

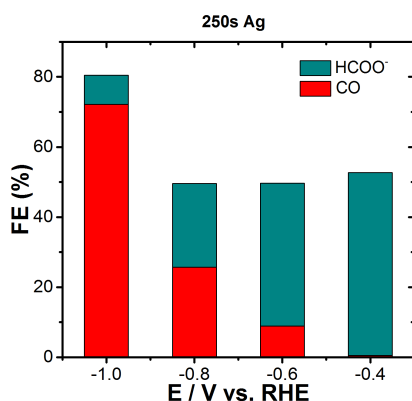
Additive assisted electrodeposition of highly faceted Ag Microcrystals: An application towards electrochemical CO₂ reduction

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Ag microcrystals were prepared via an additive-assisted electrodeposition approach. They have been applied as efficient catalysts in CO₂ reduction reaction. Differently sized Ag microcrystals were prepared through four different deposition times (50s, 100s, 250s, and 500s) on polished graphite substrate. 3,6-dithia-1,8-octanediol (OHCH₂CH₂SCH₂CH₂SCH₂CH₂OH) was used as a complexing additive during the electrodeposition process. The catalysts were physically characterized by scanning electron microscopy (SEM), energy dispersive X-Ray spectroscopy (EDAX) and X-Ray diffraction (XRD). Electrolysis was carried out in aqueous 0.5 M KHCO₃ medium and formed products were analyzed by gas chromatography (GC) and ion chromatography (IC) techniques. There is a clear switching in the product distribution from formate to carbon monoxide by going from lower to higher overpotentials. The complexing additive, adsorbed on the Ag surface, plays a crucial role for the formate formation. Different treatments (annealing, negative potential application, H₂ evolution in the acidic media etc.) were developed to chemically remove the adsorbed additive from the surface. No formate was obtained on the Ag microcrystals after application any of these treatments. Untreated Ag microcrystal with 250s deposition time gives the highest faradaic efficiency of formate at low overpotentials whereas Ag with 500s deposition time gives the highest CO efficiency at higher overpotentials.

The following faradaic efficiency plot clearly shows the switching of the CO₂ reduction product distribution from formate at lower overpotentials to CO at higher overpotentials.



[1] H. Yano, F. Shirai, M. Nakayama, K. Orura, *J. Electroanal. Chem.*, **2002**, 533, 113-118