

Photo-assisted electrochemical CO₂ reduction at boron-doped diamond cathode

G. Iwai¹, A. Fiorani¹, J. Du¹ and Y. Einaga¹

¹ Department of Chemistry, Keio University, 3-14-1 Hiyoshi, Yokohama 223-8522, Japan
goki-iwai@keio.jp

1. Introduction

Electrochemical CO₂ reduction has been an attracting method for the utilization of carbon dioxide. The use of a boron-doped diamond (BDD) as a cathode has been reported for high faradic efficiency for formic acid production.⁽¹⁾ However, the oxygen evolution reaction at the anode which is coupled with the CO₂ reduction reaction requires a high overpotential, resulting in a high voltage for the total reaction. To reduce the reliance on electrical energy required for the electrochemical CO₂ reduction, we investigated a photoelectrochemical system, comprising TiO₂ nanotubes (TiO₂ NT) as a photoanode to reduce the electrical energy by using light energy instead.

2. Experimental

BDD with a boron concentration of 0.1% were prepared on Si wafer substrates by microwave plasma-assisted chemical vapor deposition. TiO₂ NT were fabricated by applying 30 V between a Ti substrate and a Pt electrode for 3 hours in an electrolyte solution containing 1M (NH₄)H₂PO₄ and 0.5 wt% NH₄F•HF. The TiO₂ NT plate was annealed at 450 °C for 1 hour. Inside a two-chamber flow cell, BDD was used as the working electrode, TiO₂ NT as the counter electrode which was irradiated with light (wavelength range: 300 to 700 nm, power: 25.2 mWcm⁻²), and Ag/AgCl as the reference electrode. The electrolysis was conducted at fixed total voltage, E_{tot} (from 1 V to 1.6 V) between the TiO₂ NT photoanode and the BDD cathode. Formic acid from CO₂ reduction was quantified by HPLC.

3. Results & Discussion

The crystalline phase of TiO₂ has been confirmed as anatase by XRD. The main product obtained by the CO₂ reduction on BDD was formic acid. The Faradaic efficiency of formic acid production is shown in Fig. 1A. As the applied voltage was increased from 1.0 V to 1.6 V, the overpotential for CO₂ reduction to CO₂^{•-} intermediate increased, therefore the Faradaic efficiency for the production of formic acid increased consequently.⁽¹⁾ At voltages above 1.3 V, the Faradaic efficiency for the production of formic acid reached a steady level of 80 ~ 88%. The system provided an overall energy conversion efficiency of nearly 1.5 to 2%. If we consider only the electrical-to-chemical conversion efficiency, neglecting the light power input, this efficiency reaches 94 % (Fig. 1B) at 1.3 V, compared to 50% reached from previous CO₂ reduction at dark electrolyser at 2.7 V, which saved a 48% of electrical energy.⁽²⁾ This energy saving is evident in the potential at TiO₂ NT for water oxidation in the range of -0.8 to -0.6 V vs Ag/AgCl, KCl sat'd compared to theoretical 0.21 V vs Ag/AgCl, KCl sat'd.⁽³⁾ However, this electrical-to-chemical conversion efficiency could be hypothetically observed only with solar radiation, because is freely available.

4. References

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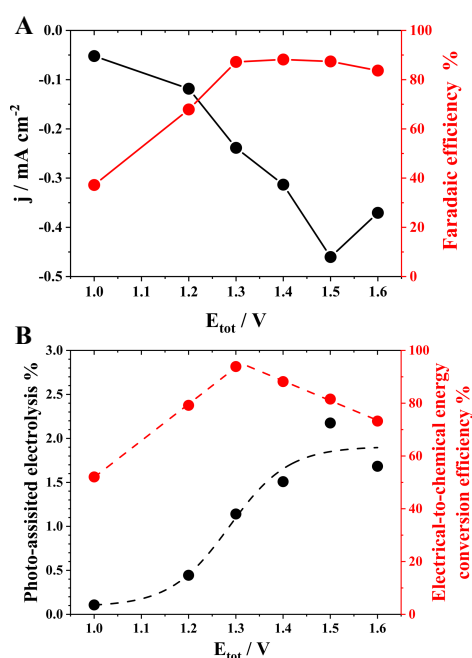


Fig. 1 A) Average current measured at the BDD cathode (black) and faradaic efficiency for the production of formic acid (red). B) Energy throughput conversion efficiency for photo-assisted electrolysis (black) and electrical-to-chemical energy conversion efficiency (red) as function of E_{tot} .