

Electrochemical CO₂ Reduction Catalyzed by Metal Porphyrin Complexes: Control of the Catalytic Activity by Reaction Media

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Keywords: CO₂ Reduction; Solvation Effect; Electrochemistry; Porphyrin; Catalyst

The development of artificial molecular catalysts for CO₂ reduction is the key to solving energy and environmental problems. Although chemical modification can generally improve the catalytic activity of this class of compounds, they often require complicated synthetic procedures. Here, we report the simple procedures that dramatically enhance electrochemical CO₂ reduction activity by metal porphyrin complexes focusing on the effect of the reaction medium.

We began by reinvestigating CO₂ reduction by a commercially available catalyst, iron(III) tetraphenylporphyrin chloride (**FeTPP-Cl**), in DMF. DMF is a common solvent for iron porphyrin systems, as it can dissolve both the complex and CO₂ at high concentration. **FeTPP-Cl** indeed exhibited a large irreversible current under CO₂, corresponding to the electrocatalytic reduction of CO₂ (Figure 1, red line). Unexpectedly, the intensity of the irreversible current increased when acetonitrile (MeCN) was added (Figure 1, dashed lines). Furthermore, **FeTPP-CIO₄**, a perchlorate salt of **FeTPP** that is well soluble in various solvent, exhibited the largest irreversible current in pure MeCN (Figure 1, blue line). To quantify the catalytic product, controlled potential electrolysis experiment of **FeTPP-CIO₄** (0.01 mM) was then performed in MeCN with 1.0 M TFE under CO₂ at -2.35 V vs. Fc/Fc⁺. The total amount of charge passed over a period of 60 min was 75.9 C, and CO was formed with a Faradaic efficiency of 97.3%. Subsequently, turnover frequency (TOF) for CO production was evaluated. Surprisingly, TOF reached 7.30 × 10⁶ s⁻¹, which is the highest among those of current best-in-class molecular catalysts.¹ These results clearly demonstrate that the electrocatalytic activity of **FeTPP** for CO₂ reduction is significantly enhanced in MeCN.

The effect of reaction medium on the catalytic activity was also observed for other metal porphyrin complex. In MeCN, a copper porphyrin complex bearing strong electron-withdrawing substituents, copper(II) tetrakis(pentafluorophenyl)porphyrin (**CuTPFP**), exhibited a TOF of 1.46 × 10⁶ s⁻¹ at an overpotential of 0.85 V.² Surprisingly, this value is more than 10⁶ times higher than those of other reported copper-based catalysts (TOF ≤ 1.15 s⁻¹). The details of the reaction medium on the catalytic mechanisms will be discussed in the presentation.

1) K. Kosugi *et al.*, *Angew. Chem. Int. Ed.* **2021**, *60*, 22070. 2) K. Kosugi *et al.*, *Chem. Commun. in press.*

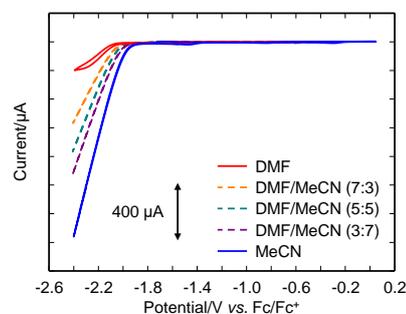


Figure 1. Cyclic voltammograms of **FeTPP** in TBAP/solvent under CO₂ with 1.0 M TFE (scan rate: 100 mV s⁻¹).