Electrochemical CO_2 reduction on Pb hydroxyapatite electrocatalyst in phosphate-based electrolyte

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Electrochemical CO_2 reduction has garnered attention because it can convert CO_2 into valuable chemicals using renewable energy sources. Pb(II)-based materials are promising electrocatalysts that can selectively produce formic acid or formate. In Pb(II)-based systems, suppressing self-reduction to metallic Pb is crucial because Pb promotes the undesirable hydrogen evolution reaction. Under typical conditions in KOH or $KHCO_3$ aqueous solutions, they often decompose into lead carbonate, which acts as the actual active species.[1)] Therefore, suppressing the formation of lead carbonate and stabilizing other phases could open the way to developing new catalysts. In this study, we performed CO_2 electrolysis in various electrolytes and found that Pb hydroxyapatite (Pb-HAP) is a stable active phase and produces formate selectively in phosphate-based electrolytes.

Pb-HAP powder was synthesized by mixing aqueous solutions of Pb(II) acetate and $Na_2HPO_4 \cdot 12H_2O$. Then, a catalyst ink was prepared by dispersing Pb-HAP powder, Ketjen Black, and binder (Sustainion® dispersion) in a mixture of ethanol and water. The ink was coated onto carbon paper and dried to prepare the working electrode. Using the electrode, constant potential electrolysis was performed in an H-type cell. Ag/AgCl and Pt were used as reference and counter electrodes. CO_2-saturated 0.2 M $KHCO_3$ aqueous solution, 0.1 M K_2HPO_4 aqueous solution, and others were used as catholytes.

CO_2 electrolysis in both electrolytes mainly produces formate, and the Faradaic efficiencies exceed 80%. (Figure 1a). However, for the electrode after the reaction in 0.2 M $KHCO_3$ aqueous solution, the X-ray diffraction (XRD) pattern shows that Pb-HAP decomposes, forming $PbCO_3$ and Pb (Figure 1b, red). By contrast, in the case of 0.1 M K_2HPO_4 aqueous solution, Pb-HAP retains its crystal structure without the formation of $PbCO_3$ or Pb (Figure 1b, blue). Therefore, Pb-HAP is a stable active phase that can produce formate with high Faradaic efficiencies in phosphate-based electrolytes.

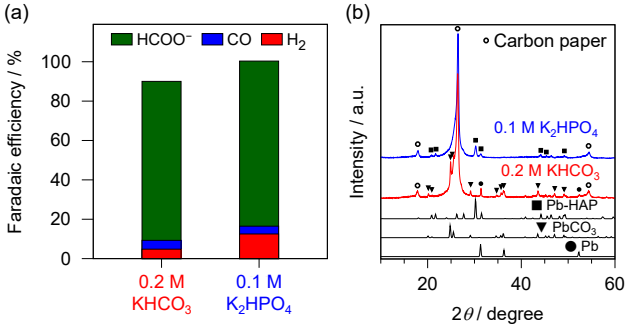

Figure 1. (a) Faradaic efficiencies and (b) XRD patterns of the electrodes after the electrolysis in each electrolyte at −1.0 V vs. RHE for 120 min.

1) Y. Shi et al., *Nat. Commun.* **2020**, *11*, 3415.