Electrochemical Production of Long Chain Hydrocarbons and Oxygenates

Boon Siang Jason Yeo[1,*]

[1.] Department of Chemistry, National University of Singapore, Singapore

*Email: chmyeos@nus.edu.sg

In this presentation, we share our works related to the development of catalysts and discovery of the mechanisms for the electroreduction of CO_2 and CO to long-chain oxygenates, such as 1-butanol and C_3-C_6 acetate esters, and long-chain hydrocarbons. In particular, we shall show how C_1-C_6 alkanes and alkenes such as *n*-hexane could be selectively formed. The catalysts that were found to work well were unexpectedly based on nickel and cobalt, rather than copper (which is generally known to reduce CO_2 to C_1-C_3 molecules).

1,3-butadiene is industrially produced as a by-product alongside ethylene from the energy-intensive thermal cracking of naphtha. We shall show that copper catalysts, after a modification with iodide anions, are efficacious for electro-converting acetylene to 1,3-butadiene at ambient temperature and pressure. 1,3-butadiene could be produced with a Faradaic efficiency of 93% at −0.85 V versus the Standard Hydrogen Electrode (SHE) and a partial current density of −75 mA cm^{-2} at −1.0 V versus SHE. The partial current density of 1,3-butadiene was at least 20 times higher than that reported in previous works. Characterisation of the catalyst using in situ spectroscopies and density functional theory calculations revealed that iodide promotes stable ensembles of neutral and partially oxidised Cu sites ($Cu^{\delta+}$–Cu^0 sites), which enhance the C-C coupling of $*C_2H_3$ intermediates to form 1,3-butadiene. We shall also showcase strategies to couple acetylene into longer-chain hydrocarbons, which could potentially be used as aviation fuel.

References

[1] W.J. Teh, E. Romeo, S.B. Xi, B. Rowley, F. Illas, F. Calle-Vallejo and B.S. Yeo. Selective electroreduction of acetylene to 1,3-butadiene on iodide-induced $Cu^{\delta+}$-Cu^0 sites. *Nature Catal.* 7, 1382, (**2024**).

[2] P. Preikschas, J. Zhang, R.R. Seemakurthi, Z. Lian, A.J. Martin, S.B. Xi, F. Krumeich, H. Ma, Y. Zhou, N. López, B.S. Yeo and J. Pérez-Ramírez. CO_2 Electroreduction to Long-Chain Hydrocarbons on Cobalt Catalysts. *Adv Energy Mater.* 14, 2401447, (**2024**).

[3] Y. Zhou, A.J. Martín, F. Dattila, S.B. Xi, N. López, J. Pérez-Ramírez, B.S. Yeo. Long-chain hydrocarbons by CO_2 electroreduction using polarized nickel catalysts. *Nature Catal.* 5, 545, (**2022**)