

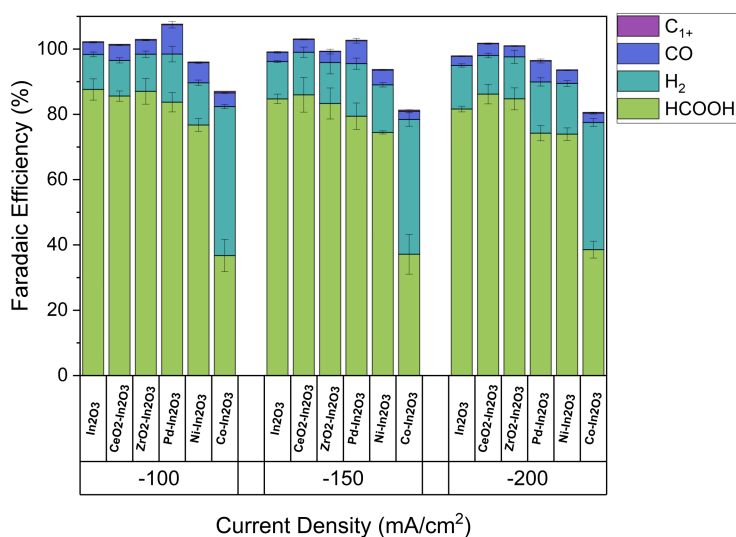
# Transition metal doped In<sub>2</sub>O<sub>3</sub> for CO<sub>2</sub> reduction to formate: How to retain the oxide phase for improved stability

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The electrocatalytic reduction of CO<sub>2</sub> to formic acid has been reported with promising faradaic efficiencies [1]. Moreover, it is one of the first reduction products of CO<sub>2</sub> and H<sub>2</sub>O having a relatively high added value per kWh among the reported products.[2] For industrial applications, several requirements should be met. For example, the current density needs to surpass at least 100 mA/cm<sup>2</sup>, [3] and the catalyst needs to be stable and active for preferable thousands of hours. [4] Several reports suggest the importance of a (mixed) oxide surface state of the catalyst for a high faradaic efficiency of CO<sub>2</sub> reduction to formic acid.[5],[6],[7] Nevertheless, these studies were performed for relatively short times (<5h) and low current densities (<5mA/cm<sup>2</sup>). These oxide phases might not be stable in the long run during the high current densities required for industrial applications.

By studying the effect of doping In<sub>2</sub>O<sub>3</sub> with transition metals and redox-active CeO<sub>2</sub> and ZrO<sub>2</sub>, we intend to gain an understanding of how to retain the high faradaic efficiencies at higher current density and reduction times. Flame Spray Pyrolysis (FSP) was used to synthesize nanoparticles. FSP offers optimal precision in nanoparticle size and incorporation of the dopants in the cubic In<sub>2</sub>O<sub>3</sub> crystal structure as was studied by TEM and XRD. We found that doping In<sub>2</sub>O<sub>3</sub> with metal oxides such as CeO<sub>2</sub> and ZrO<sub>2</sub> improves and maintains its high faradaic efficiency at larger current densities, while Ni, Pd, or Co decrease the efficiency towards formic acid alongside increased efficiency towards H<sub>2</sub> and CO. We analyze the catalyst by XPS and RAMAN spectroscopy and relate the improved efficiency to the persisted presence of the oxidic character on the catalyst of the Ce- and Zr- doped In<sub>2</sub>O<sub>3</sub>.



Chrono Potentiometry on doped In-oxide GDE's for one hour in 0.5 M KHCO<sub>3</sub>, 15 mL/min CO<sub>2</sub>, 200 mL/min electrolyte flow, at room temperature and 1 atm.

- [1] Y. Hori. (2008). *Modern Aspects of Electrochemistry*, DOI: [10.1007/978-0-387-49489-0](https://doi.org/10.1007/978-0-387-49489-0)
- [2] Na Han, Pan Ding, Le He, Youyong Li, Yanguang Li. (2019). *Adv. Energy Mater.*, 11, 1902338. DOI: [10.1002/aenm.201902338](https://doi.org/10.1002/aenm.201902338)
- [3] Jan-Bernd Vennekoetter, Robert Sengpiel, Matthias Wessling. (2019). *Chemical Engineering Journal*, 89. DOI: [10.1016/j.cej.2019.01.045](https://doi.org/10.1016/j.cej.2019.01.045)
- [4] Matthew Jouny, Wesley Luc, Feng Jiao. (2018). *Ind. Eng. Chem. Res.*, 6, 2165. DOI: [10.1021/acs.iecr.7b03514](https://doi.org/10.1021/acs.iecr.7b03514)
- [5] Abhijit Dutta, Akiyoshi Kuzume, Motiar Rahaman, Soma Vesztergom, Peter Broekmann. (2015). *ACS Catal.*, 12, 7498. DOI: [10.1021/acscatal.5b02322](https://doi.org/10.1021/acscatal.5b02322)
- [6] Maor F. Baruch, James E. Pander, James L. White, Andrew B. Bocarsly. (2015). *ACS Catal.*, 5, 3148. DOI: [10.1021/acscatal.5b00402](https://doi.org/10.1021/acscatal.5b00402)
- [7] Zachary M. Detweiler, James L. White, Steven L. Bernasek, Andrew B. Bocarsly. (2014). *Langmuir*, 25, 7593. DOI: [10.1021/la501245p](https://doi.org/10.1021/la501245p)