Exploring tuneable ethylene production via the electrochemical oxidative coupling of methane (EOCM): a case study of doped titanates

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Ethylene (C_2H_4) is one of the most valuable compounds in the chemical industry but the current ethylene production pathway is the second-biggest CO_2-generating process in industry. In 1982, an alternative ethylene production pathway, the oxidative coupling of methane (OCM), was proposed. Unfortunately, this OCM approach suffers from significant "deep oxidation" where CH_4 is instead combusted to CO/CO_2 and H_2O.[1] To improve the C_2 selectivity and yield of OCM processes, recent works have focused on integrating OCM activity into solid oxide electrolyser systems. In this electrochemical OCM (EOCM) approach, O^{2-} ions from the cathode are transported to the anode where they oxidise CH_4 molecules to yield the desired C_2 (C_2H_4 and C_2H_6) products.[2]

In this study, we use $La_{0.3}Sr_{0.7}TiO_3$ as the anode material and catalyst for EOCM. By using combined electrochemical and gas chromatographic analyses, we demonstrate that this anode can successfully yield the desired C_2 products and can respond to changes in the O^{2-} flux. We highlight that the C_2 selectivity can be tuned using the applied potential: we show an unprecedented tuneability in the C_2 selectivity with enhancements of >3x at higher currents relative to lower currents. We rationalize these results mechanistically and demonstrate that the oxygen species active for selective OCM can be selectively produced at the anode surface. These results furnish the ability to increase both the methane conversion and C_2 selectivity and have finally broken the inverse relationship between the methane conversion and the C_2 selectivity. Additionally, we characterise the anode stability using methods such as X-ray photoelectron spectroscopy, Auger spectroscopy and energy dispersive X-ray spectroscopy. These results illustrate that the anode material is stable under the EOCM operational conditions with no phase decomposition, a notorious limitation of other EOCM anodes.[3] Our results thus demonstrate that titanate-based systems are ideal candidates for EOCM.

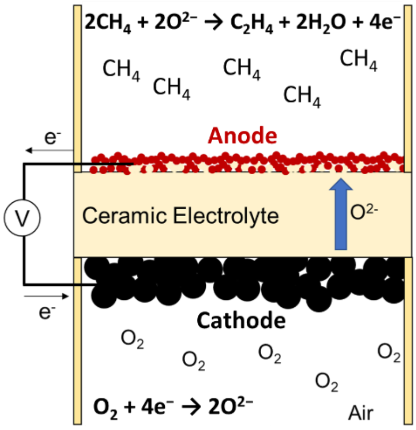

Fig. 1. Schematic representation of the EOCM reactor and the associated reactions.

[1] M.A. Barteau, Journal of Catalysis, **408**, 173 (2022)
[2] C. Zhu, S. Hou, X. Hu, J. Lu, F. Chen, K. Xie, Nature Communications, **10**, 1173 (2019)
[3] K.P. Ramaiyan, L.H. Denoyer, A. Benavidez, F.H. Garzon, Communications Chemistry, **4**, 139 (2021)