



Short communication

Effect of halides on nanoporous Zn-based catalysts for highly efficient electroreduction of CO₂ to CO

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ABSTRACT

The effects of halide ions (F⁻, Cl⁻, Br⁻, or I⁻) on nanoporous Zn-based electrocatalysts were assessed. All catalysts in the presence of halides exhibited high electrocatalytic performances of CO₂ reduction reaction (CO₂RR) and efficient suppression of hydrogen evolution reaction (HER) with a maximum Faradaic efficiency of up to 97%. The increasing adsorption strength from F⁻ to I⁻ is proposed to form more porous structures and higher oxidized Zn species, thus facilitating the protonation of CO₂ and stabilizing the adsorbed intermediates induced by charge donation from the adsorbed halides on Zn surface to CO₂, enhance CO₂RR and simultaneously suppress HER.

1. Introduction

Electrocatalytic reduction of CO₂ to fuels is a potential strategy to address environmental issues caused by the heavy usage of fossil fuels [1]. However, CO₂ reduction reaction (CO₂RR) in aqueous electrolytes encounters a challenging fact that CO₂-reducing catalysts also facilitate hydrogen evolution reaction (HER). In fact, HER is often more competitive because CO₂RR requires relatively high potential due to the formation of a thermodynamically unstable intermediate [2, 3]. Noble metals such as Au and Ag are well known to have selectively high activity in CO₂RR to CO [4–6] and recently Zn-based electrocatalysts have been highlighted to replace precious metals in electroreduction of CO₂ to CO due to material cost [7–9]. In the case of Zn-based catalyst, chloride ion has been effectively used to develop selective Zn-based electrocatalysts for CO production from electrochemical carbon dioxide reduction reaction. A high Faradaic efficiency for CO (FE_{CO}) production (> 90%) was achieved in the presence of chloride anions, while HER was suppressed [10, 11]. Based on surface analysis, it is proposed that the adsorption of chloride ions on surface could selectively facilitate the protonation step of CO₂ to adsorbed COOH*, which improves CO₂RR and blocks the HER activity [10, 12]. However, more studies are required to understand how halide ions on Zn-based catalyst surface affect the catalytic activity.

Meanwhile, zinc is facily oxidized (oxidation may also occur even in the bulk state), while halide anions are well-known for high electronegativity and nucleophilicity. Therefore, the adsorption of halides on zinc nanostructured surface or the interaction of halide anions on oxidized zinc surfaces is likely to occur. These may have a strong influence on the nanostructure, morphology or chemical states of Zn-based catalysts, which are considered significant factors determining the CO₂ reduction activity [13–17]. However, no systematic work studied the effects of halides on oxide-derived Zn electrocatalysts to the best of our knowledge.

Herein, the extensive effects of various halides were assessed on nanoporous structured Zn-based catalysts derived from ZnO by cyclic voltammetry (CV) electroreduction in different halide electrolytes for the first time. A maximum FE_{CO} value larger than 95% was achieved at –1.1 V_{RHE} in KCl, KBr and KI, which efficiently suppressed HER resulting in high CO production rates. A slight decrease of FE_{CO} (89%) was observed at –1.0 V_{RHE} in KF due to increased H₂ current density. Our results revealed that the effect of adsorbed halides with a different coverage on porous Zn-based catalysts during the reaction might change some properties of the porous structures, such as the morphology and roughness of nanostructure along with the chemical states of zinc, which were critical in order to stabilize the adsorbed intermediates and improve the CO₂ to CO electrocatalytic activity.

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2. Experimental

The synthesis of Zn-based catalysts was achieved from an as prepared ZnO film (AP-ZnO). The latter was fabricated by a cathodic electrodeposition method as previously reported [11]. Porous Zn-based electrocatalyst (denoted as p-Zn) was obtained from AP-ZnO by applying cyclic voltammetry (CV) from -0.75 to -1.25 V_{RHE} at a scan rate of 50 mV/s for 45 cycles. The reduction step and CO_2RR measurements were performed in a gas-tight polyether ether ketone (PEEK) cell having two compartments separated by a proton exchange membrane (Nafion[®], 117). Ag/AgCl reference and Pt counter electrodes were used. p-Zn/KF, p-Zn/KCl, p-Zn/KBr and p-Zn/KI electrodes were prepared from the reduction of AP-ZnO in the CO_2 saturated aqueous 0.5 M KF (pH 6.30), KCl (pH 3.91), KBr (pH 2.96) and KI (pH 2.53) electrolytes, respectively. A simplified schematic diagram of the experimental procedure is presented in the provided Electronic Supplementary Information (ESI) (Scheme S1).

CO_2RR with Zn-based catalyst was conducted immediately after CV treatment without air exposure to avoid oxidative changes that might occur on the Zn surface. The electrolyte was continuously flowing with 20 sccm CO_2 gas during the CO_2RR measurements. CO_2RR activities were evaluated under chronoamperometry mode at each fixed potential by a potentiostat (CH Instruments), and all measured currents were normalized by the masked geometric electrode area (ca. 0.5 cm^2). The gaseous products i.e. H_2 , CO and CH_4 were analyzed by gas chromatography (GC, Younglin 6500). Liquid products were also analyzed by ion chromatography (IC, Dionex IC25A). The applied potentials for CO_2RR activity measurements were converted versus reversible hydrogen electrode (RHE): $E_{RHE} = E_{Ag/AgCl} + 0.197V + (0.0591 \times pH)$. Further details on the preparation procedures, characterization techniques and electrochemical surface area measurement methods are provided in the ESI.

3. Results and discussion

All porous Zn-based electrodes pre- and post- CO_2RR were characterized by SEM images and XRD patterns (Figs. 1 and S1 in ESI). As reported in a previous work [11], the original hexagonal nanowires of AP-ZnO changed to p-Zn samples that have porous nanostructures after CV treatment; but there are slight morphological variations depending on the types of halide ions present during the electrode preparation (Fig. 1a). The average particle size increased with next halide in series, except for p-Zn/KBr and p-Zn/KI having similar feature sizes (Fig. 1a), while p-Zn/KF distinctively appears to be more compact. The porous nature of all p-Zn catalysts was maintained after CO_2RR (Fig. S1a). The particle size of p-Zn/KF and p-Zn/KCl catalysts post- CO_2RR seems stable. However, p-Zn/KBr and p-Zn/KI catalysts underwent noticeable increase of particle size that ranged over 100 nm.

Crystal structures of all p-Zn electrodes were analyzed and compared with Zn foil and AP-ZnO electrode pre- and post- CO_2RR (Fig. 1b and S1b, respectively). The XRD pattern of Zn foil is matched with that of metallic Zn, while that of AP-ZnO indicates the presence of ZnO with very weak diffraction peaks of $Zn(OH)_2$ due to its incomplete decomposition [18]. The p-Zn/KF and p-Zn/KCl catalysts pre- CO_2RR have similar XRD patterns to those of metallic Zn foil as a result of the electrochemical reduction (Fig. 1b). Meanwhile, p-Zn/KBr and p-Zn/KI electrodes still show some ZnO patterns, indicating that ZnO was not completely reduced during CV treatment, which might be the reason that caused morphology changes after CO_2RR (see Fig. S1a). Furthermore, all post- CO_2RR p-Zn electrodes have similar XRD patterns to those of metallic Zn, suggesting that ZnO was reduced during CO_2RR by the negative potential.

Fig. 2 compares CO_2RR activities of all p-Zn catalysts, and p-Zn/KF shows noticeably different performance to other p-Zn. Only CO and H_2 gases were the main products according to GC measurements, while the amount of liquid products (such as formic acid) produced was under the

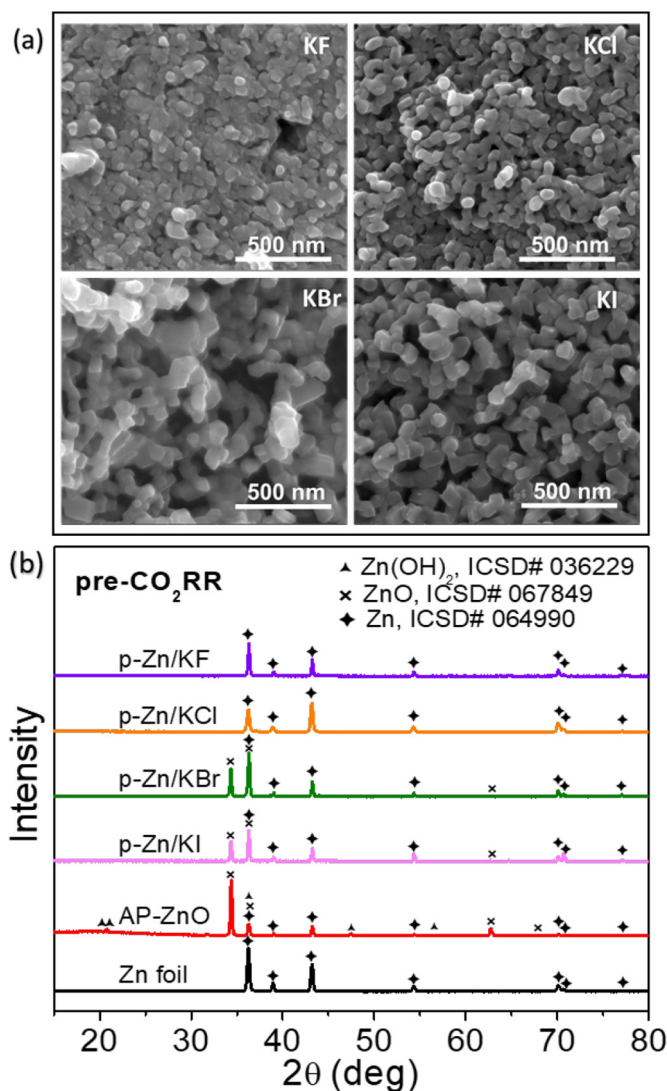


Fig. 1. SEM images (a) and XRD patterns (b) of p-Zn/KF, p-Zn/KCl, p-Zn/KBr and p-Zn/KI pre- CO_2RR .

detection limit of IC, consistent with some previous studies [7, 10, 11]. High FE_{CO} values over 90% are achieved on p-Zn/KCl, p-Zn/KBr and p-Zn/KI catalysts in a wide potential range (-0.95 to -1.25 V_{RHE}), with a maximum value of 97.1, 95.9 and 96.5% at -1.1 V_{RHE} , respectively (Fig. 2a). Meanwhile, the FE_{CO} on the p-Zn/KF reached the value of 84.5% at the same potential, which is more than 10% lower. Also, unlike the others, the p-Zn/KF reached the maximum FE_{CO} of 89.4% at a lower potential (-1.0 V_{RHE}). AP-ZnO sample was reduced and tested in the same manner with p-Zn catalysts in CO_2 saturated 0.5 M $KHCO_3$ electrolyte (denoted as RE-Zn) as previously reported [11], which exhibited overall lower CO Faradaic efficiencies than p-Zn/KX (X = F, Cl, Br or I) due to the excellent ability of p-Zn/KX catalysts to suppress H_2 production.

The CO partial current density (j_{CO}), H_2 partial current density (j_{H_2}), and the total current density (j) of p-Zn catalysts were also compared. A gradual decrease of j_{CO} (Fig. 2b) and j (Fig. S2, ESI) is observed from p-Zn/KF to p-Zn/KI, while there is a unique disparity in j_{H_2} on p-Zn/KF (Fig. 2c). Compared with j_{H_2} of p-Zn prepared in $KHCO_3$ electrolyte (-4.7 $mA\ cm^{-2}$ at -1.1 V_{RHE}) previously reported [11], HER was significantly suppressed to -1.4 $mA\ cm^{-2}$ on p-Zn/KF in KF electrolyte. However, the suppression of HER was more extreme on other p-Zn catalysts which exhibited j_{H_2} of only about -0.2 $mA\ cm^{-2}$.

To understand the halide-dependent CO_2RR trend and the uniquely

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