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Electrocatalytic CO₂ reduction toward liquid fuels : on heterogeneous electrocatalysts and heterogenized molecular catalysts

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Supporting Information to Chapter 7

Optimization of Electrolyte Composition for
Electrocatalytic CO₂ Reduction on Immobilized
Indium(III) protoporphyrin

D.1 Materials and Experimental procedures

The experimental procedures are similar to those reported before.^[1,2] High purity chemicals were used for the preparation of the electrolyte solutions: KH_2PO_4 , K_2HPO_4 , KHCO_3 , KI (TraceSELECT, Honeywell), K_2SO_4 , KClO_4 , KCl, KBr (EMSURE, Merck), KOH (semiconductor grade, Honeywell) and NaB_2O_7 (trace metal basis, Sigma Aldrich). The pH was measured with a SI Analytics Lab 855 pH meter. Indium(III) protoporphyrin IX was purchased from Frontier Scientific and used without further purification.

High Performance Liquid Chromatography (Prominence HPLC, Shimadzu) was utilized for the analysis of non-volatile reaction products. The samples were placed in an auto-sampler (SIL-20A) which injects 20 μl of the sample into the column. An Aminex HPX 87-H (Bio-Rad) column with a Micro-Guard Cation H Cartridge (Bio-Rad) in front were used. The eluent was 5 mM H_2SO_4 and the eluent flow rate 0.6 ml min^{-1} . The column and the refractive index detector (RID-10A) were maintained at a temperature of 45 °C. The setup utilized for online HPLC experiments has been described before.^[3] The reported concentrations of liquid products or subsequently calculated faradaic efficiency (FE) are an average of at least two independent experiments. Additionally, the data points for each experiment were obtained by the average of three injections of the same sample. The dominant contribution of the uncertainty in concentration/FE resulted from the different experiments.

D.2 Electrolyte effect

It can be seen in Figure D.1a, that the bulk pH of the different buffer electrolytes after CO_2 saturation is as follows: $\text{pH}_{\text{borate}} < \text{pH}_{\text{phosphate}} < \text{pH}_{\text{bicarbonate}}$. The pH after CO_2 saturation for the KCl electrolytes is higher for the electrolytes with higher initial pH, as shown in Figure D.1b.

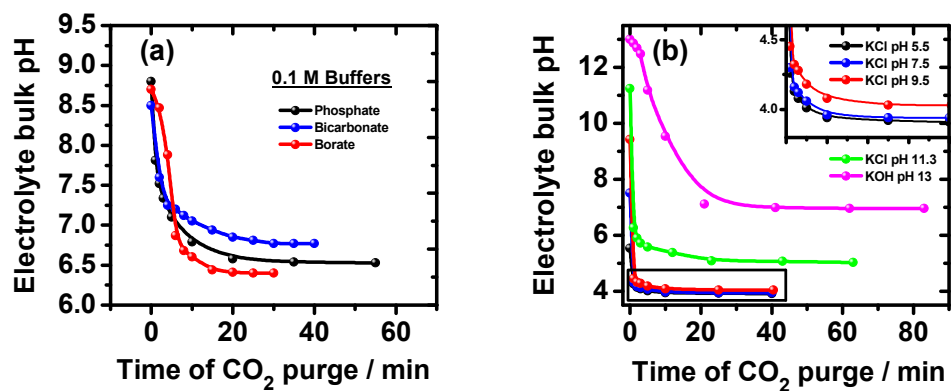


Figure D.1 (a) pH of the different buffer electrolytes as a function of CO₂ purging time and (b) pH of KCl electrolytes with different initial pH as a function of CO₂ purging time.

D.3 Buffer capacity effect

In addition to the experiments in Figure D.2, we previously performed online HPLC experiments in phosphate buffers with three different buffer capacities for CO₂RR on immobilized InPP. As shown in Figure B.10 in Appendix B, higher buffer capacity leads to higher current density throughout the whole potential range, but not necessarily to higher HCOOH formation. The increase in current density is therefore mainly the result of enhanced HER, in agreement with Figure D.2d.

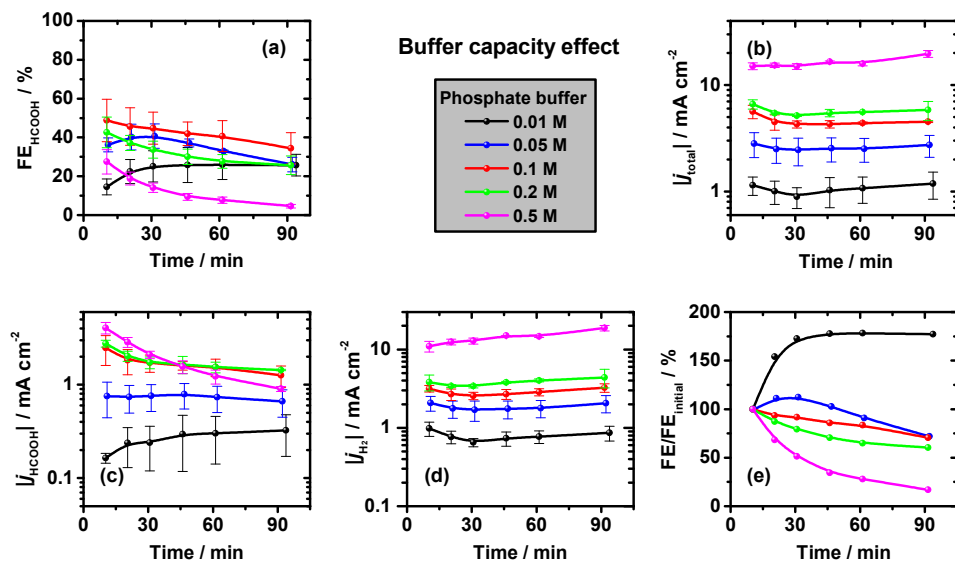


Figure D.2 (a) Faradaic efficiency toward HCOOH, (b) absolute total current density, (c) absolute partial current density for HCOOH, (d) absolute partial current density for H₂, (e) stability during CO₂ reduction on immobilized InPP on PG in phosphate buffers (initial pH $\approx$ 9.6) with different buffer capacity. Lines to guide the eye.

D.4 Effect of Ionic species

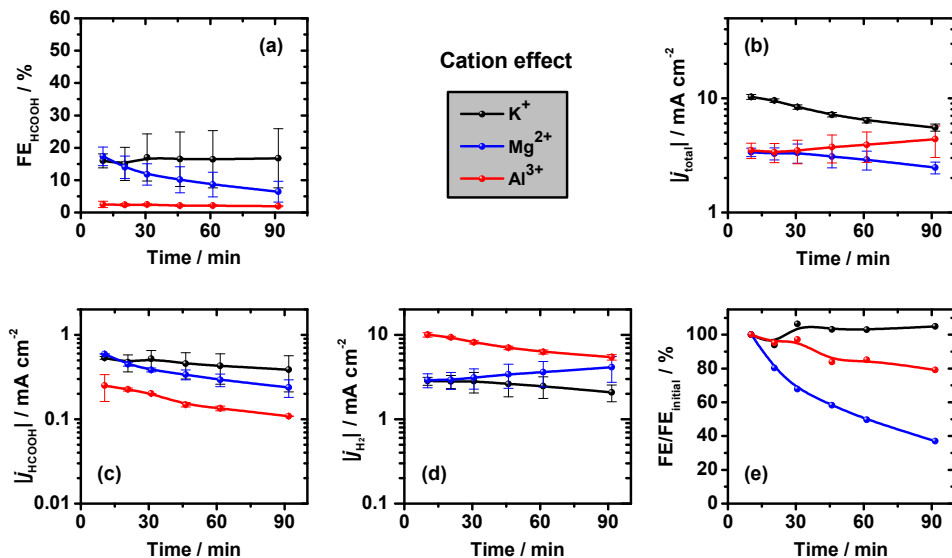


Figure D.3 (a) Faradaic efficiency toward HCOOH, (b) absolute total current density, (c) absolute partial current density for HCOOH, (d) absolute partial current density for H_2 , (e) stability during CO_2 reduction on immobilized InPP on PG in 0.001 M HClO_4 (pH $\approx$ 3) with 0.099 M K^+ , Mg^{2+} and Al^{3+} . Lines to guide the eye.

To investigate the influence of Mg^{2+} and Al^{3+} , a HClO_4 electrolyte was used. It can be seen that these cations in solution worsen the selectivity, reactivity and stability of CO_2RR . The total and partial current densities corresponding to the experiments in Figure 7.4a and Figure 7.4b are given in respectively Figures D.4 and Figure D.5.

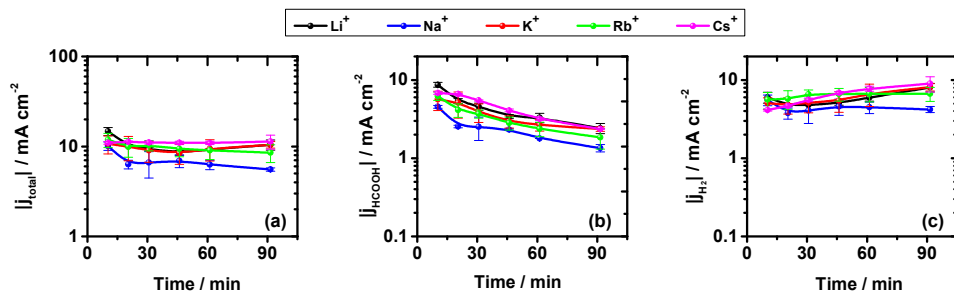


Figure D.4 (a) absolute total current density, (b) absolute partial current density for HCOOH , (c) absolute partial current density for H_2 during CO_2 reduction on immobilized InPP on PG in phosphate buffer (pH 9.6) with $25 \mu\text{M}$ alkali cations in solution. Lines to guide the eye.

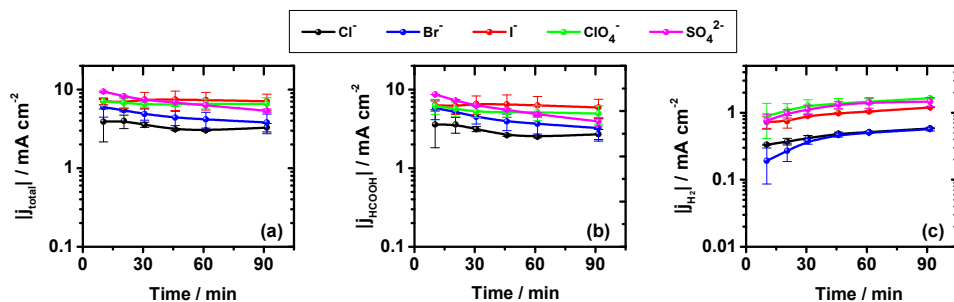


Figure D.5 (a) absolute total current density, (b) absolute partial current density for HCOOH , (c) absolute partial current density for H_2 during CO_2 reduction on immobilized InPP on PG in 0.1 M KX electrolyte brought to $\text{pH} \approx 9.6$, where X stands for different anions. Lines to guide the eye.

D.5 References

- [1] Y. Y. Birdja, J. Shen, M. T. M. Koper, *Catal. Today* **2017**, *288*, 37–47.
- [2] Y. Y. Birdja, R. E. Vos, T. A. Wezendonk, L. Jiang, F. Kapteijn, M. T. M. Koper, *ACS Catal.* **under revision**.
- [3] Y. Kwon, M. T. M. Koper, *Anal. Chem.* **2010**, *82*, 5420–5424.

