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MOF-derived Co₃O₄/Nitrogen-doped Carbon Composite for Chlorine-assisted Production of Ethylene Oxide

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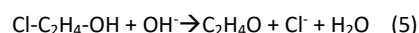
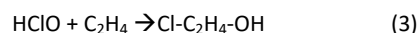
Ethylene oxide (EO) is one of the most crucial materials in plastic industries. The traditional catalytic process requires high temperature and pressure to produce EO. A chlorine-assisted system has been reported to produce EO, but it required noble metal catalysts, which significantly increased the cost. In this work, a MOF-derived Co₃O₄/nitrogen-doped carbon composite (Co₃O₄/NC) prepared through a two-step calcination method has demonstrated remarkable chlorine evolution reaction (CIER) activity as compared with a commercial RuO₂ catalyst, which can be attributed to higher specific surface area and lower resistance of its porous structure and nitrogen-doped carbon. Further, the Co₃O₄/NC maintained a stable potential and a high faradaic efficiency throughout the 10-hour electrolysis test.

Introduction

Ethylene oxide (EO), one of the most crucial chemicals for manufacturing consumer products and intermediates, was mass-produced with an annual production of over 34.5 Mt (2021)¹. Taking great advantage of its strained ring structure, EO can participate in various addition reactions to open the ring. One major use of EO is its conversion to ethylene glycol², which is one of the most important precursors in the plastic industry. In addition, EO can be used to produce ethanol amines³ and various polymers with novel architectures⁴. Patented by Lefort in 1935⁵ and numerous follow-up studies^{6–9}, ethylene can be directly oxidized to EO on silver-based catalysts through thermal catalytic processes. However, relatively high temperature (220 ~ 280 °C) and high pressure (1 ~ 3 MPa) are required for this chemical transformation¹⁰.

Alternatively, EO can be produced by a chlorohydrin process (RXN 2,3,5)². Powered by renewable electricity generated from solar and wind sources, chlorine (Cl₂) can be *in-situ* generated through the electrochemical process under ambient conditions (RXN 1). Then, EO can be produced from a chlorine-assisted process in the formation of ethylene chlorohydrin (RXN 2-3), followed by its chemical reaction with OH[–] that was accumulated at the cathode (RXN 4) to produce ethylene oxide via a dehydrochlorination process (RXN 5) (Fig. 1a). At the meantime, hydrogen is generated on the cathode.¹¹ Iridium oxide (IrO₂)¹² and barium oxide-loaded IrO₂¹³ were reported to achieve EO production with high faradaic efficiency (FE) of >70%. Besides, the dimensional stable anode (DSA), made of ruthenium oxide and titanium oxide, has been proven as an active and durable catalyst for Cl₂ evolution reaction (CIER) and is expected to be active for the chlorine-assisted EO generation process¹⁴. However, all those catalysts are based on noble metals, which significantly increases the overall process costs. Exploration of low-cost, robust, non-noble metal catalysts is highly desirable. Although several works showed

that non-noble cobalt oxide (Co₃O₄) was an active and durable catalyst in the CIER process^{15–17}, their performances are generally inferior to noble metal-based catalysts.



In this work, a metal-organic framework (MOF)-derived porous cobalt oxide/nitrogen-doped carbon composite (Co₃O₄/NC) was studied for chlorine-assisted EO production. MOF-derived materials are well known for their unique porous structure that can offer high specific area that is desirable for various applications, such as sensing, energy storage and catalysis^{18–20}. However, they have been rarely studied for chlorine evolution reaction (CIER). Benefiting from the highly porous structure and carbonized organic linker of MOF as sacrificing template, Co₃O₄ catalysts with high specific surface area and low charge transfer resistance were prepared. Compared to the generally used direct calcination in the air to turn MOF into metal oxides, we investigated a two-step calcination method and observed that the calcination method and temperature significantly influenced the structure and CIER activity. The optimized catalyst has exhibited comparable CIER catalytic activities to commercial ruthenium oxide (RuO₂) catalyst, while the Co₃O₄ costs two orders of magnitude lower than RuO₂. Finally, the Co₃O₄/NC exhibited long-term durability for chlorine-assisted EO production.

Results and Discussion

Characterization of MOF-derived Co₃O₄

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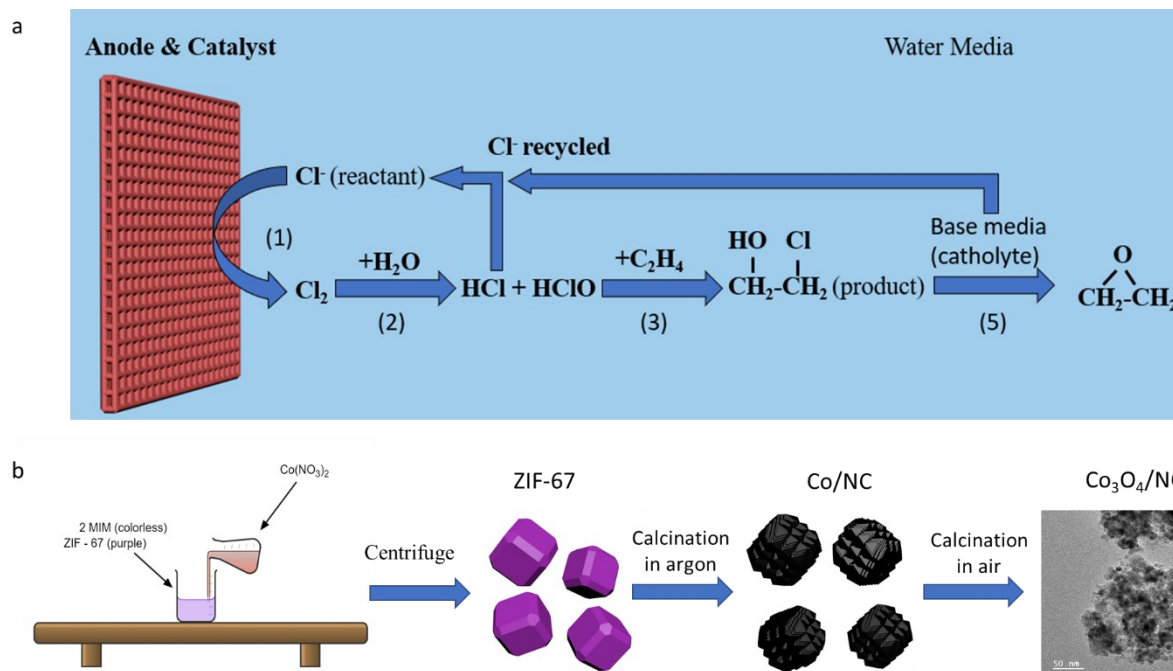


Figure 1. a) Scheme of the chlorine-assisted EO generation process, b) Synthesis process

Cobalt containing zeolite imidazole framework (ZIF-67) was chosen as the sacrificing template due to its facile hydrothermal synthesis process and nitrogen containing organic linker. MOF-derived $\text{Co}_3\text{O}_4/\text{NC}$ samples were prepared from a two-step calcination treatment of ZIF-67. (Fig. 1b). Samples are named after thermal treatment temperatures. For example, ZCO-700-300 (ZCO is short for ZIF-derived cobalt oxide) was obtained by calcinating ZIF-67 at 700 °C under argon for 1 hour, followed by calcination at 300 °C in the air for 1 hour. The morphology and crystal structure of the pristine ZIF-67 after the hydrothermal synthesis were characterized by SEM (Fig. 2a) and XRD (Fig. 2d), showing a typical polyhedral morphology with the particle size of 150-200 nm²¹. After the first calcination step at 700 °C in argon atmosphere, SEM (Fig. 2b) showed a slight decrease in the particle size (~100 nm). XRD (Fig. 2e) indicated the transformation of ZIF-67 into metallic Co, and the organic linker was converted to nitrogen-doped carbon (Fig. S1a). The pore size distribution was well maintained after the first step calcination at 700 °C (Fig. S2a). Therefore, the first step temperature was not further optimized. The metallic Co/NC can be further converted into desirable $\text{Co}_3\text{O}_4/\text{NC}$ through the second calcination step in the air, which shows a similar size to the sample after first step calcination as evidenced by SEM (Fig. 2c). The successful conversion of metallic Co into Co_3O_4 was also supported by XRD patterns (Fig. 2f), and XPS fitting spectra further suggested the existence of C-N bond (Fig. S3).

As the temperature of second thermal treatment largely affects the content species and porous structure (Fig. S1, S2), it is critical to optimize its operating temperature. An extremely high temperature could collapse the small pores of MOF and remove nitrogen-doped carbon, but a relatively low temperature would not fully oxidize Co to Co_3O_4 . We kept the first step calcination temperature at 700 °C in argon and optimized the second step calcination temperature in air. As suggested by the TGA and TPO curves (Fig. S4), ZCO-700-NA (NA indicates the second step has not been done yet) starts to decompose at 250 °C while ZIF-67 starts to decompose at 350 °C. As such, the second step of calcination was designed to perform at 250,

300 and 350 °C. To compare our developed two-step method with the generally used one-step method, samples were prepared via one-step calcination at 350 and 400 °C in the air. If the second step temperature is lower than 300 °C, Co can only be partially oxidized into Co_3O_4 . For instance, as shown in the XRD patterns (Fig. S5), ZCO-700-250 possesses both Co and Co_3O_4 phases, as compared to ZCO-700-300 with a solely Co_3O_4 phase (Fig. 2f). Further increasing the second step temperature to 350 °C would decompose all the nitrogen-doped carbon, as shown in TGA and TPO curves (Fig. S4), which could undesirably increase the internal resistance of metal oxide catalysts. Energy dispersive spectroscopy (EDS) (Fig. S1) and TGA (Table S1) were performed to further confirm the species composition after the calcination at different temperatures. EDS and TGA showed a similar trend: with the second step calcination temperature increasing, a reduction in the amount of carbon and nitrogen was observed, along with an increase in the active content of Co_3O_4 . With the second step calcination temperature over 300 °C (i.e., ZCO-700-300 and ZCO-700-350), the samples showed similar oxygen to Co ratio, indicating that Co was fully oxidized to Co_3O_4 , and 300 °C was the ideal temperature for the second step calcination.

To further understand how temperature affects the pore size distribution and surface area of ZCO samples, nitrogen physisorption was performed. BET curves and pore size distributions were shown in Fig. S2. All samples showed a type IV hysteresis loops (Fig. S2a), which indicates their mesoporous structures. As the second step calcination temperature increasing, large-size pores appeared with an increase in their portion (Fig. S2b). BET surface area measured by nitrogen physisorption showed that the original pore structure in the ZIF-67 precursor collapsed during the calcination treatment, leading to a decrease in surface area (Table S1). Therefore, the optimized second step calcination temperature is 300 °C, consistent with the EDS and TGA suggestions. TEM image of the ZCO-700-300 showed a d-spacing of 0.243 nm (Fig. 2i), which can be assigned to the Co_3O_4 (311) plane, in line with the XRD results. The above synthesis and

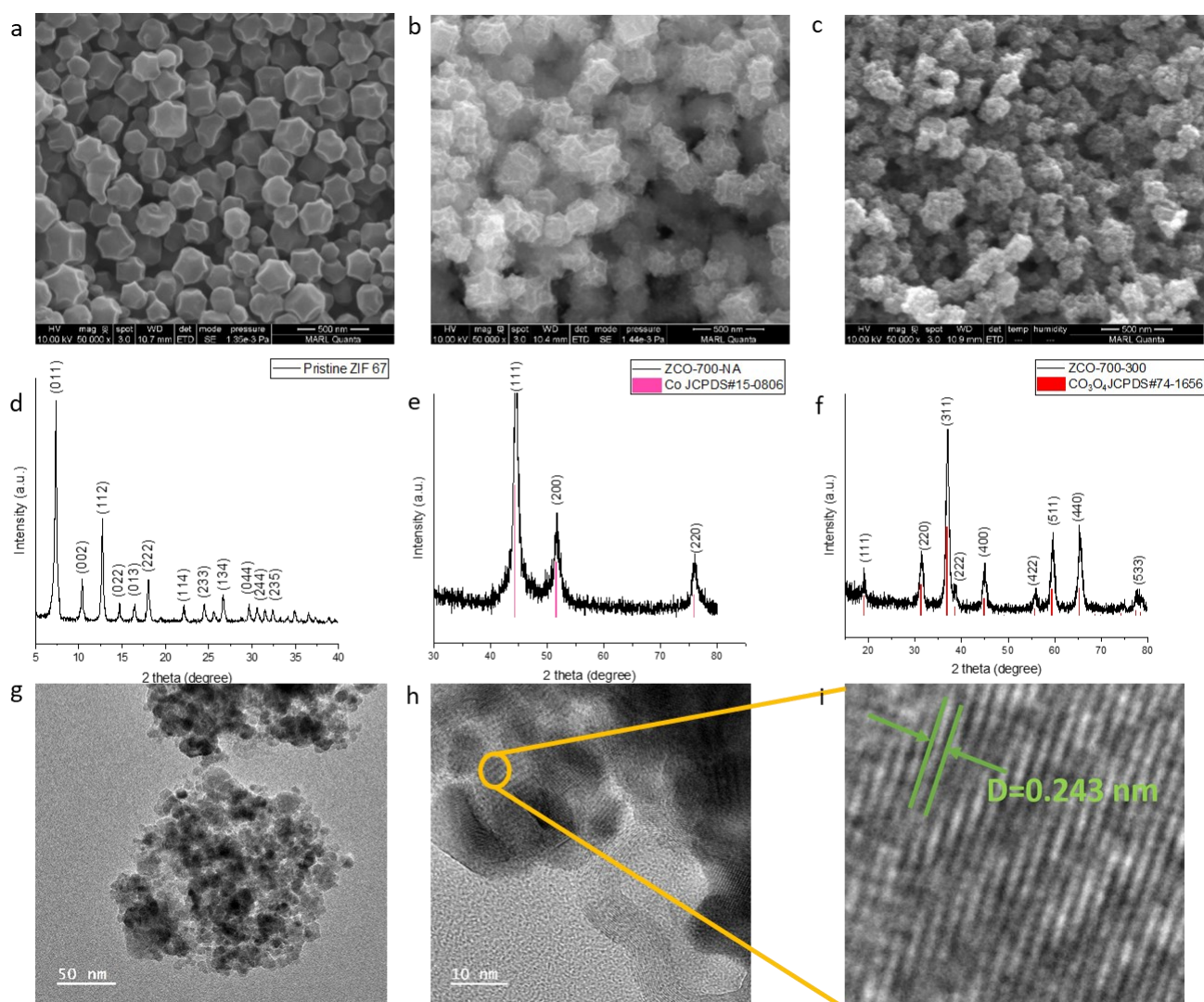


Figure 2. Characterization of catalysts. SEM images and XRD patterns of **a,d**) as-synthesized ZIF-67, **b,e**) ZCO-700-NA, and **c,f**) ZCO-700-300. **g,h**) TEM images of ZCO-700-300 at different magnifications. **i**) A zoom-in image of Figure 2h.

characterization results showed the successful preparation of MOF-derived Co_3O_4 .

Electrochemical measurements on MOF-derived Co_3O_4

Performance comparisons are evaluated by linear scan voltammetry (LSV), as shown in **Fig. 3a, S6**. ZCO-700-300 exhibited comparable performance to RuO_2 , and superior to commercial Co_3O_4 (C- Co_3O_4). At 100 mA/cm^2 , only 0.04 V difference in CIER was observed between RuO_2 and ZCO-700-300. Similar kinetics between ZCO-700-300 and RuO_2 was also supported by examining their Tafel slopes (**Fig. 3b**). The potential dependence of the CIER on ZCO-700-300 was also investigated. The FE of EO (FE_{EO}) and current density increased by positively shifting the anodic potential, and the FE_{EO} maintained $>70\%$ at the potential of $>1.22 \text{ V}$ vs. Ag/AgCl (**Fig. S7**). No active chlorine was detected in the absorbing vessel, and the ethylene chlorohydrin amount in the absorbing vessel was $<1\%$ in the anolyte. We reasoned that this was due to the facile reaction between ethylene and hypochlorous acid (HClO). Since HClO was consumed, the reversible reaction between chlorine gas and water will always favour production of HCl and HClO, with negligible chlorine escaped from the anolyte. Furthermore, by comparing the samples prepared

by different calcination temperatures, the sample with the second step calcination temperature of 300°C showed a superior performance to other samples (**Fig. 3c**), consistent with our characterizations that Co was not only fully oxidized to Co_3O_4 , but also maintained a better porous structure with optimal nitrogen doped carbon content. EIS tests were further carried out on these samples to compare the charge transfer resistance (**Fig. S8**). ZCO-700-300 showed the lowest charge transfer resistance, contributing to its good CIER activity. Although ZCO-700-250 possessed both high surface area and low charge transfer resistance, Co was not fully oxidized to Co_3O_4 and the remaining Co could transform to $\text{Co}(\text{OH})_2$ in the aqueous electrolyte under an anodic potential. XPS confirmed the presence of $\text{Co}(\text{OH})_2$ species in the ZCO-700-250 sample (**Fig. S8**). It has been known that $\text{Co}(\text{OH})_2$ is an active oxygen evolution reaction (OER) catalyst²², which is the main side reaction competing for CIER. This can be the reason to the decreased activity and selectivity of CIER on ZCO-700-250. At the second step calcination temperature of $>300^\circ\text{C}$, a lower CIER performance could be due to the decrease in surface area (**Table S1**) and increase in internal resistance. Taken all together, the optimized MOF-derived $\text{Co}_3\text{O}_4/\text{NC}$

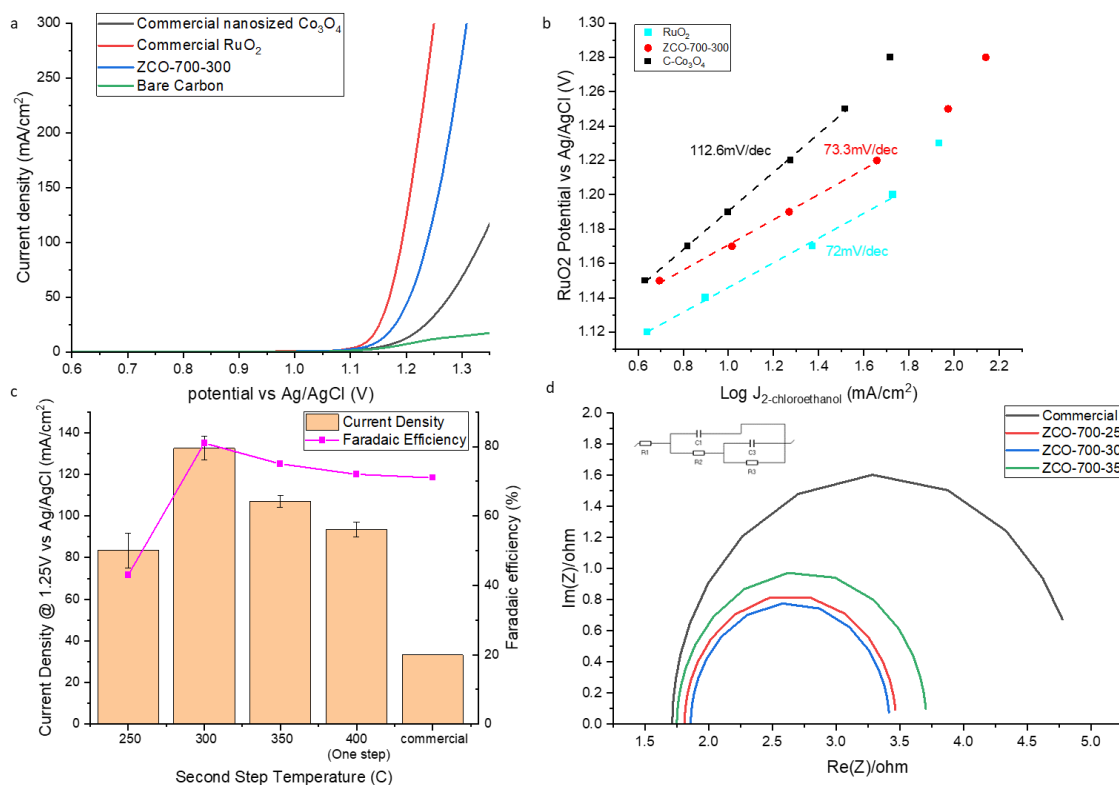


Figure 3. CIER performance of **a)** LSV test, **b)** Tafel slope, **c)** Current density and FE of samples prepared by different temperatures, **d)** EIS test (equivalent circuit inserted).

exhibited an outstanding performance for CIER, and careful control over the second step calcination temperature at 300 °C is critical for optimizing the CIER activity and selectivity. The performance for CIER reached lowest potential at 100 mA/cm² compared to other cobalt oxide catalyst and even comparable to some noble metal catalysts, as shown in **Table S2**.

The intrinsic activity was also examined by comparing their specific activity. However, it is challenging to quantify the Co₃O₄ surface area in ZCO-700-300. As we use either the nitrogen physisorption (i.e., BET) method or the double-layer capacitance method, we always obtain the total areas of both carbon and Co₃O₄. Instead, we used chemical surface area (CSA) to calculate the area-specific activity of CIER of our reported catalysts to compare their intrinsic activity. ZCO-700-300, C-Co₃O₄, and C-Co₃O₄ mixed with the same nitrogen doped carbon in ZCO-700-300 was examined (C-Co₃O₄-NC). As shown in **Figure S9**, C-Co₃O₄-NC showed similar performance compared to C-Co₃O₄. The specific activity of ZCO-700-300 is about 50% better than C-Co₃O₄ and C-Co₃O₄-NC. The possible reason could be attributed to 1) the heterojunction formed between carbon and Co₃O₄ during MOF calcination facilitated the electron transfer; 2) Co₃O₄ particles in ZCO-700-300 was separated by carbon, which increase the utilization of particle surface area.

Furthermore, the durability of Co₃O₄/NC was evaluated at the constant current density of 100 mA/cm² for 10-hour electrolysis. The electrolyte was replaced by fresh electrolytes at each 2-hour interval to compensate for the consumption of reactant Cl⁻. The electrolysis was carried out in both 0.2 M phosphate-buffered electrolyte at pH

of 6 and unbuffered 2 M KCl electrolyte. Buffered solution pH was set to 6 because it is the highest pH in which HClO is the dominant species²³. When the electrolyte pH is > 6, ClO⁻ ion would be the dominant species that could not oxidize ethylene to ethylene chlorohydrin. Whether in the buffered or unbuffered system, ZCO-700-300 maintained a remarkably stable performance in terms of both low cell potential and high FE to EO (**Fig. 4a**). ICP-MS confirmed a very trace number of cobalt ions in the buffered anolyte (equal to <0.002% of Co₃O₄ leaching). In the unbuffered system, although the anolyte pH continuously decreased and eventually formed a strong acid environment, we did not observe significant dissolution of Co₃O₄ after 10-hour electrolysis (3.6% Co₃O₄ leaching obtained from ICP-OES results). The slow cobalt dissolution rate may benefit from effective protection of Co₃O₄ by the carbon residual^{24, 25}. The slightly lower FE_{EO} in the buffered system may be attributed to the use of phosphate-buffered electrolyte, which can enhance the OER activity as phosphate has been reported to be able to facilitate the proton-coupled electron transfer process^{26, 27}. In addition, in terms of thermodynamic potential, the acidic environment in the unbuffered system increased OER equilibrium potential (e.g., 0.876 V at pH 6 and 1.171 V at pH 1), while the CIER potential was unchanged (no proton participated, 1.36 V in all pH). Therefore, the standard reduction potential difference is reduced from 0.484 V to 0.136 V when the pH is changed from 6 to 1, this can also explain slightly higher FE_{EO} in the unbuffered electrolyte. To confirm the OER is the dominating side reaction, online gas chromatography (GC) was utilized to identify gas product and NMR was employed to identify soluble by-products. No signal of other C₂H₄ partial products was observed (**Figure S10, S11**). XPS was conducted to study the durability of ZCO-700-300 after 10-

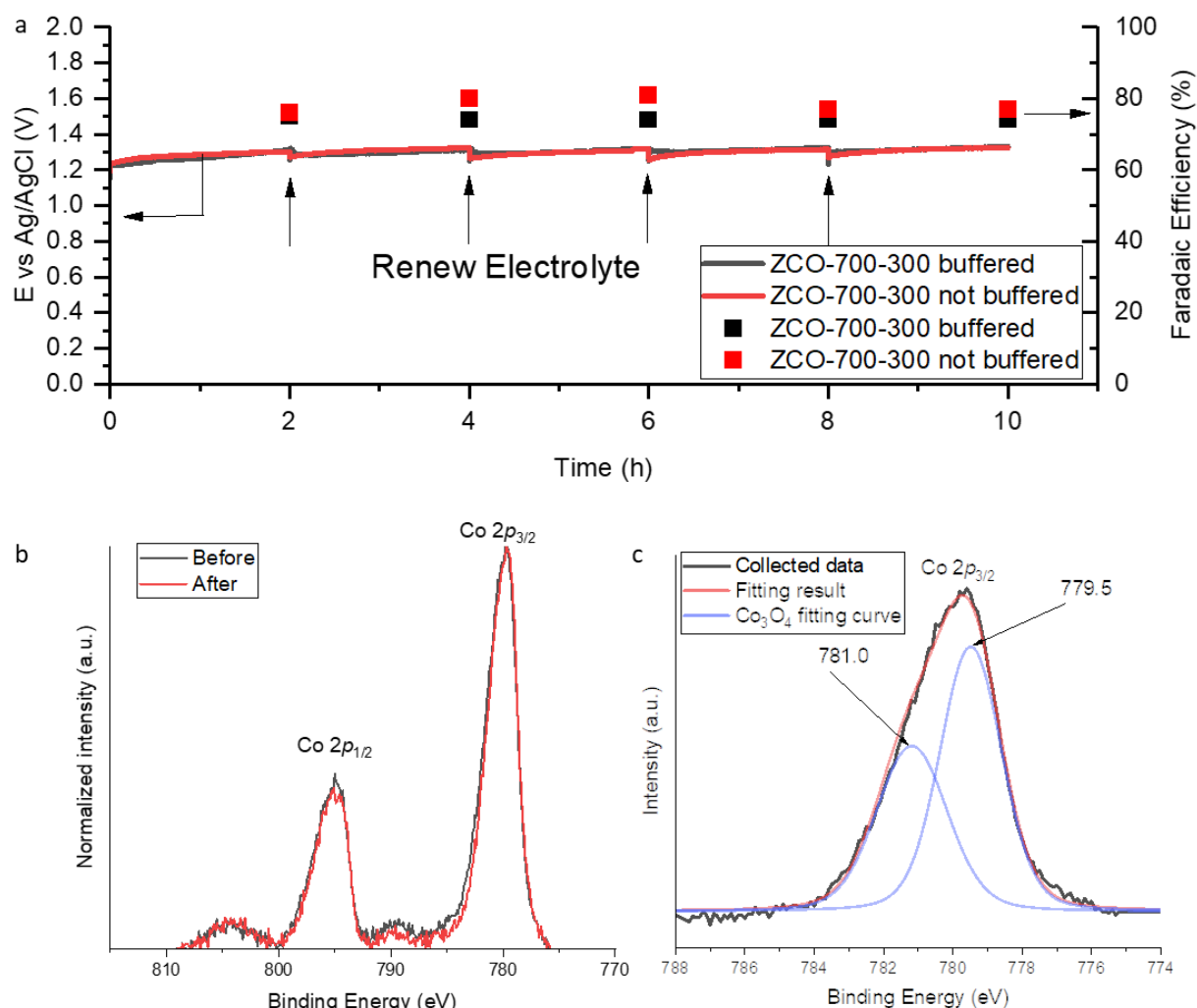


Figure 4. a) CP test result (90% IR compensated), b) XPS result before and after the durability test. c) Co₃O₄ 2p_{3/2} peak fitting curve,

hour electrolysis. Peaks at 779.5 and 781.0 eV in the XPS fitting curve can be assigned to Co³⁺ and Co²⁺ in Co₃O₄, respectively. The overlapped XPS spectrum between the fresh catalyst (before the electrolysis) and spent catalyst (after 10-hour electrolysis) showed unchanged valence state of Co (Fig. 4b, 4c), which indicated the robust durability of Co₃O₄/NC catalyst.

Conclusions

In summary, we have demonstrated MOF-derived Co₃O₄/NC through our self-developed two-step calcination method can serve as a highly active catalyst for chlorine-assisted production of ethylene oxide. The effects of calcination method and temperature on the CIER activity and FE_{EO} on the ZCO samples were investigated and optimized. Benefitting from the porous structure with more exposed active sites and improved charge transfer, high CIER activity was obtained on Co₃O₄/NC catalyst, which is comparable to a commercial RuO₂ catalyst. In the 10-hour chronoamperometry test, the optimized Co₃O₄/NC catalyst exhibited remarkable stability in buffered electrolyte, in terms of CIER activity, FE_{EO}, and catalyst

phase stability. The strategy to synthesizing the MOF-derived Co₃O₄/NC materials could be used for the synthesis of efficient catalysts for other electrochemical reactions.

Experimental Methods

Materials and chemicals

All materials and chemicals were used as received without further purification. Platinum foil (25 x 25 x 0.025 mm, 99.99%) was purchased from Strem Chemicals Inc. Cobalt(II) nitrate hexahydrate (Co(NO₃)₂•6H₂O, 98%), 2-Methyl Imidazole (2-MIM, 99%), ethylene oxide (EO, 50mg/mL in methanol), dimethylmalonic acid (DMMA, 99%) were purchased from Sigma-Aldrich. Potassium Chloride (KCl, 99%), ethylene glycol (EG) was purchased from Fisher Chemicals. Anion exchange membrane (AEM, Fumasep FAA-3-50) was purchased from Fuel Cell Store. Commercial Co₃O₄ was purchased from US Nano Research, Inc. Commercial RuO₂ was purchased from Premetek Co.

Preparation of precursor ZIF-67

The precursor ZIF-67 was synthesized by hydrothermal method²¹. Typically, 0.45g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved into 3 mL of deionized (DI) water, and 5.5g of 2-methylimidazole (2-MIM) was dissolved into 20 mL of DI water separately. Then cobalt nitrate solution was added into 2-MIM solution slowly under stirring. The solution was kept stirring for 6 hours at room temperature. The purple precipitate was collected by centrifuging at 8000 rpm for 15 min and washed with water and methanol, respectively. The obtained precipitate was dried in a vacuum oven at 80 °C for 24 hours.

Preparation of ZCO samples

ZIF-derived cobalt oxide (ZCO) samples were prepared through a two-step calcination method (**Fig. 1b**). The first step calcination was conducted at 700 °C in a tube furnace under an argon atmosphere for 1 hour²⁸. The second step was performed in a muffle furnace under an air atmosphere for 1 hour at different temperatures of 250, 300, and 350 °C to study the temperature effect on samples' activity. To compare the effect of the calcination method, samples made by the one-step calcination method were also prepared at 350 and 400 °C under an air atmosphere.

Preparation of C- Co_3O_4 -NC samples

ZIF-8 is a similar MOF as compared to ZIF-67, which replaces Co by Zn as the metal source. We chose ZIF-8 instead of ZIF-67 because Zn is easier to be removed, so we can obtain the nitrogen-doped carbon (without metal). ZIF-8 was then synthesized with the same molar ratio of metal ion to the organic linker as the ZIF-67 (reported in this work). The product was calcinated in Ar at 700 °C for 1 hour with a temperature ramp of 5 °C/min. The product after calcination is denoted as Zn/NC composite, which should be similar to ZCO-700-NA. Then Zn/NC was soaked in 0.5 M H_2SO_4 overnight to remove Zn²⁹. The remaining Zn is <1 wt%, as confirmed by EDS. We mixed the ZIF-8 derived carbon with a commercial Co_3O_4 (C- Co_3O_4) with a 14: 86 weight ratio, same as that for ZCO-700-300 according to the TGA results shown in Table S1. The mixture was grounded and dispersed in isopropanol alcohol and sprayed on 1 x 1 cm² carbon paper to reach the Co_3O_4 loading of 1 mg/cm². This sample was named as C- Co_3O_4 -NC.

Preparation of electrodes

Commercial nanosized cobalt oxide (C- Co_3O_4), commercial ruthenium oxide (RuO_2), and various self-prepared samples were loaded on hydrophilic carbon paper by spray coating. The spray ink was made of active content and isopropanol (IPA) at 5 mg/mL concentration. The amounts of catalyst were normalized to 1 mg/cm² of Co_3O_4 or RuO_2 according to TGA results. Commercial samples were directly sprayed on carbon paper. Self-prepared samples were loaded by spray coating their precursor (ZIF-67 for one-step and ZCO-700-NA for two-step method) on carbon paper followed by calcination at designed temperatures. This loading method would enhance the contact with carbon paper and prevent physical peel-off.

Characterization of samples

Scanning electron microscopy (SEM) images and energy dispersive spectroscopy (EDS) spectra were obtained from FEI Quanta 250 FE-SEM. X-ray diffraction (XRD) data were collected from the Rigaku SmartLab diffractometer, with Cu K α radiation (λ = 0.15418 nm) working at 40 kV and 44 mA. Transmission electron microscopy (TEM)

images were captured using a JEOL 200kV JSM-2100 scanning transmission electron microscope with a Gatan OneView 4K camera. X-ray photoelectron spectroscopy (XPS) was performed with a Kratos Amicus/ESCA 3400 instrument. Nitrogen physisorption was carried out on Micromeritics ASAP 2020 Surface Area and Porosity Analyzer. It needed to be noted that BET measured both carbon and Co_3O_4 surface area while carbon was inert in CLER. Temperature-programmed oxidation was completed on the Micromeritics AutoChem II chemisorption Analyzer. Leached cobalt during durability test was determined by inductively coupled plasma-optical emission spectrometer (ICP-OES) on PerkinElmer Optima 8000 ICP-OES instrument and Agilent Technologies 7700 Inductively coupled plasma mass spectrometry (ICP-MS). Gas product was identified by gas chromatography (SRI instrument 8610C #3) equipped with HayeSep D and MolSieve 5Å columns. A thermal conductivity detector was used to quantify H_2 , and a flame ionization detector was employed to detect CO_2 and possible gaseous side products.

Electrochemical tests

Electrochemical tests were conducted on a BioLogic VSP-300 electrochemical workstation. Measurements were carried out in a typical H-type cell with an additional absorbing vessel (**Fig. S12**). Anode was prepared as described in section 2.4. The cathode was platinum foil. A saturated Ag/AgCl electrode was utilized as a reference electrode. The electrolyte was 2 M KCl solution at both the anode and cathode. An anion exchange membrane was used to separate the two compartments of this cell. Ethylene gas was purged into anolyte through a gas diffuser. An additional compartment was added to capture the chlorine gas generated on the anode.

Linear sweep voltammetry (LSV) was conducted to evaluate the activity performance of CLER. The scanning rate of LSV was 5 mV/s. A 90% IR compensation was used to eliminate the effect of solution resistance. Electrochemical impedance spectroscopy (EIS) was measured at 1.15 V vs. Ag/AgCl electrode to measure charge transfer resistance. Chronopotentiometry (CP) mode was utilized to test the durability of the catalyst at 100 mA/cm². The electrolyte was replaced with fresh electrolyte solution every 2 hours during the durability test to compensate for the consumption of chloride ions.

Product quantification.

The amount of product was measured by nuclear magnetic resonance (NMR) on Bruker NEO 400 instrument. An internal standard method was employed to quantify the product¹⁷. Typically, the solution was made of 200 μL D_2O , 100 μL 15mM DMMA solution, and 400 μL anolyte. Quantity was obtained by calculating the peak area ratio of the product to the internal standard and comparing it to the calibration curve. Peak area was obtained in MestReNova software with auto phase and baseline correction. A calibration curve made from the known product concentration in 2M KCl solution was used to quantify the product. An example of the NMR result and calibration curves for EG and EO were shown in supplementary information (**Fig. S11**). Faradic efficiency was calculated by:

$$FE = \frac{2 \times F \times n}{Q}$$

Where F is faraday constant, 96485.33 C/mol; 2 is the number of electrons transferred when one ethylene molecule is oxidized to ethylene chlorohydrin; n is the total amount of product measured by

NMR; Q is the total amount of electrons transferred in the circuit during the whole reaction.

Active chlorine was tested by WaterWorks free chlorine test strip. The lower detection limit is 25ppm, corresponding to 2 C charge. Typically, the experiment was carried out at 100 mA for 2h, which was 720 C total charge. If the color change of the strip was not observed, we assumed all active chlorine was consumed through reacting with ethylene.

Calculation of specific activity

It is challenging to quantify the specific area as mentioned above. Instead, chemical surface area (CSA) is a good alternative to calculate the area-specific activity of CLER of our reported catalysts to compare their intrinsic activity. By using Debye-Scherrer equation, the average particle size of the metal nanoparticles could be estimated from the diffraction peak of an isolated crystal plan in XRD patterns. The average size of the Co_3O_4 nanoparticles obtained is 8 nm. The TEM image also shows that the Co_3O_4 particle size ranges from 5 – 13 nm. The specific surface area of Co_3O_4 thus can be calculated by the following equation.

$$CSA = \frac{S}{m} = \frac{S}{\rho * V} = \frac{4 * \pi * r^2}{\frac{4}{3} * \pi * r^3} = \frac{3}{\rho * r}$$

Where S is surface area of a spheric Co particle; m is mass; ρ is density of cobalt oxide ($6.11\text{g}/\text{cm}^3$); V is volume of the particle, and r is radius of the particle. The total specific surface area of Co_3O_4 in ZCO-700-300 would be $122.75\text{ m}^2/\text{g}$. Then the current density based on geometric electrode surface area could be converted to the current density based on the specific surface area. The specific activity of ZCO-700-300 was $0.108\text{ mA}/\text{cm}^2$, which is 60% greater than the specific activity of commercial Co_3O_4 ($0.067\text{ mA}/\text{cm}^2$). Although the surface area of the Co_3O_4 particles cannot be all available to the reaction, we actually can compare the intrinsic activity between our MOF-derived Co_3O_4 with commercial Co_3O_4 sample, if we assume they have same catalyst utilization (electrochemical active surface area / specific surface area).

Author Contributions

T. Li synthesized and characterized MOF-derived Co_3O_4 materials, and conducted most of electrochemical tests. H. Liu helped with setting up electrochemical cells for initial electrochemical tests and data analysis. J. Yu and W. Huang performed the ICP-MS tests and data collection and analysis. Y. Chen helped with GC tests. W. Li proposed and supervised the research. T. Li, H. Liu and W. Li wrote the manuscript, and all authors discussed results and edited the manuscript.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

‡ Footnotes relating to the main text should appear here. These might include comments relevant not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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