

Flower-like NiCo_2O_4 spinel microspheres for efficient chlorine evolution under neutral conditions

Ran Zhang, Jing Cao^{*}, Ting Peng, KeXuan Wu, Yinqiang Shu

College of Chemistry, Xiangtan University, Xiangtan 411100, China

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ABSTRACT

Dimensional stability anodes (DSA), constructed using noble metal oxides like RuO_2 and IrO_2 , is widely used in industrial chlorine production. The DSA electrode demonstrates exceptional chlorine evolution capabilities in acidic solutions and high-chloride concentrations. However, under neutral conditions, its chlorine evolution efficiency diminishes significantly. In this paper, a low-cost, high-efficiency 3D flower-like NiCo_2O_4 catalyst was fabricated that exhibits high catalytic activity in neutral sodium chloride solutions. The 3D flower-like NiCo_2O_4 catalyst exhibits good chlorine evolution efficiency, achieving 90 % at 30 mA/cm^2 in NaCl solutions. Furthermore, its chlorine evolution efficiency of the electrocatalyst surpasses that of commercial DSA electrode at various current densities, making it a highly promising candidate for electrocatalytic applications.

1. Introduction

The chlor-alkali industry, through the electrolysis of saturated salt water, produces caustic soda and chlorine gas, which are extensively utilized in various industries, including the chemical industry, textiles and pipes. During the electrolysis process, reactive chlorine species (RCS) are produced [1], specifically free chlorine in the forms of HOCl , OCl^- , and Cl_2 . These species can be effectively utilized for disinfection and bleaching. Simultaneously, chlorine free radicals [2] such as $\bullet\text{Cl}$, $\bullet\text{Cl}_2^-$, and $\bullet\text{OCl}$ are generated, which further contribute to the advanced oxidation degradation of wastewater and pollutants. As a result, the chlor-alkali industry plays a crucial role in national life, providing essential resources and processes for various industries and applications.

The chlor-alkali reaction primarily involves the chlorine evolution reaction (CER) at the anode and the hydrogen evolution reaction (HER) at the cathode [1]. Among these reactions, CER plays a particularly crucial role in the chlor-alkali process, and the electrode material significantly impacts the chlorine evolution efficiency. Common chlorine evolution electrodes include noble metal oxide anodes based on RuO_2 , such as $\text{Ti}/\text{RuO}_2\text{-Sb}_2\text{O}_5\text{-SnO}_2$ [3,4], $\text{RuO}_2/\text{TiO}_2$ [5–10], $\text{RuO}_2\text{-SnO}_2\text{-TiO}_2$ [11], $\text{Ru}_{0.9}\text{Eu}_{0.1}\text{O}_x/\text{TP}$ [12], $\text{RuO}_2\text{-IrO}_2\text{-TiO}_2$ [13], $\text{RuO}_2\text{-IrO}_2\text{-SnO}_2\text{-Sb}_2\text{O}_5$ [4], $\text{Ru}_{1-x}\text{Ni}_x\text{O}_{2-y}$ [14], and $\text{RuO}_2\text{-Nb}_2\text{O}_5$ [15, 16]. However, Ru is susceptible to forming into thermodynamically stable substances, such as soluble ruthenium chlorides or gaseous ruthenium oxides, which can ultimately lead to catalyst deactivation or

degradation [17,18].

In recent years, numerous scholars [19,20] have discovered that the transition metal oxide Co_3O_4 exhibits comparable or superior CER activity than the RuO_2 -based electrode, while also exhibiting better stability. Specifically, Peng Wang et al. [19] prepared a Co_3O_4 anode composed of nanobelt arrays (NBA) on the FTO substrate, which displayed outstanding chlorine evolution performance. The cobalt antiminate (CoSb_2O_6) has been demonstrated to possess exceptional stability and chlorine evolution activity. Even after 250 h of long-term electrocatalytic degradation, there is no noticeable deterioration, significantly outperforming RuTiO_x under identical conditions [17]. Xina Zhang et al. [18] were the first to confirm that the chlorine evolution mechanism of Co_3O_4 under neutral seawater conditions follows the Krishtalik mechanism, as determined by density functional theory (DFT) calculations.

According to Petr Krtil's research [14], a 10 % Ni-doped $\text{Ru}_{1-x}\text{Ni}_x\text{O}_2$ electrode exhibits noteworthy chlorine evolution selectivity and activity. More recently, Haiying Wang et al. [21] discovered that Co^{2+} at tetrahedral sites and Co^{3+} at octahedral sites in Co_3O_4 may be substituted by other elements, leading to increased catalytic activity and thermal stability. Crucially, the spinel metal cobaltate (MCo_2O_4), which is composed of several transition metals and oxides, exhibits exceptional redox characteristics. These unique properties lead to remarkable catalytic activity and superior energy storage capability. According to Do Heui Kim et al. [22], the insertion of Ni^{2+} ions into the octahedral site of the Co_3O_4 spinel structure enhances the activity of the resulting NiCo_2O_4

^{*} Corresponding author.

E-mail address: caojing8088@xtu.edu.cn (J. Cao).

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material.

NiCo₂O₄, with its straightforward preparation process, low cost, and abundant reserves, is widely utilized in oxygen evolution reaction (OER). This material boasts a noteworthy oxygen evolution activity and serves as a robust oxidant [23,24]. Notably, Gengfeng Zheng et al. [25] utilized NiCo₂O₄ to generate Cl* intermediates, thereby enhancing the electrocatalytic oxidation of methane. While numerous studies have centered on the OER of NiCo₂O₄, there is limited research and literature on the utilization of NiCo₂O₄ catalysts for CER.

In this article, we present the synthesis of a low-cost 3D flower-like NiCo₂O₄ spinel catalyst through a straightforward preparation method. We investigate and compare the effects of NiCo₂O₄ catalysts with varying Ni/Co molar ratios on chlorine evolution performance. For the first time, a series of electrochemical tests are conducted on the fabricated NiCo₂O₄ catalyst in 2 M NaCl electrolyte to assess its for chlorine evolution activity.

2. Experimental

2.1. Materials and reagents

Ni(NO₃)₂·6H₂O, Co(NO₃)₂·6H₂O, hexamethylenetetramine (HTM), ethanol (C₂H₅OH), acetone (C₆H₁₂O₂), and oxalic acid (H₂C₂O₄) were purchased from Macklin (Shanghai, China). N-methyl-2-pyrrolidone (NMP) was purchased from Aladdin Chemical Reagent Co., Ltd. Polyvinylidene fluoride (PVDF) was purchased from Dongguan Kelude Innovation Technology Co., Ltd. All reagents were used as originally intended without further purification. Pure titanium plate was obtained from Schur Technology Co., Ltd., and commercial DSA electrode was obtained from Hanston Technology Development Co., Ltd.

2.2. Preparation of 3D flower-like NiCo₂O₄

Ni(NO₃)₂·6H₂O, Co(NO₃)₂·6H₂O and HTM (the molar ratio of total metal ions to HTM is 1/1.2) with Ni/Co molar ratios of 1/1, 1/2, 1/3, 1/4 and 1/9 were dissolved in 100 mL deionized water and stirred for 30 min. The reaction was carried out in a polytetrafluoroethylene reactor at 95 °C for 18 h. After the reaction, it was centrifuged and washed several times with ethanol and water, dried at 60 °C for 8 h, and calcined at 400 °C for 3 h at a heating rate of 1 °C/min in a muffle furnace. Ni₁Co₁, Ni₁Co₂, Ni₁Co₃, Ni₁Co₄ and Ni₁Co₉ were named according to their proportions.

2.3. Preparation of working electrodes

Pure titanium plates (20 mm×20 mm×0.5 mm) were polished with 600-mesh and 800-mesh sandpaper, and then immersed in acetone, ethanol and deionized water and sonicated for 15 min, respectively. After ultrasonic treatment, it was further etched in 10 wt% boiling oxalic acid solution for 2 h. After acid etching, ultrasonic treatment in deionized water for 5–10 min, dried and placed in anhydrous ethanol for use. The active material (80 wt%), PVDF (10 wt%) and acetylene black (10 wt%) were put into the centrifuge tube, and a small amount of NMP was added to make it into slurry by ultrasound. This slurry was then applied to the pretreated titanium plates until the desired coating thickness of 2–2.5 mg/cm² was achieved. The prepared anodes were then dried overnight at 120 °C.

2.4. Characterizations

The surface morphology and chemical composition of the samples were characterized by Scanning electron microscopy (SEM, JSM-6610LV) and binding energy dispersive X-ray spectroscopy (EDX, Sigma 300). The crystal phase of the samples were detected via X-ray diffraction (XRD, Bruker D8-Advance) with Cu Kα radiation (40 kV, 250 mA) across a degree range of 10° to 80° at a scan rate of 5°/min. The

surface chemical state was determined by the X-ray photoelectron spectroscopy (XPS) with a Thermo Scientific K-Alpha⁺ X-ray photoelectron spectrometer. In order to identify the functional groups and chemical bonds of the samples investigated by the fourier transform infrared spectrometer (FTIR, Nicolet 6700) in the range of 4000–400 cm⁻¹. The N₂ adsorption-desorption isotherm is obtained from the Tristar II 3020 specific surface area and pore size analyzer. The microstructure and crystallinity of the NiCo₂O₄ were investigated by the transmission electron microscopy (TEM, JEM-2100) and selective area electron diffraction (SAED) analysis.

2.5. Electrochemical measurements

All electrochemical experiments were performed on a CHI 660E (Chenhua) electrochemical workstation. Using a three-electrode setup, the electrochemical characteristics of the anode were investigated using cyclic voltammetry (CV), linear cyclic voltammetry (LSV), and electrochemical impedance spectroscopy (EIS). The platinum electrode served as the counter electrode, the saturated calomel electrode as the reference electrode, and the Ti/NiCo₂O₄ electrode as the working electrode. CV measurements were recorded at various scanning rates from 0.2 V vs. SCE to 0.6 V vs. SCE. LSV were performed at a scan rate of 10 mV/s in the potential range of 1.0 V vs. SCE to 1.5 V vs. SCE. In order to clarify the behavior of the Ti/NiCo₂O₄ electrode for CER and OER in 2 M NaCl and 2 M NaNO₃ aqueous solutions were used, respectively [26]. It should be noted that NaCl is utilized as an electrolyte to examine chlorine evolution, whereas NaNO₃ examines oxygen evolution under neutral circumstances (i.e., the pH value of NaNO₃ solution is similar to that of NaCl solution.) [27]. In 2 M NaCl, EIS measurements were performed at open circuit voltage from 10⁴ Hz to 0.01 Hz with a 10 mV amplitude. In addition, the catalyst's stability is investigated by the chronoamperometry.

2.6. Current efficiency of the CER

The CER experiment of 20 mm×20 mm Ti/NiCo₂O₄ electrode and 20 mm×20 mm DSA electrode were carried out in 50 mL 2 M NaCl and 0.6 M NaCl solution at different current densities (5, 10, 20, 30, 40 mA/cm²) for 7 min. The effective chlorine content was determined using the iodometric technique [8]. Current efficiency was calculated using Eq. (1) [10]:

$$CER(\%) = \frac{c v n F}{I t} \times 100\% \quad (1)$$

Where c is the concentration of free chlorine produced by electrolysis (mol/L), v is the volume of electrolyte (L), n is the number of electrons involved in the CER (2 equiv. mol⁻¹), F is the Faraday's constant (96485 C equiv.⁻¹), I is the electric current (A), t is the electrolysis time (s).

3. Results and discussion

3.1. Structural characterizations

To synthesize NiCo-layered double hydroxide (NiCo-LDH) precursors with different Ni/Co ratios, a reaction was conducted at 95 °C for 18 h using Ni(NO₃)₂·6H₂O and Co(NO₃)₂·6H₂O as raw materials, with HTM serving as the precipitant (Fig. 1). Subsequently, NiCo₂O₄ was obtained by calcining the precursor in a muffle furnace at 400 °C for 3 h. The formation of NiCo₂O₄ mainly involves the following reactions (2–6) [28–30]:

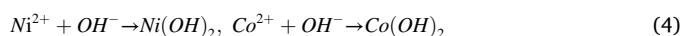
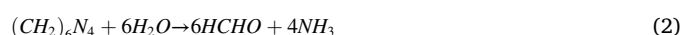
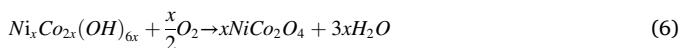
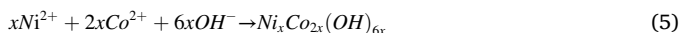




Fig. 1. Synthesis procedures of NiCo_2O_4 .



The morphology and elemental composition of oxides produced with nickel cobalt mixed oxides with various Ni/Co ratios were investigated by SEM and EDX. The uncalcined precursor (Fig. S1i-j) is explicitly observed that flower-like microspheres with some burrs on the edge. After calcination, only the flower-like microspheres, which are constructed from nanosheets, remain (Fig. S1a-h and S1k-l). The SEM image of the $\text{Ti}/\text{Ni}_1\text{Co}_4$ electrode (Fig. 2a-c) reveals the presence of numerous flower-like nanospheres on the titanium substrate. These microspheres are composed of several polygonal sheets with smooth surfaces. This microsphere shape enhances the exposure of active sites and provides efficient electron transport pathways, thereby enhancing catalytic efficiency and playing a crucial role in electrochemical performance. The EDX analysis of the elemental composition of Ni_1Co_4 , as presented in Fig. 2e-h, reveals that it consists of Ni, Co, and O elements. It is noteworthy that these elements are evenly distributed within the microsphere structure. Additionally, the corresponding EDX result (Fig. 2d)

demonstrates that the atomic content of Ni reaches up to 8.53 %, emphasizing its significant presence in the composition.

TEM images of NiCo_2O_4 (Fig. 3a-b) illustrate the nanosheets morphology. Furthermore, the diffraction rings in Fig. 3d correspond solely to the (111), (220), (311), (400), (422), (511) and (533) crystal planes of NiCo_2O_4 . The exposed crystal planes in Fig. 3c only belong to the (111), (331) and (400) crystal planes of NiCo_2O_4 . Additionally, the SAED pattern also confirms the formation of a crystalline material with a cubic spinel structure.

In Fig. S2, XRD pattern of the precursor shows typical peaks at 2θ of 10° , 18° , 33.2° , 35.8° , 38° and 59.7° , corresponding to (003), (006), (012), (015), (018), (110) planes, respectively, of typical LDH phase [28]. XRD patterns of the nickel cobalt mixed oxides with various Ni/Co ratios (Fig. 4a) show typical peaks at 2θ of 19.3° , 31.12° , 36.7° , 44.6° , 59.2° , and 64.9° , corresponding to the crystal planes (111), (220), (311), (400), (511), and (440) of spinel NiCo_2O_4 (PDF#20-0781) [31,32]. $2\theta=37.16^\circ$, 43.21° , 62.34° , 75.19° , and 79.24° correspond to the (111), (200), (220), (311), and (222) planes of NiO, respectively (PDF#73-1523) [33]. As a result, the NiO and NiCo_2O_4 peaks are mainly shown in Ni_1Co_1 , Ni_1Co_2 , and Ni_1Co_3 , NiCo_2O_4 peaks in Ni_1Co_4 and Ni_1Co_5 . It reveals that NiO is gradually formed when the Ni content exceeds 25 %, as evidenced by the increase in the (200) crystal plane of NiO corresponding to the rise in Ni content.

The functional groups and chemical bonds of the nickel cobalt mixed oxides with various Ni/Co ratios investigated by FTIR. Fig. 4b shows that the peaks at 1630 cm^{-1} and 3450 cm^{-1} are attributed to the bending and tensile vibration of water molecules within the structure. For a NiCo-LDH of the NO_3^- type, the strong band observed at 1390 cm^{-1} corresponds to the symmetric stretching band of NO_3^- [28]. The lattice vibration modes of M-O and M-O-M (M being Ni or Co) are responsible for the absorption band in the low wavenumber range ($500\text{--}1000\text{ cm}^{-1}$). The strong peaks centered at 570 cm^{-1} and 654 cm^{-1} are attributed to the tensile vibration of the Co-O group [34]. The peaks at 453 cm^{-1} and 525 cm^{-1} are attributed to the stretching vibration of the Ni-O group [35].

Catalysts usually require a highly specific surface area. Therefore, the specific surface areas (SSAs) of nickel cobalt mixed oxides with various Ni/Co ratios was evaluated by analyzing the N_2 adsorption-desorption isotherms and pore size distribution presented in Fig. 5a. A typical type IV isotherm is observed in nickel cobalt mixed oxides with various Ni/Co ratios. Notably, when the relative pressure P/P_0 exceeds 0.7, an evident adsorption hysteresis loop emerges in the curve, indicating that the sintered sample possesses mesoporous properties. The pore size distribution of oxides with nickel cobalt mixed oxides with various Ni/Co ratios exhibits a broad peak structure, indicating a mesoporous structure with a hole diameter greater than 2 nm, as shown in

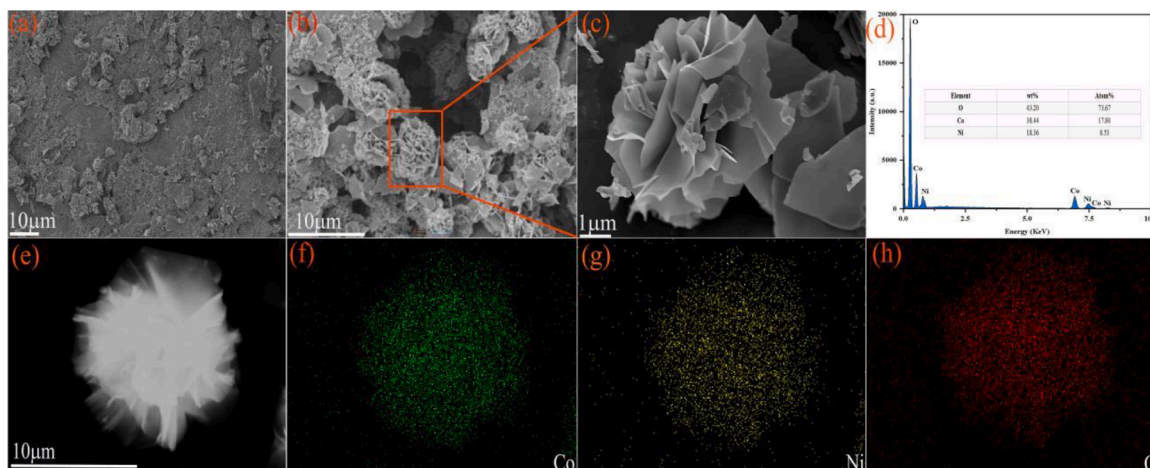


Fig. 2. (a-c) SEM of $\text{Ti}/\text{Ni}_1\text{Co}_4$ electrode under different scales, (d) EDX plot of the Ni_1Co_4 , (e-h) TEM-Mapping images of the Ni_1Co_4 .

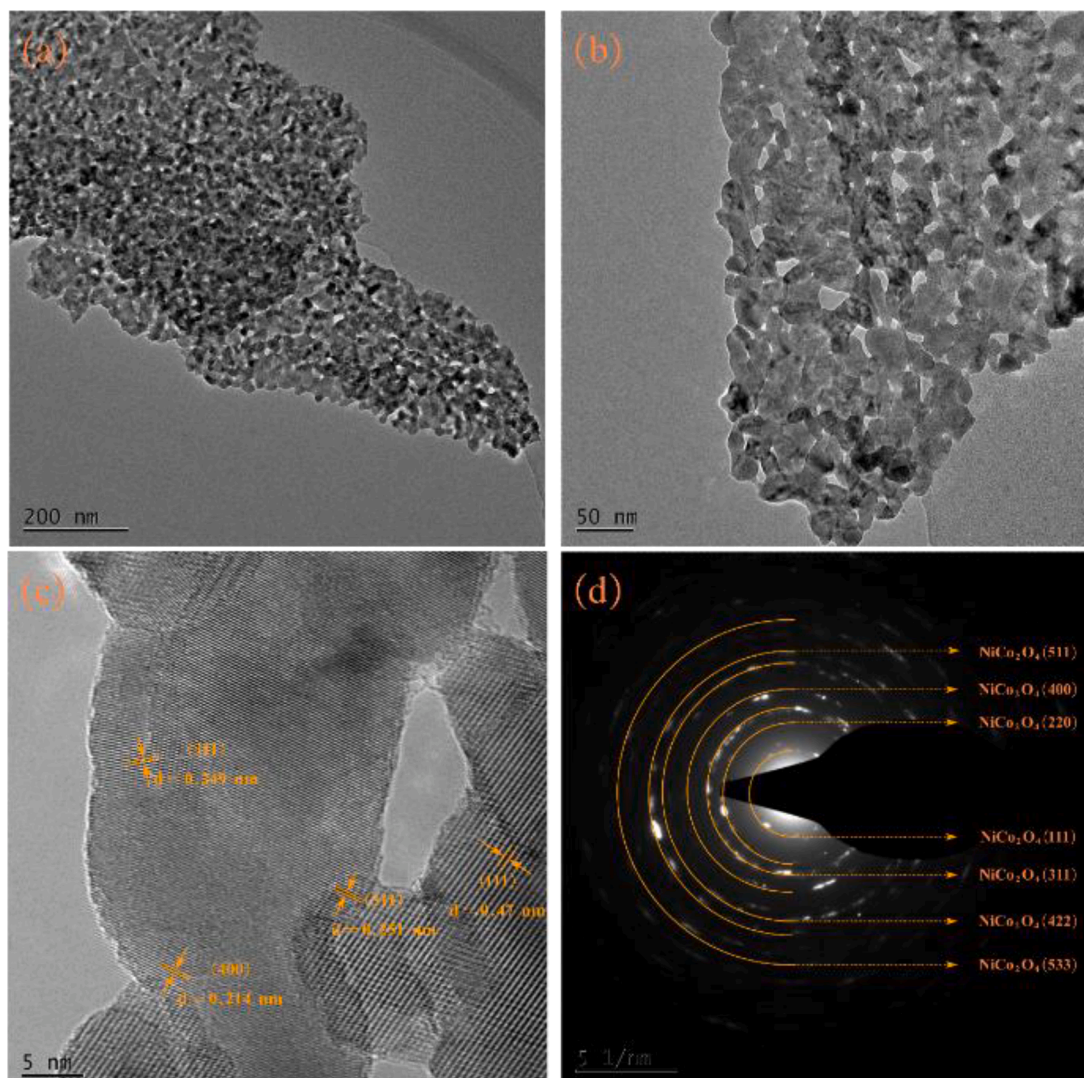


Fig. 3. (a-b)TEM micrographs at different magnifications for Ni_1Co_4 (c) TEM image of the Ni_1Co_4 , (d) SAED pattern of the Ni_1Co_4 .

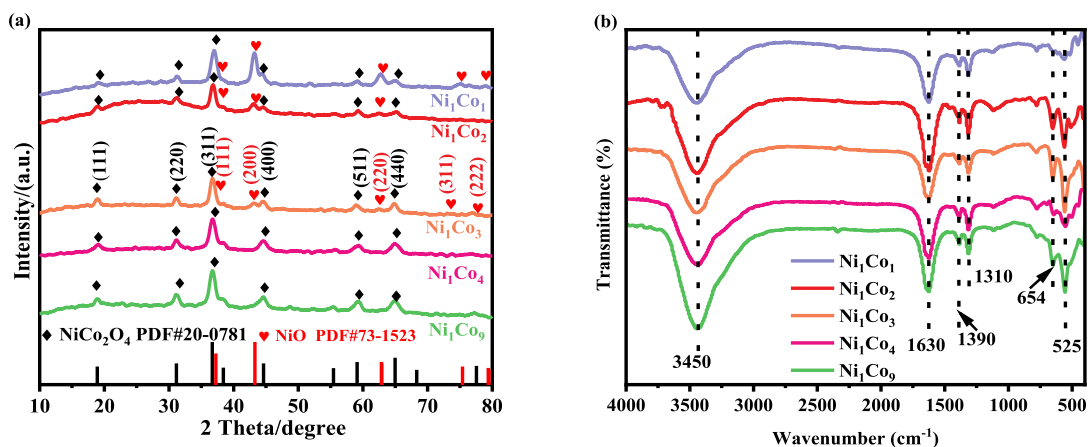


Fig. 4. Nickel cobalt mixed oxides with various Ni/Co ratios (a) XRD, (b) FTIR.

Fig. 5b. The SSAs of Ni_1Co_1 , Ni_1Co_2 , Ni_1Co_3 , Ni_1Co_4 , and Ni_1Co_9 are $10.57 \text{ m}^2/\text{g}$, $13.49 \text{ m}^2/\text{g}$, $12.51 \text{ m}^2/\text{g}$, $46.00 \text{ m}^2/\text{g}$, and $38.46 \text{ m}^2/\text{g}$, respectively, as shown in Table 1. Among these, Ni_1Co_4 exhibits the largest SSAs, whereas Ni_1Co_1 has the smallest SSAs. Additionally, Do

Heui Kim et al. [22] also reported that when the annealing temperature reaches 400°C and the Ni/Co ratio is equal to 1/1, the NiO phase in NiCo_2O_4 becomes dominant, leading to a decrease in surface area. In Table 1, the pore diameters of nickel cobalt mixed oxides with various

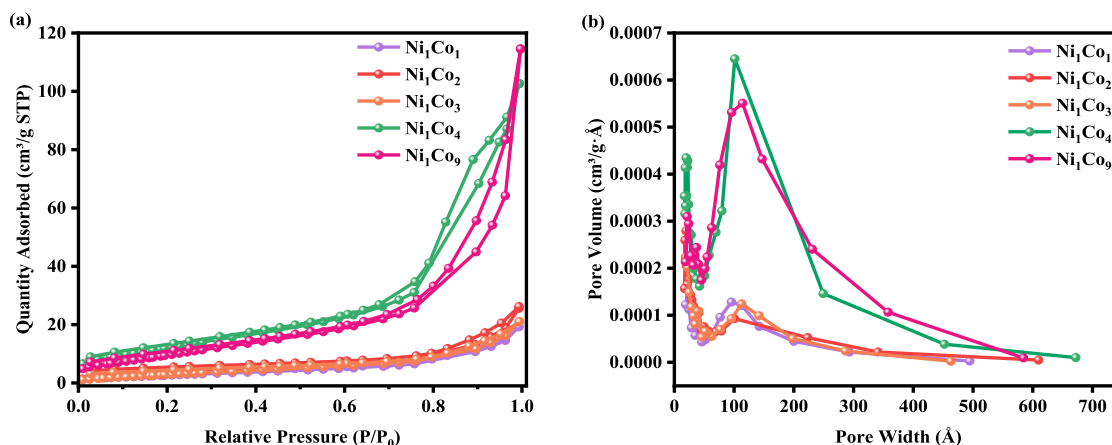


Fig. 5. Nickel cobalt mixed oxides with various Ni/Co ratios (a) N_2 adsorption-desorption isotherms, (b) pore size distribution curves.

Table 1

Basic parameters of N_2 adsorption-desorption isotherms and pore size for nickel cobalt mixed oxides with various Ni/Co ratios.

Sample	Surface area (m^2/g)	Pore Volume (cm^3/g)	Pore size (nm)
Ni ₁ Co ₁	10.57	0.02981	11.28
Ni ₁ Co ₂	13.49	0.03964	11.75
Ni ₁ Co ₃	12.51	0.03254	10.40
Ni ₁ Co ₄	46.00	0.15874	13.68
Ni ₁ Co ₉	38.46	0.1777	18.43

Ni/Co ratios are 11.28 nm, 11.75 nm, 10.40 nm, 13.68 nm, and 18.43 nm, respectively. Notably, the pores of Ni₁Co₄ are smaller compared to those of Ni₁Co₉. Consequently, the larger SSAs, increased pore volume, and narrower pore width observed in Ni₁Co₄ nanoflowers are highly advantageous for CER. This is because the expanded surface area elevates the number of exposed active sites, while the pores facilitate rapid mass transfer of both reactants and products. Additionally, the presence of more pores enhances the electrolyte solution's permeability, promoting Cl_2 release and minimizing the bubble shielding effect [6]. As a result, Ni₁Co₄ exhibits the highest catalytic activity, followed by Ni₁Co₉, with Ni₁Co₁ exhibiting the lowest activity.

The surface chemical composition and chemical state of the nickel cobalt mixed oxides with various Ni/Co ratios were investigated by XPS. As shown in Fig. 6a, nickel cobalt mixed oxides with various Ni/Co ratios consist of three elements: O, Ni, and Co. Fig. 6b presents the fitted Ni 2p peaks. Ni 2p_{3/2} (856.1 eV, 854.2 eV) and Ni 2p_{1/2} (874.3 eV, 872.0 eV) correspond to the peaks of Ni²⁺ and Ni³⁺. The satellite peaks of Ni²⁺ and Ni³⁺ correspond to the weak peaks on the left side of the two major peaks, respectively [32,36,37].

Fig. 6c presents the O 1s signal, which primarily consists of lattice oxygen (529.37 eV, O_L), oxygen vacancies (530.56 eV, O_V) and chemisorbed and dissociated oxygen species of O₂⁻, O₂²⁻, O⁻ and OH⁻ (532.58 eV, O_C) [18,38,39]. Table 2 lists the contents of O_V, O_L and O_C. Notably, Ni₁Co₁, Ni₁Co₂, Ni₁Co₃, Ni₁Co₄, and Ni₁Co₉ exhibit O_V values of 59.02 %, 56 %, 53.92 %, 51.10 %, and 49.99 %, respectively.

The fitting peaks of high-resolution Co 2p are presented in Fig. 6d. Co 2p_{3/2} (779.54 eV, 781.22 eV) and Co 2p_{1/2} (794.58 eV, 796.15 eV) correspond to the peaks of Co³⁺ and Co²⁺, respectively, and Sat. is its satellite peak [32,40]. The contents of Co³⁺ and Co²⁺ are also listed in Table 2. The contents of Co³⁺ in Ni₁Co₁, Ni₁Co₂, Ni₁Co₃, Ni₁Co₄ and Ni₁Co₉ are 49.86 %, 55.37 %, 56.77 %, 59.25 % and 61.06 %, respectively. Notably, the content of Co³⁺ in Ni₁Co₉ was observed the highest, while the content of Co³⁺ in Ni₁Co₁ is found the lowest.

NiCo₂O₄ is similar to Co₃O₄ and has a spinel structure, in which Ni and Co ions have different oxidation states. Co ions occupy tetrahedral sites and octahedral sites, whereas Ni ions are solely present at

octahedral sites [41]. In addition, the ratio of Co³⁺/Co²⁺ serves as a metric for gauging the extent of Ni²⁺ ion insertion into the octahedral site of the Co₃O₄ spinel structure [22]. Table 2 shows that with the increase of Ni content, the ratio of Co³⁺/Co²⁺ gradually diminishes, while the content of Ni³⁺/(Co³⁺+Ni³⁺) rises.

3.2. Electrochemical measurements

Fig. 7 shows the electrochemical performance of various Ni/Co ratio oxide electrodes. Notably, the Ti/Ni₁Co₄ electrode exhibits the highest feed current and the greatest voltammetric charge in 2 M NaCl (Fig. 7a), indicating the finest chlorine evolution activity. When the voltage exceeds 1.0 V vs. SCE during the positive scan direction, the current density rapidly climbs, indicating the onset of a robust chlorine evolution reaction process [42]. During the negative potential scan, a notable reduction peak at 0.8 V vs. SCE, attributed to chlorine reduction [6,43], is observed (Fig. 7a). The LSV test was conducted to evaluate the electrode performance of the five electrodes. As shown in Fig. 7b, at a current density of 20 mA/cm², the Ti/Ni₁Co₄ electrode has less positive evolution potential and the best chlorine evolution performance. In addition, the catalytic activities of the nickel cobalt mixed oxides electrodes with various Ni/Co ratios follow the sequence: Ti/Ni₁Co₄ (64.85 mA/cm² @1.30 V) > Ti/Ni₁Co₉ (46.35 mA/cm² @1.30 V) > Ti/Ni₁Co₃ (44.2 mA/cm² @1.30 V) > Ti/Ni₁Co₂ (35.05 mA/cm² @1.30 V) > Ti/Ni₁Co₁ (25.8 mA/cm² @1.30 V) (Fig. S3). Therefore, the Ti/Ni₁Co₄ electrode has a good catalytic performance.

The Tafel slope is commonly applied to study the kinetics of the CER process. Small Tafel slope suggests quick increase in the CER rate and decrease in the overpotential. The lower the value of the Tafel slope, the slower the growth rate of the overpotential [18]. The Tafel slopes of the Ti/Ni₁Co₁, Ti/Ni₁Co₂, Ti/Ni₁Co₃, Ti/Ni₁Co₄, and Ti/Ni₁Co₉ are 99.91 mV dec⁻¹, 93.18 mV dec⁻¹, 80.55 mV dec⁻¹, 76.12 mV dec⁻¹, and 78.10 mV dec⁻¹, respectively, as shown in Fig. 7c. As a result, the Ti/Ni₁Co₄ electrode has the smallest Tafel slope while also having the highest electrocatalytic activity. The Ti/Ni₁Co₁ electrode has the largest Tafel slope and the lowest electrocatalytic activity. To confirm the high efficiency and CER selectivity of the Ti/Ni₁Co₄ electrode, LSV curves were measured in both chlorine-containing and chlorine-free solutions, with a commercial DSA electrode serving as reference. Fig. 7d shows that the electrocatalytic activity of the Ti/Ni₁Co₄ electrode in 2 M NaCl solution surpasses that of the commercial DSA electrode, whereas its activity in 2 M NaNO₃ solution falls short of the commercial DSA electrode. Consequently, the Ti/Ni₁Co₄ electrode exhibits superior CER selectivity compared to commercial DSA electrode.

To investigate the electrochemical active area of nickel cobalt mixed oxides electrodes with various Ni/Co ratios. The double layer capacitance (C_{dl}) was measured using CV plots, the CV scans were performed at

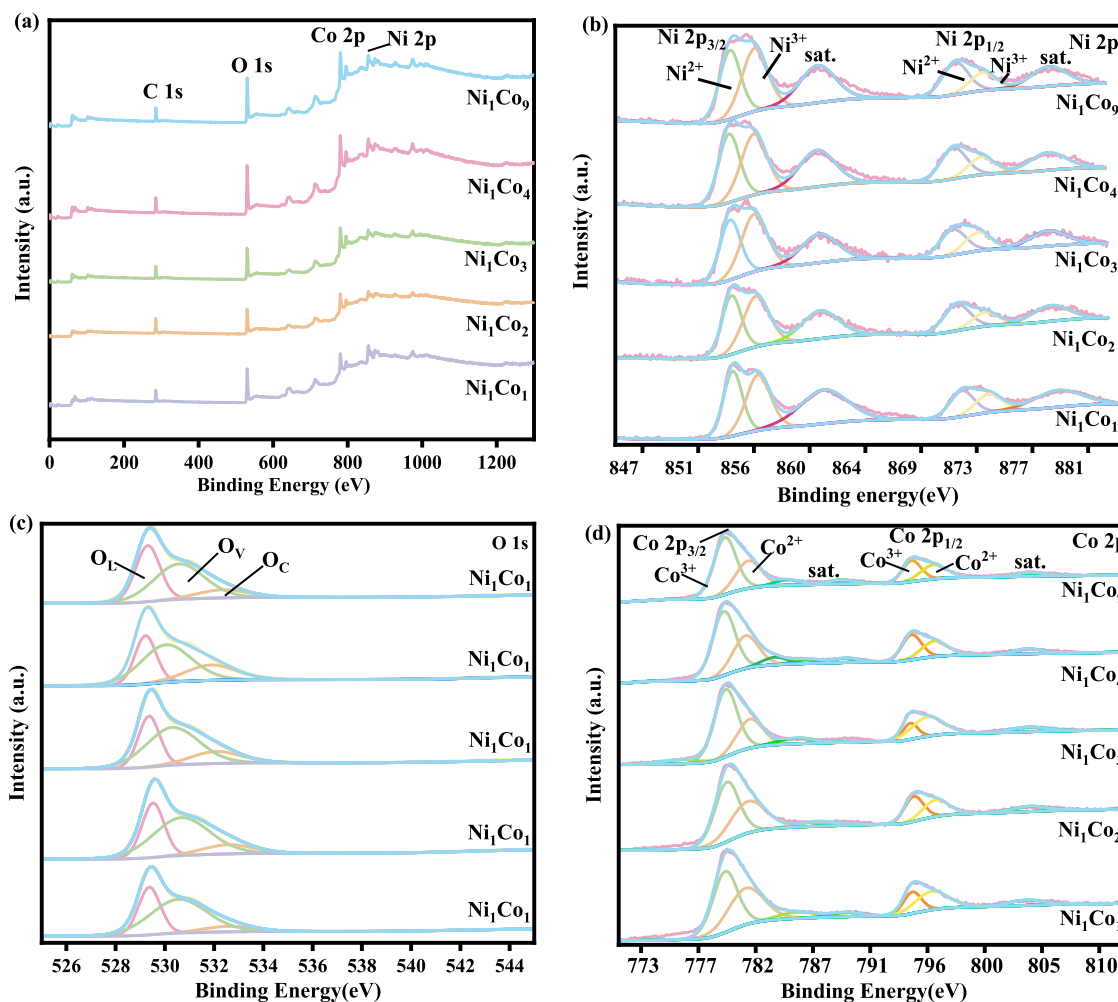


Fig. 6. XPS of nickel cobalt mixed oxides with various Ni/Co ratios (a) Survey spectrum, (b) Ni 2p, (c) O 1s, (d) Co 2p.

Table 2

XPS results for the O_V , O_L , O_C , Co^{3+} , Co^{2+} , Ni^{3+} , Ni^{2+} of nickel cobalt mixed oxides with various Ni/Co ratios. (atom %).

Sample	O_V	O_L	O_C	Co^{3+}	Co^{2+}	Co^{3+}/Co^{2+}	Ni^{2+}	Ni^{3+}
Ni_1Co_1	59.02 %	32.45 %	8.53 %	49.86 %	50.14 %	0.994	46.11 %	53.89 %
Ni_1Co_2	56.00 %	31.83 %	12.17 %	55.37 %	44.63 %	1.241	50.55 %	49.45 %
Ni_1Co_3	53.92 %	29.72 %	16.36 %	56.77 %	43.23 %	1.313	55.61 %	44.39 %
Ni_1Co_4	51.10 %	27.99 %	20.91 %	59.25 %	40.75 %	1.454	58.75 %	41.25 %
Ni_1Co_9	49.99 %	38.57 %	11.44 %	61.06 %	38.94 %	1.568	59.42 %	40.58 %

scan speeds of 10, 30, 50, 30, 70, and 90 mV/s in the non-Faradaic response potential window (0.2–0.6 V vs. SCE). The current density at 0.4 V vs. SCE voltage was used to calculate C_{dl} , which was employed to estimate the electrochemical active surface area (ECSA) at the contact between the electrolyte and the electrode surface. The C_{dl} is estimated by plotting the Δj ($j_a - j_c$) at 0.4 V vs. SCE against the scan rate, where the slope is twice C_{dl} [42,44]. CV of the nickel cobalt mixed oxides electrodes with various Ni/Co ratios at different scan rates is shown in Fig. 8a–e, exhibiting the ideal rectangular curve.

Furthermore, the following relationship between C_{dl} and ECSA, such as Eq. (7) [42,45,46]:

$$ECSA = C_{dl}/C_s \times GSA \quad (7)$$

The C_s is the specific capacitance of the smooth surface and can be used in the range of 20–60 $\mu F/cm^2$, which is 60 $\mu F/cm^2$ in our work [47, 48], GSA is the geometric surface area of the electrodes (4 cm^2).

As a result, ECSA is proportional to C_{dl} of the electrocatalyst. From

Fig. 8f and Table S1, the values size of C_{dl} is Ti/Ni_1Co_4 (7.16 mF/cm^2) > Ti/Ni_1Co_9 (5.76 mF/cm^2) > Ti/Ni_1Co_3 (1.17 mF/cm^2) > Ti/Ni_1Co_1 (1.35 mF/cm^2). Notably, the C_{dl} value for the Ti/Ni_1Co_4 electrode is the largest at 7.16 mF/cm^2 . Conversely, the Ti/Ni_1Co_1 electrode has the lowest C_{dl} value of 1.35 mF/cm^2 . Table S1 shows that the Ti/Ni_1Co_4 electrode exhibits the largest ECSA value of 477.2 cm^2 , while the Ti/Ni_1Co_1 electrode has the least ECSA value, just 90 cm^2 . Additionally, we also analyze the ECSA-normalized CER performance of these electrodes (Table S2). As we can see, the ECSA-normalized electrochemical activities follow the sequence: Ti/Ni_1Co_1 (1.14 $mA/cm^2 @ 1.30V$) > Ti/Ni_1Co_2 (0.93 $mA/cm^2 @ 1.30V$) > Ti/Ni_1Co_4 (0.54 $mA/cm^2 @ 1.30V$) > Ti/Ni_1Co_9 (0.39 $mA/cm^2 @ 1.30V$). Furthermore, the N_2 adsorption-desorption curve (Fig. 5a) shows that Ni_1Co_4 has the largest SSAs, Ni_1Co_1 has the smallest SSAs. Crucially, in Fig. S4, the current efficiency of Ti/Ni_1Co_1 , Ti/Ni_1Co_2 , Ti/Ni_1Co_3 , Ti/Ni_1Co_4 and Ti/Ni_1Co_9 electrodes are 76 %, 83 %, 87 %, 90 %, 88 % at 30 mA/cm^2 in 0.6 M NaCl solution. Therefore, these findings suggest that

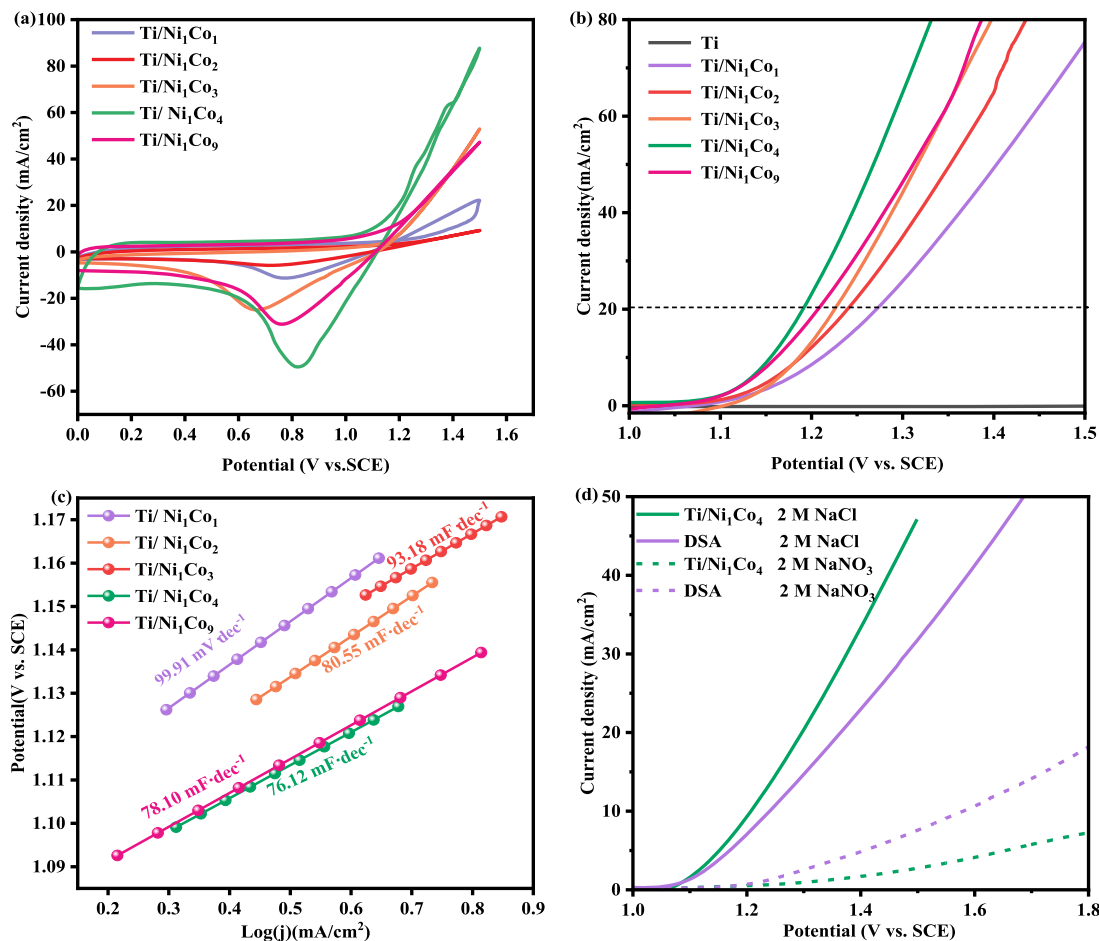


Fig. 7. (a) CV of nickel cobalt mixed oxides electrodes with various Ni/Co ratios, Operating conditions: electrolyte=2 M NaCl, scan rate=100 mV/s, electrode surface area=20 mm×20 mm, (b) LSV of nickel cobalt mixed oxides electrodes with various Ni/Co ratios. Operating conditions: electrolyte=2 M NaCl, scan rate=10 mV/s, electrode surface area=20 mm×20 mm, (c) Corresponding Tafel slope of nickel cobalt mixed oxides electrodes with various Ni/Co ratios, (d) LSV curves of DSA and Ti/Ni₁Co₄ electrodes in 2 M NaCl and 2 M NaNO₃ solutions. Operating conditions: scan rate=10 mV/s, electrode surface area=20 mm×20 mm.

the ECSA of the Ti/Ni₁Co₄ electrode was enhanced, probably due to the large specific surface area of Ni₁Co₄ nanosheets.

EIS was employed to determine the electron transfer efficiency of the nickel cobalt mixed oxides electrodes with various Ni/Co ratios in the CER process, as presented in Fig. 9a. Fig. 9a gives the AC impedance diagram of the electrode and its equivalent circuit diagram. R_s represents the resistance of the electrolyte system, and the parallel connection of C_{dl} and R_{ct} (charge transfer resistance) represent the difficulty of charge transfer, which directly reacts to the reaction kinetics of the electrode [18,49]. We also analyze the ECSA-normalized charge transfer resistances of these electrodes (Table S3). The parameter R_{ct} obtained with the Ti/Ni₁Co₄ electrode is higher than that with other electrodes, which can be related to the reduced pore diameter in interfacial film [50]. In addition, Helmholtz double layer capacitance (DLC) is calculated by using EIS at the same potentials as CV. Table S1 and S3 reveal that when comparing capacitances calculated using differential capacitance measurement (DCM) and EIS, the capacitance values determined by EIS are generally larger than the ones obtained by DCM [51]. The capacitance values obtained from EIS the nickel cobalt mixed oxides electrodes with various Ni/Co ratios exhibit a consistent trend with those obtained through DCM. The Ti/Ni₁Co₁ electrode shows lower capacitance values, while Ti/Ni₁Co₄ electrode exhibits larger ones.

Chronopotentiometry was employed to evaluate the electrode's long-term stability. The voltage shift was minimal after approximately 55 h of continuous testing, as shown in Fig. 9b. However, the current

efficiency of the Ti/Ni₁Co₄ electrode at current density of 10 mA/cm² decreased from 83 % to 70 %, due to the number of microspheres was greatly reduced after the prepared electrode is repeated use. Additionally, in the stability test, the dissolved cobalt and nickel (Table S4) were quantified by ICP-MS to be 81.676 ug/L and 252.4 ug/L at 55 h, standing for 0.41 % and 1.26 % of the anode catalyst content, respectively. Therefore, the Ti/Ni₁Co₄ electrode has a certain degree of stability. It's important to keep in mind that the industrial current density may not necessarily be 10 mA/cm². Based on the experimental data reported by Malkin and Hine et al. [4,52]. The relationship exists between electrode service life (SL) and current density (i) as Eq. (8):

$$SL \propto \frac{1}{i^n} \quad (8)$$

According to Eq. (8), the service life of the (SL_{SE}) at a certain current density (i_{SE}) can be estimated according to the following Eq. (9) [4]:

$$SL_{SE} = SL_a \left(\frac{i_a}{i_{SE}} \right)^n \quad (9)$$

Where i_a is the anode current density and SL_a is the life under accelerated life conditions, i_{SE} is the anode current density and SL_{SE} is the service life at a certain current density. The range of n is from 1.4 to 2.0.

Therefore, among the nickel cobalt mixed oxides electrodes with various Ni/Co ratios prepared in this paper, the Ti/Ni₁Co₄ electrode exhibits the largest electrocatalytic activity area, indicating the best

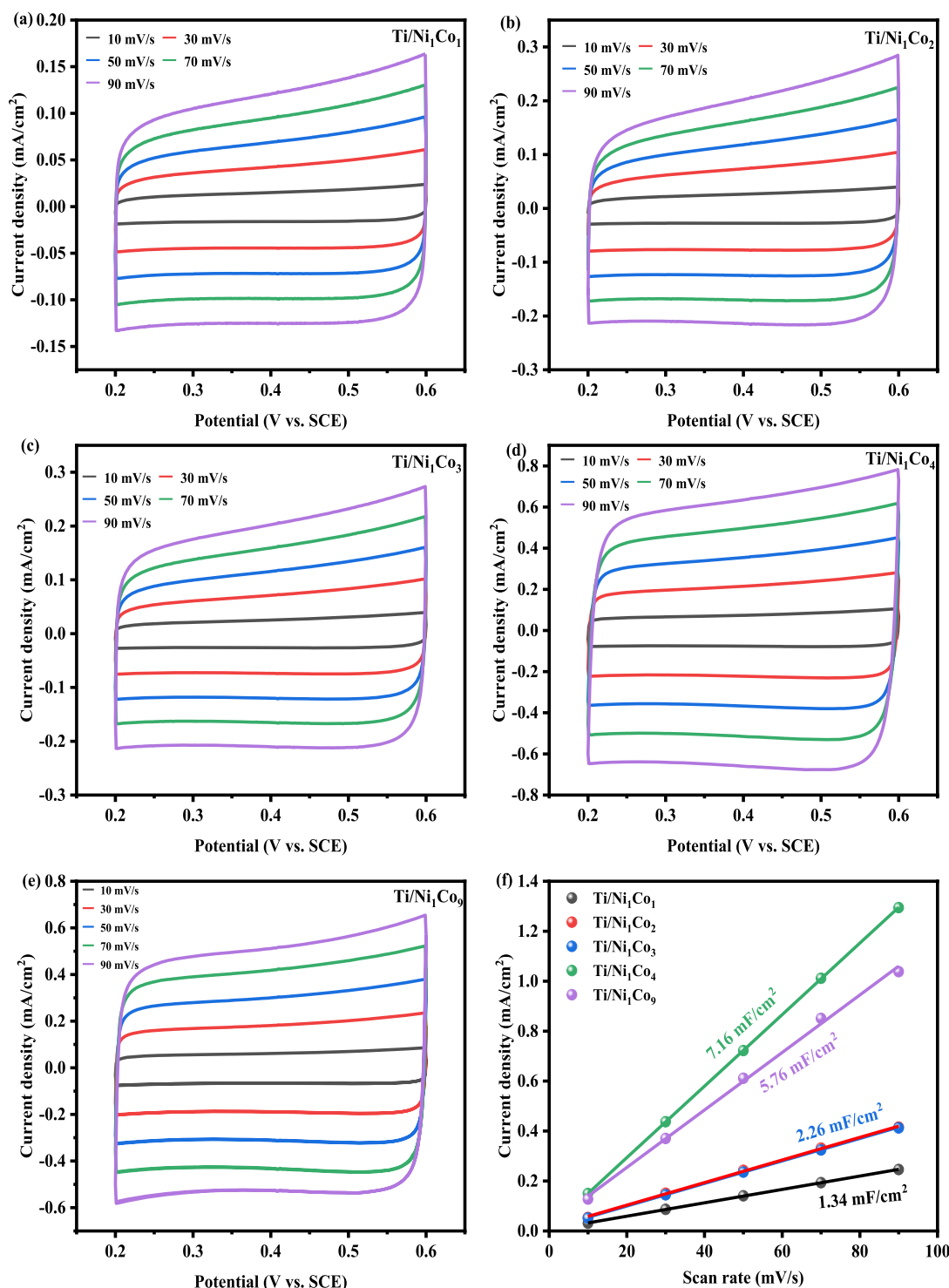


Fig. 8. Cyclic voltammetry curves, (a) Ti/NiCo₁, (b) Ti/NiCo₂, (c) Ti/NiCo₃, (d) Ti/NiCo₄, (e) Ti/NiCo₉ in 2 M NaCl electrolyte solution with different scan rates, (f) C_{dl} of nickel cobalt mixed oxides electrodes with various Ni/Co ratios.

electrocatalytic performance.

3.3. Electro-catalytic chlorination

Given the excellent electrochemical performance of the Ti/NiCo₄ electrode, we conducted electrocatalytic chlorine evolution tests using this electrode. Fig. 10a and b illustrate the effects of current density on the Ti/NiCo₄ electrode and the DSA electrode. In 0.6 M NaCl and 2 M

NaCl solutions, the chlorine evolution efficiency of the Ti/NiCo₄ electrode surpasses that of DSA electrode at any current density. When the current density reaches 30 mA/cm², the chlorine evolution efficiency is the highest, which can reach 90 %. It is worth noting that the current efficiency of the Ti/NiCo₄ electrode and the DSA electrode decreases slightly with increasing current density, which is inevitable because of OER competition and current loss at high anode potential [18]. As a result, the Ti/NiCo₄ electrode outperforms commercial DSA by

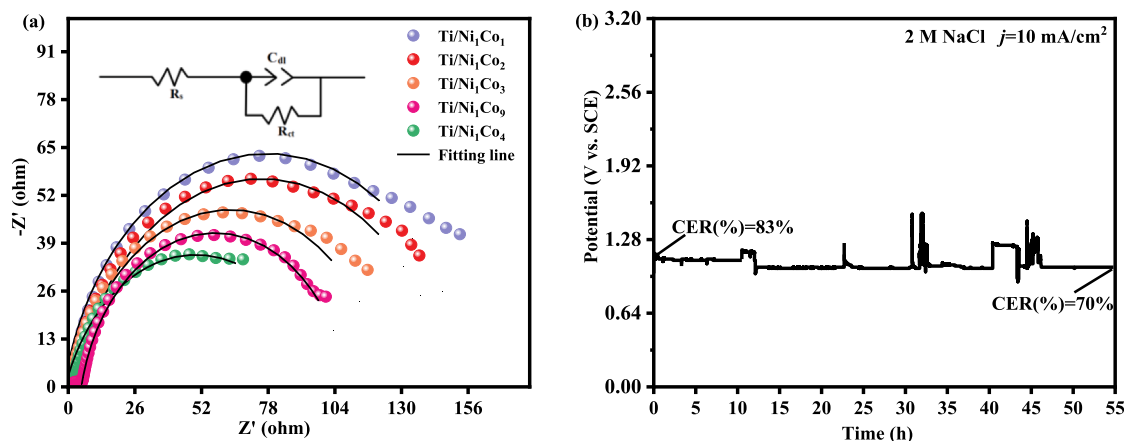


Fig. 9. (a) Nyquist plots, (b) Long-term stability of Ti/Ni₁Co₄ electrode.

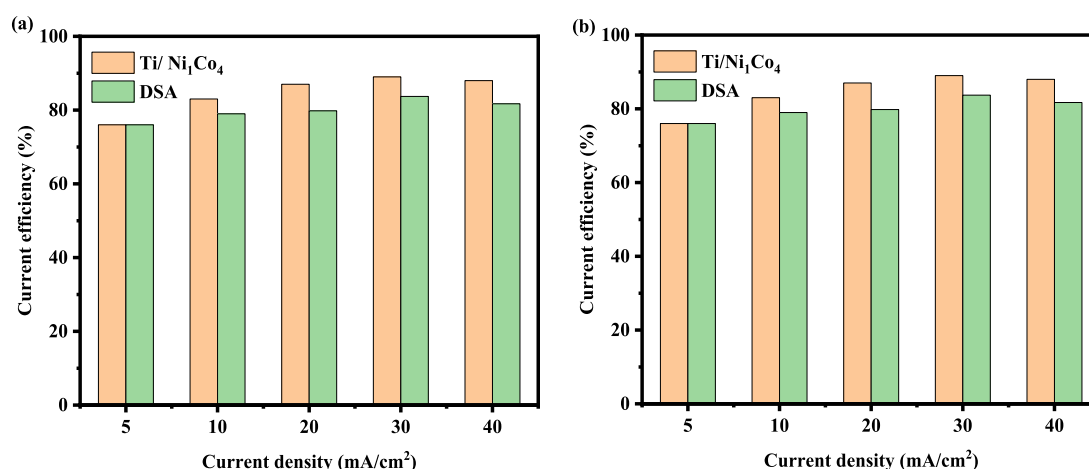


Fig. 10. Current efficiencies at different current densities of Ti/Ni₁Co₄ electrode in (a) 0.6 M, (b) 2 M.

achieving more than 80 % chlorine evolution efficiency in chlorides with approximate seawater content (Concentration of seawater $\approx$ 0.6 M NaCl). This is primarily attributed to the high specific surface area, large pore volume, and small pore size of the Ni₁Co₄ flower-like nanosheet microspheres, which facilitate efficient mass transfer of reactants and products.

4. Conclusion

In this research, a simple approach was employed to create a 3D flower-like NiCo₂O₄ microsphere, which has potential applications in CER. NiCo₂O₄ exhibits a high SSAs (46.00 m²/g) when Ni/Co=1/4. Moreover, NiCo₂O₄ exhibits the largest pore size (0.1777 cm³/g) when Ni/Co=1/9, enhancing electron transport. Notably, the NiCo₂O₄ electrode demonstrates excellent chlorine evolution activity in 0.6 M NaCl solutions. When the current density is 30 mA/cm², the current efficiency of the Ti/NiCo₂O₄ electrode is 90 %. Furthermore, at any current density, the chlorine evolution activity of NiCo₂O₄ surpasses that of commercial DSA electrode. We conducted a study to investigate the impact of varying Ni/Co ratios on chlorine evolution activity and discovered that excessively high Ni content is not conducive to chlorine evolution.

CRediT authorship contribution statement

Ran Zhang: Writing – original draft. **Jing Cao:** Writing – review & editing. **Ting Peng:** Investigation. **KeXuan Wu:** Investigation. **Yinqiang Shu:** Investigation.

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

Data will be made available on request.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.electacta.2024.144166](https://doi.org/10.1016/j.electacta.2024.144166).

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