Application and challenges of CO_2 reducing gas diffusion electrodes in renewable value chains

Guenter Schmid & Team, Thomas Haas, M. Demmler, L. Reinicke, A. Hecker (Evonik Operations)

Siemens Energy Global GmbH & Co. KG, Freyeslebenstrasse 1, 91058 Erlangen, Germany
Email: guenter.schmid@siemens-energy com

Siemens Energy evaluated the application of CO2-reducing gas diffusion electrodes for almost one decade. The presentation will cover three applications, mainly differing in their maturity level (TRL) of the catalyst and the ability to scale.

1. CO_2-to-CO

Silver-based gas diffusion electrodes are able to selectively reduce CO_2-to-CO with Faradic efficiencies above 90% at a current density of 300 mA/cm² at the application relevant operation temperature of 60°C. Methane or formate formation could be suppressed below in total 1%. Endurance was proven several thousands of hours at a scaling level of 300 – 5000 cm². The inherent CO_2-cross over to the anode could be suppressed below 10% to make an application viable.

The combination of electrolysis and syngas fermentation was found to provide access to C_4-C_6 based value chains. The Kopernikus and Rheticus projects together with Evonik Operations GmbH & Co.KG focused on a sustainable synthesis of C6 oxygenates for specialty chemicals, food additives and even fuels. The technology was successfully implemented in chemical plant environment at Marl with an annual production capacity of ~15t. The scaling into the multimillion-ton annual production range depends on various boundary conditions, such as the availability of renewable energy at competitive cost, the political situation as well as its customer acceptance.

2. CO_2-to Hydrocarbons, mainly Ethylene and Ethanol

Copper-based gas diffusion electrodes might open multi-million-ton sustainable value chains by reducing CO_2 in a single step towards ethyene or ethanol in aqueous media. In the presentation paramelaconite (Cu_3O_4) derived electro catalysts consisting of mixed Cu^{+I}, Cu^{+II} will be discussed. Upon in-situ reduction the paramelaconite pure phase collapses into highly active electro catalyst species (template effect). Faradaic efficiencies of C_{2+} compounds (mainly ethylene, ethanol and acetate) at CO_2-reduction of 60 – 70% at 300 – 400 mA/cm² have been achieved, while CO-reduction achieved even around 80% at the same current density. Further insight was gained by substitution of Cu+I by Ag+I while maintaining the paramelaconite crystal structure. Surprisingly, the upon in-situ reduction collapsed catalyst with its 50% silver content produced hydrocarbons. In CO-reduction FE (C_{2+}) > 90% could be reproducibly obtained. While the initial performance seems to be sufficient for industrialization, endurance of the oxide derived copper catalysts still is the major challenge for industrialization. Electrolyte work-up is demanding to ensure continuous operation of the electrolyzer at scale.

Besides the challenges already discussed, especially sizing of the gas diffusion electrode, continuous operation and energy efficiency of the electrolyzer need to be solved to get into the MW scale and beyond.

Acknowledgement

The investigations reported in the presentation on CO2 reducing gas diffusion electrode was partly funded by the BMBF under the contract numbers Kopernikus I & II (FKZ: 03SFK2J0-2), Rheticus I & II (FKZ: 03SF0574B), eEthylene (FKZ 033RC004A) and PhasKat (FKZ 033RC028A).