1 cm × 2 cm Ni foam washed sequentially using ethanol, acetone and deionized water. The Co-Cl-C/Ni foam was used as the working electrode, the reference electrode and counter electrode are Hg/HgO and graphite respectively. In all measurements, the measured potentials vs. 0.931 V were calibrated according to the reversible hydrogen electrode (RHE).

2.4. Characterization

The surface topography and element mapping of the powders were analysed using JSM-7800F scanning electron microscope (SEM). The test carrier is a silicon substrate. The microstructure, morphology and element mapping of the powders were characterized by JEM-2100 transmission electron microscope (TEM). The elemental compositions were performed by Thermo Fisher ESCALAB250XI X-ray photoelectron spectroscopy (XPS).

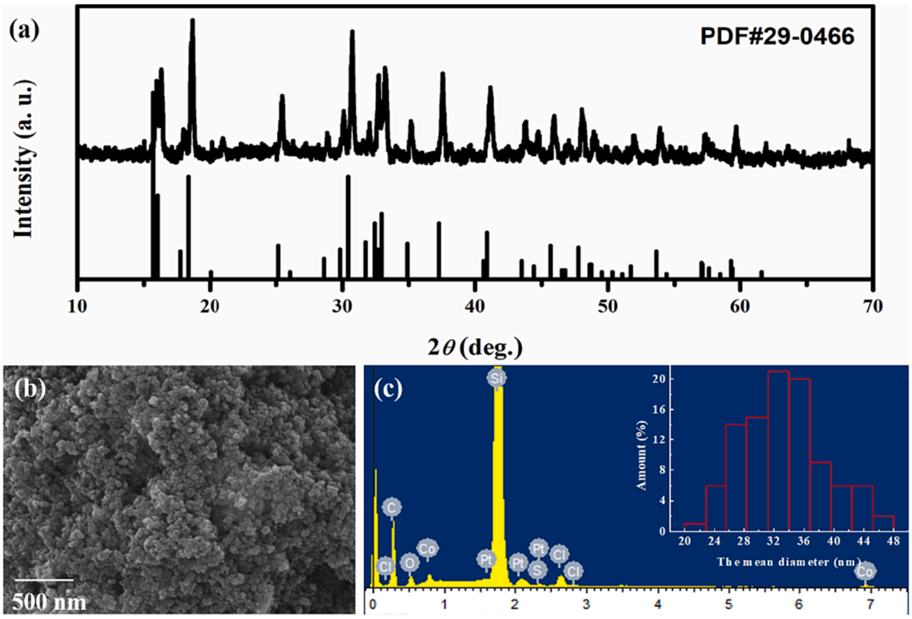

Fig. 2. (a) XRD pattern, (b) SEM image and (c) energy spectrum Co-Cl-C composited powder, the insert is the distribution of the mean diameter.

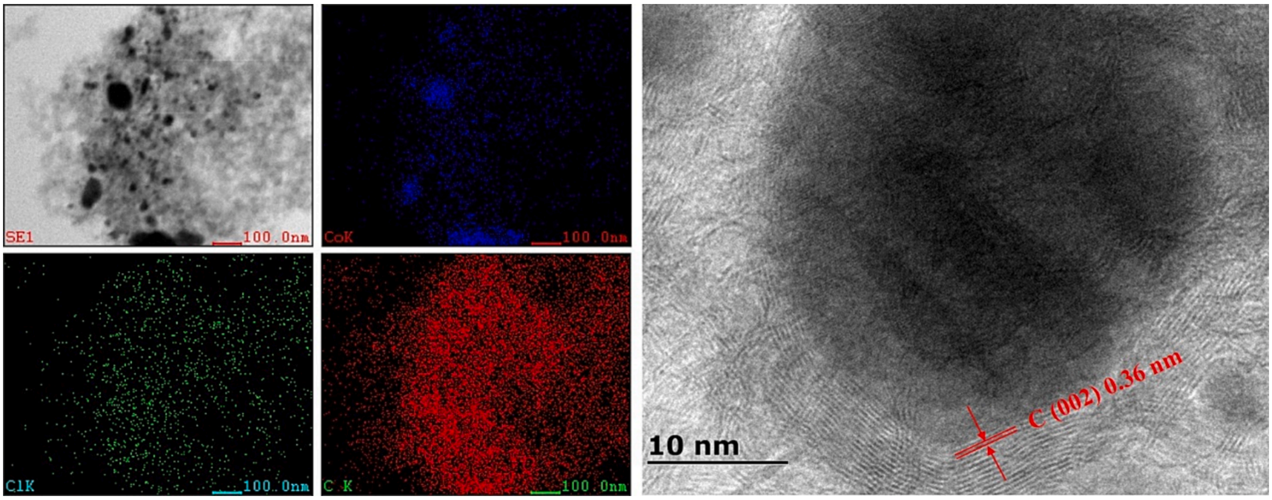

Fig. 3. TEM images, elemental mapping and HRTEM image of $CoCl_2$-C composited powder.

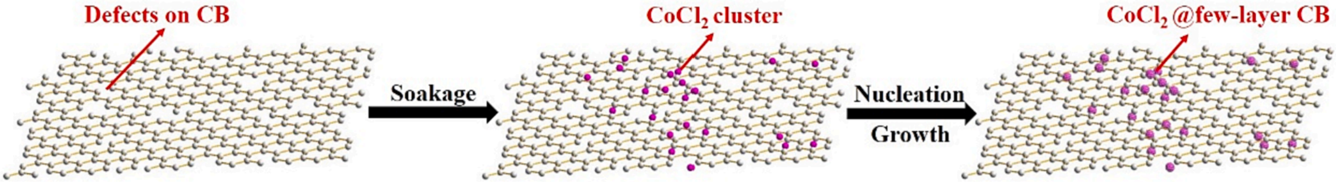

Fig. 4. Schematic illustration of the synthesis.

3. Results and discussion

3.1. Co-Cl-C composited powder prepared by flash Joule heating system

XRD pattern of the powder sample with flash Joule heating is shown in Fig. 2 (a). It is well consistent with JCPDS#29-0466, which exemplifies that anhydrous cobalt chloride of monoclinic crystal system is obtained after heating. SEM image and energy spectrum of the Co-Cl-C composited powder prepared by flash Joule heating system are shown in Fig. 2 (b, c). We can investigate that the particle size distribution of the powder is relatively uniform. The mean diameter of the composited powder is 33.20 nm, suggesting that flash Joule heating unifies the particles of the composited powder. For the energy spectrum, S peak is from the impurities in the conductive carbon black. The atomic ratio of Cl and Co decreases from 2 ($CoCl_2$-C) to 1.34 (Co-Cl-C), which indicates certain atoms sublimate during the process of the flash Joule heating. We can also observe the air mass releasing from the sample cell (Fig. 1a) after heating. The air mass may be chlorine (See the support information for more details). Then the chlorine production reduces the chloride content of the cobalt dichloride.

In order to investigate further the distribution of the elements, the TEM images, elemental mapping and HRTEM image of Co-Cl-C composited powder are shown in Fig. 3. Part of the cobalt atom aggregates, while chlorine and carbon distribute uniformly. From the HRTEM image, we observe that the cobalt-based compounds are coated by the crystalline carbons which act as a protection and isolation. In general, cobalt chloride and carbon black are mixed in heterogeneous. The above distribution mode cannot be achieved using the ordinary heating method. In our work, we apply a voltage at both ends of the quartz tube, the current is transmitted along the path with minimal resistance,

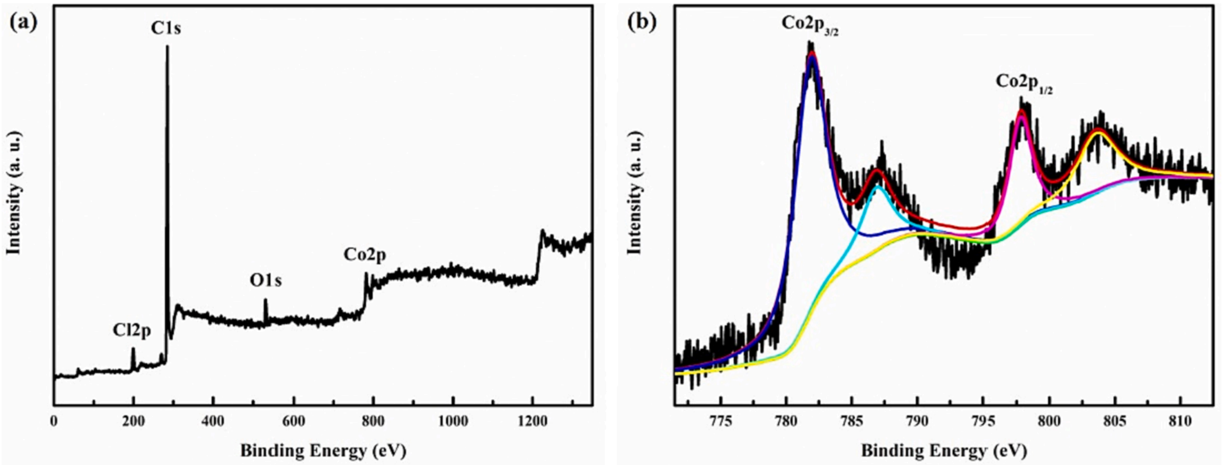

Fig. 5. (a) XPS survey spectrum of Co-Cl-C composite and (b) high-resolution Co2p XPS spectra.

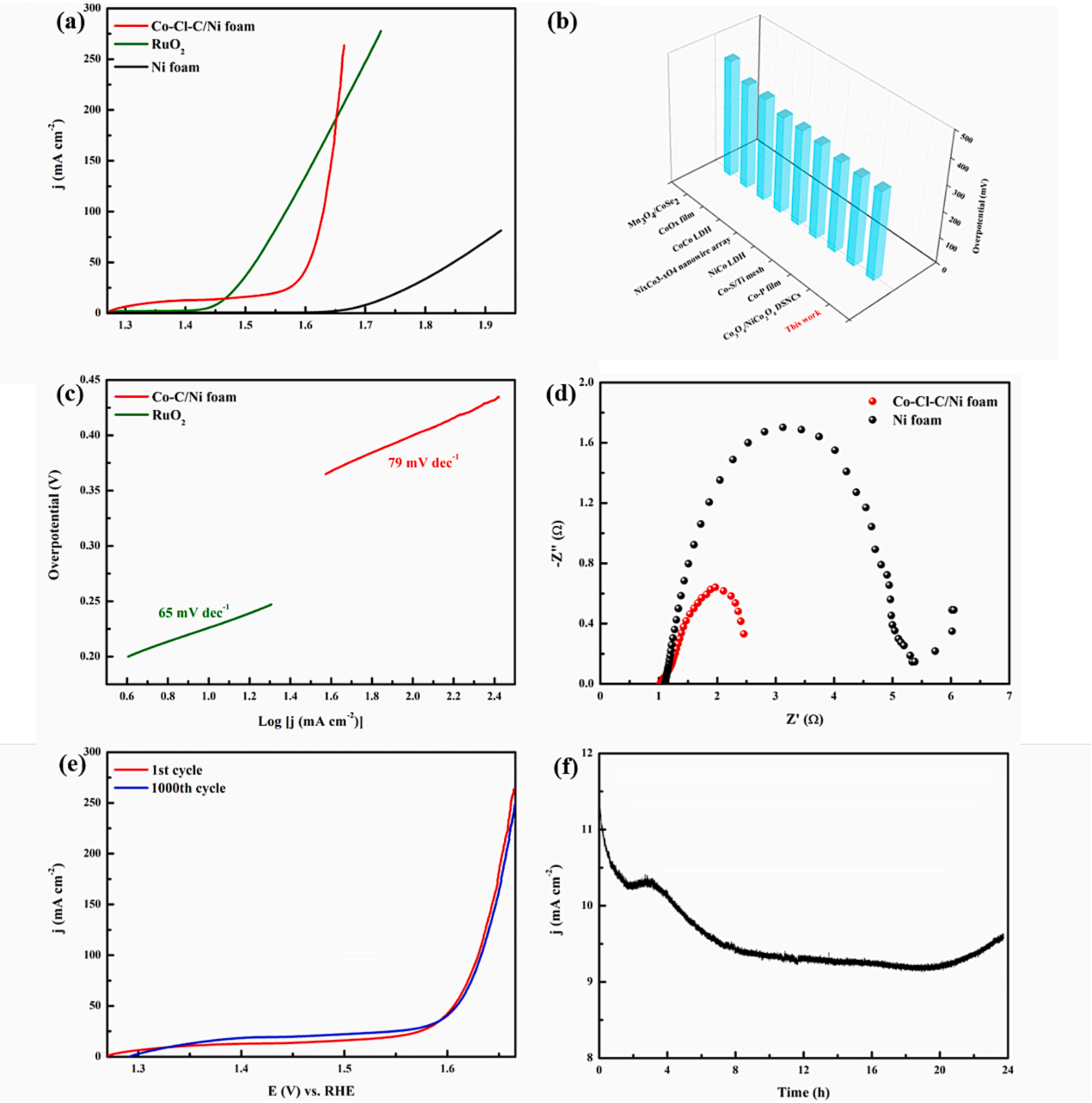

Fig. 6. (a) LSV curves of $CoCl_2$-C/Ni foam, RuO_2 on the Ni foam and the blank Ni foam in 1.0 M KOH for OER, (b) Integrated OER performance chart providing a comparison with recent representative works, (c) Tafel plots of $CoCl_2$-C/Ni foam and RuO_2 on the Ni foam, (d) EIS plots, (e) LSV curves recorded for $CoCl_2$-C/Ni foam before and after 1000 CV cycles, (f) Time-dependent current density curve for $CoCl_2$-C/Ni foam under a static overpotential of 458 mV for 24 h.

providing the maximum heat to the conductive area, and the heat is released in the form of the black body radiation. The conduction path and the surrounding materials undergo significant annealing and graphitization during the flash Joule heating process. Due to the existence of other impurities in carbon black and chlorine-containing component, the sublimation of heteroatoms provides more activity path for amorphous carbon atoms. Carbon atoms begin to nucleate, crystal, and grow, then cover on cobalt chloride. Schematic illustration of the synthesis is shown in Fig. 4.

The surface composition of Co-Cl-C composited powder is observed in the XPS spectra. As shown in Fig. 5, the survey spectrum confirms the elements of chlorine, carbon, oxygen and cobalt. A typical Co2p XPS spectrum exhibits two peaks at 797.9 and 782.0 eV, which corresponds to Co2$p_{1/2\text{-}3/2}$ doublets. And minor doublet shows the satellite peaks at 803.7 and 787.1 eV. Such spectrum shape relates to Co(II) [15]. These results suggest that cobalt chloride exists as a compound in the powder. The cobalt-based compound has an excellent electrocatalytic activity toward OER and HER [16].

3.2. Co-Cl-C/Ni foam

OER of Co-Cl-C/Ni foam (Co-Cl-C loading: 1.33 mg cm^{-2}) is evaluated using a three-electrode cell with a scan rate of 0.005 V s^{-1} in 1.0 M KOH. A blank Ni foam and RuO_2 on the Ni foam were also investigated

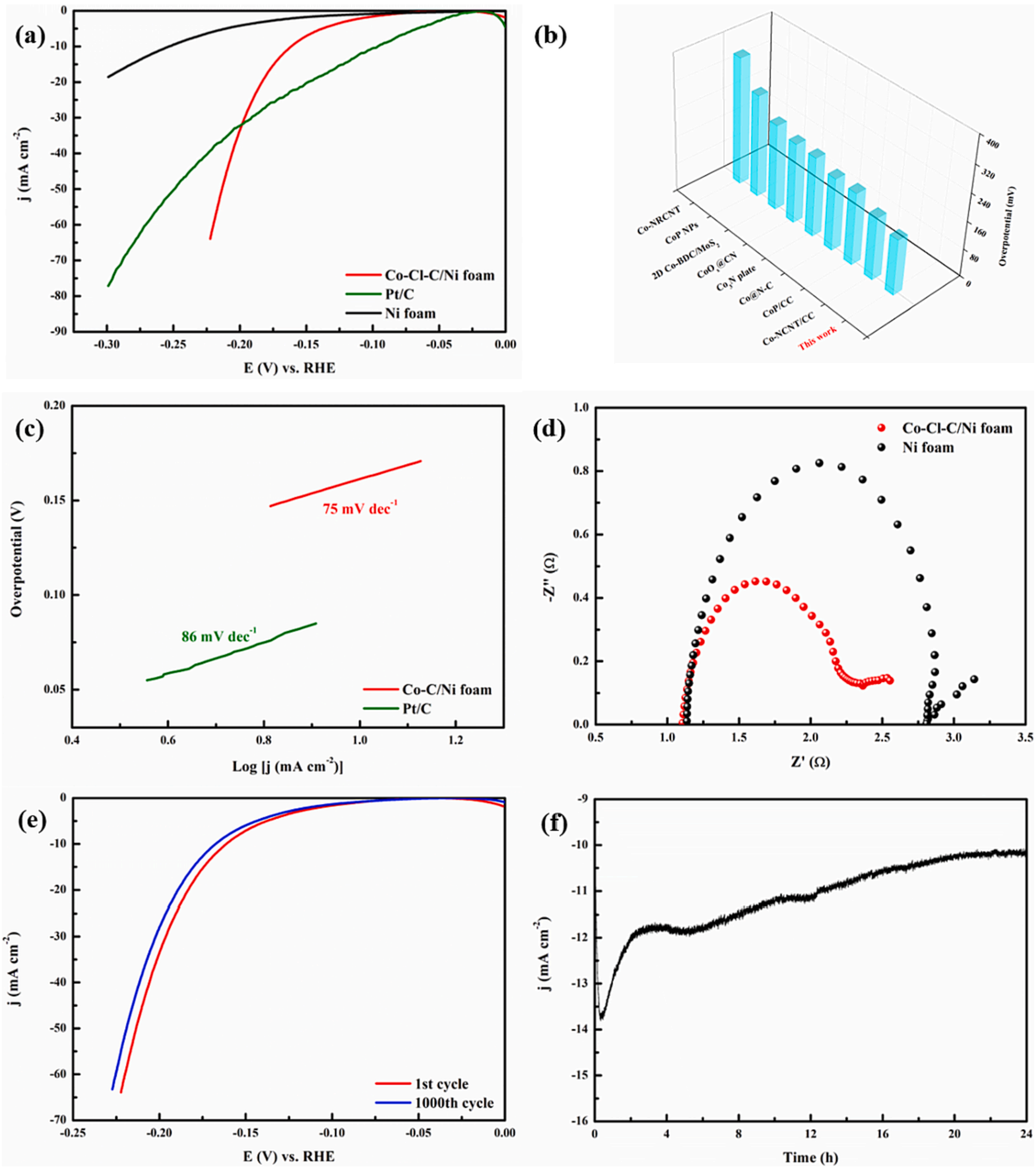

Fig. 7. (a) LSV curves of Co-Cl-C/Ni foam, Pt/C on the Ni foam, and the blank Ni foam in 1.0 M KOH for HER, (b) Integrated HER performance chart providing a comparison with recent representative works, (c) Tafel plots of Co-Cl-C/Ni foam and Pt/C on the Ni foam, (d) EIS plots, (e) LSV curves recorded for Co-Cl-C/Ni foam before and after 1000 CV cycles, (f) Time-dependent current density curve for Co-Cl-C/Ni foam under a static overpotential of 173 mV for 24 h.

for comparison purpose. Fig. 6 (a) shows linear sweep voltammetry (LSV) curves of the sample on the reversible hydrogen electrode (RHE) scale. To avoid the effect of ohmic resistance on the measured anodic currents, an *iR* correction must be applied to all initial data for further analysis. At a current density of 10 mA cm^{-2}, the blank Ni foam has an OER catalytic activity with a high overpotential of 484 mV, and RuO_2 shows an OER activity with a low overpotential of 226 mV. While the Co-Cl-C/Ni foam has the moderate OER activity with the overpotential of 339 mV at the same current density. As shown in Fig. 6 (b), this overpotential is superior to Co-containing catalysts [17–24] and some other noble-metal-free OER catalysts in alkaline solutions [25,26]. The Tafel plots are shown in Fig. 6 (c). The Tafel slope with linear fitting can reflect the catalytic kinetics for oxygen evolution. The Tafel slope value of Co-Cl-C/Ni foam (79 mV dec^{-1}) is higher than that of RuO_2 (65 mV dec^{-1}), implying that Co-Cl-C/Ni foam has a slow OER kinetics compared with RuO_2. Electrochemical impedance spectroscopy (EIS) measurements were then conducted at an operating voltage of 400 mV, and Nyquist curves are shown in Fig. 6 (d). Comparing the charge transfer resistance (Rct) values, the value of Co-Cl-C/Ni foam (2.063 Ω) is obviously smaller than that of Ni foam, indicating that the OER process of Co-Cl-C/Ni foam has fast electron transport and is weakly affected by mass transfer. Furthermore, we investigate the durability of Co-Cl-C/Ni foam by continuous cyclic voltammetry (CV) scanning between 1.4 and 1.7 V vs. RHE with a scan rate of 0.1 V s^{-1}. Fig. 6 (e) shows the LSV curves of the initial and 1000th CV scanning. At a current density of 10 mA cm^{-2}, the overpotential decreases to 343 mV, indicating that the appropriate number of CV scanning could motivate the surface activation and stabilize the catalytic properties of the catalyst. Moreover, the 24 h chronoamperometric test of Co-Cl-C/Ni foam leads to 10.9% degradation in current density, as shown in Fig. 6 (f). The bubbles from oxygen evolution reaction make the catalyst fall off from Ni foam and weaken catalytic performance of the catalyst. These results indicate Co-Cl-C/Ni foam has an excellent OER catalytic activity and relatively good long-term stability in 1.0 M KOH.

The HER performances of Co-Cl-C/Ni foam, Pt/C loaded on the Ni foam, and the blank Ni foam were also evaluated in the same electrolyte. Fig. 7 (a) shows the linear sweep voltammetry (LSV) curves. For the current density of 10 mA cm^{-2}, Pt/C has an outstanding activity and the blank Ni foam has a poor activity, while Co-Cl-C/Ni foam shows the moderate activity with an overpotential of 161 mV. As shown in Fig. 7 (b), the overpotential is less than Co-containing catalysts [27–32,10,33] and some other noble-metal-free HER catalysts in same solution environment [34,35], suggesting that Co-Cl-C/Ni foam has a superior HER activity. Fig. 7 (c) shows the Tafel plots for Co-Cl-C/Ni foam and Pt/C. The Tafel slope of Co-Cl-C/Ni foam is lower than that of Pt/C, suggesting that Co-Cl-C/Ni foam has a fast HER kinetics compared with Pt/C. Fig. 7 (d) shows Nyquist curves measured at an operating voltage of 300 mV. The value of Co-Cl-C/Ni foam (1.262 Ω) is still smaller than that of Ni foam, demonstrating that the HER process of Co-Cl-C/Ni foam has fast electron transport and is weakly affected by mass transfer. After 1000 cycles by continuous CV scanning between 0 and −0.5 V vs. RHE with a scan rate of 0.1 V s^{-1}, the LSV curves of the initial and 1000th CV scanning are shown in Fig. 7 (e). There is 13.6% degradation in current density for 24 h chronoamperometric test of $CoCl_2$-C/Ni foam, as shown in Fig. 7 (f). These results indicate that Co-Cl-C/Ni foam is suitable for a catalyst of hydrogen evolution reaction.

4. Conclusions

Co-Cl-C composited powders were prepared by flash Joule heating system. The particles of the composited powder were refined and the cobalt-based compounds were coated in the crystal carbon after the flash Joule heating. This is a novel preparation method. Our work is the first report on the preparation of composited materials using this method, and the ink mixture with the prepared composited powders have achieved a demonstrable effect in catalytic performance of OER and HER. The overpotential of OER and HER for Co-Cl-C composited film with good catalytic stability are 339 and 161 mV at the current density of 10 mA cm^{-2}. Although the performance is not very high, the preparation method of the composited powders provides a new inspiration. Next, we will continue to work on preparing composites using flash Joule heating and constantly improve their performance and application of the catalyst under high current density.

CRediT authorship contribution statement

Wei Li: Data curation, Writing – original draft, Investigation, Methodology. **Xianhua Sheng:** Writing – review & editing, Supervision. **Zhaoliang Yu:** Writing – review & editing, Supervision. **Qian Tang:** Writing – review & editing, Supervision. **Jinghua Geng:** Data curation. **Dangzheng Hu:** Data curation. **Xiangdong Meng:** Visualization, Resources. **Yumei Zhang:** Visualization, Resources.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cplett.2023.140762.

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