New insights into CO₂ electro-reduction over different metal surfaces

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Introduction
While most energy and chemicals are currently obtained from fossil fuels. Concerns about oil depletion and CO₂ emissions have spurred a great deal of research into alternative processes.[1] Among them, CO₂ electro-reduction may play a key role in the replacement fossil fuels using renewable energy sources, and to mitigate CO₂ emissions.[2, 3] However, we still know very little detail about the factors that govern this thrilling process, i.e. influence of metal, electrolyte or operating conditions.

In this communication we present the design of a newly developed reactor cell that allows working under continuous flow or in batch mode. By in-situ monitoring the evolution of CO₂ in the liquid phase, and by controlling temperature, pressure of anode and cathode and voltage, combined with a thorough analysis of both liquid and gas phase, we are now able to extract very important kinetic information, crucial for the further development and understanding of this technology. The electrocatalytic reduction of CO₂ over Cu, Ag, and Sn has been studied in this new cell and will be thoroughly discussed.

Materials and Methods
Electrochemical experiments were performed in a new two compartment cell made from Poly(methyl methacrylate) (Fig 1). A proton conductive membrane (Nafion N117) was used to separate the anode and cathode compartment. An Ag/AgCl was used as a reference, Pt gauze as counter electrode and metal plates of 11 cm² as working electrodes. Electrocatalytic conversion of CO₂ was carried out at 293 K. In a typical experiment the two compartments are filled with 0.1M KH₂PO₄/K₂PO₄ and CO₂ is bubbled through until the buffer solution is saturated. CO₂ in the liquid phase is in-situ monitored, CO₂ and gas products are detected by on-line gas chromatography. Liquid phase CO₂ reduction products are analyzed off-line by UPLC.

Results and Discussion
By using the reactor depicted in Figure 1 we are able to follow the time evolution concentration of CO₂ in both gas and liquid phase and to fully quantify formation of products. In figure 2 a continuous gas flow experiment over an Ag electrode is depicted. For Ag a quasi-steady state operation is achieved after circa 5 h of operation at a voltage of -1.22 V vs. RHE, with CO and formic acid being the major reaction products.

Figure 1. The new two compartments electrocatalytic reactor.

Figure 2. CO₂ in the liquid and gas phase (left) and main CO₂ products formation (right) over time for a continuous gas flow experiment using Ag as working electrode and -1.22 V vs. RHE.

During this presentation the influence of the operation parameters on the product distribution for Cu, Ag, and Sn is discussed, both in batch and in continuous flow experiments.

Significance
Understanding CO₂ electrocatalytic reduction is of vital importance for future application of this technology. The developed reactor allows in-situ monitoring of reactants and products in both the liquid and the gas phase, opening the door to a much better understanding of this challenging process.

References