The change of product selectivity in the electrochemical methanol oxidation reaction with decreasing water content in the Nafion membrane

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Abstract

The electrochemical methanol oxidation to valuable products like formaldehyde (FA) or dimethoxymethane (DMM) offers several advantages compared with the established thermal production routes such as the opportunity to use renewable energy sources and to produce hydrogen in a separated cathode compartment.
Already in 1992 Fedkiw et al.[1] presented a gas-phase electrolyzer system that selectively oxidized methanol to products like DMM, FA and methylformate at the anode. The anode consisted of a porous Pt film, which penetrated 0.5 µm deep into in a Nafion 117 membrane.[1,2] The cathode was filled with 85 wt.%H_3PO_4 to achieve high FA and DMM selectivities. In this cell methanol vapor entered the anode through a gas diffusion layer, and the products and unreacted methanol also left the anode compartment in the gas phase. At the cathode hydrogen evolution reaction occurred: $2\ H^+ + 2\ e^- \rightarrow H_2$, while the electrochemical reactions at the anode were assumed to be: (1) $CH_3OH \rightarrow CH_2O + 2\ e^- + 2\ H^+$, (2) $CH_2O + H_2O \rightarrow HCOOH + 2\ e^- + 2\ H^+$, (3) $HCOOH \rightarrow CO_2 + 2\ e^- + 2\ H^+$ and additionally the following reversible thermal side reactions at the anode were assumed: (4) $CH_3OH + HCOOH \leftrightarrow H_2O + HCOOCH_3$, (5) $2\ CH_3OH + CH_2O \leftrightarrow H_2O + CH_2(OCH_3)_2$, (6) $CH_3OH + CH_3OH \leftrightarrow H_2O + CH_3OCH_3$.
The electrolyzer design was claimed to have the advantage of having FA production with low water content and therefor low energy input for the subsequent separation of water and FA. In our work we adapted the cell design by Fedkiw et al.[1] and initially planned to increase the production rate of FA. The FA production rate and the applied current were limited for high FA selectivities, as low methanol mole fractions of 1 % in the anode gas stream had to be used.[1] Upon using the same conditions as Fedkiw et al.[1] for high FA selectivity, which included 100 °C cell temperature and a potential of 1 V vs RHE, a dilemma was identified regarding FA production with low water content. When keeping the cell temperature for many hours at 100 °C, the amount of gas-phase water leaving the anode decreased from initially around 5 % to 0.25 % after ca. 95 h of heating. This gas-phase water originated from water diffusing though the membrane and evaporating. Therefore, a decrease in the amount of gas-phase water indicated a decrease in the water content in the membrane. With the water vapor content in the anode effluent decreasing from 0.71 to 0.32 %, the product distribution towards FA decreased from 40 % to 25 %, while the product distribution towards DMM increased from 7 % to 41 %. DMM is formed from methanol and formaldehyde with water as coupled product (see anode reaction (5)) in the presence of an acid catalyst in a reversible condensation reaction. Therefore, at the desired low water content in the membrane for FA production the equilibrium is shifted towards the DMM formation rather than FA formation.
These insights can help to improve the conditions for high DMM selectivity and also show that the synthesis of water-free FA is not possible electrochemically in the used electrolyzer with a Nafion membrane.

[1] R. Liu, P. Fedkiw, *J. Electrochem. Soc.,* **1992,** *139, 3514*
[2] R. Liu, W.-H. Her, P. Fedkiw, *J. Electrochem. Soc.,* **1992,** *139, 15*
[3] R. Sun, I. Delidovich, R. Palkovits, *ACS Catal*. **2019**, *9, 1298*