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Supplementary Information

Designing CO_2 Reduction Electrode Materials by Morphology and Interface Engineering

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Note 1. The definition of activity descriptors

1) Overpotential (η): Theoretically, an electrochemical reaction has its thermodynamic equilibrium potential (E_0), which can be calculated by the Nernst equation.[1]

To make CO_2RR going forward to the generate products, an external potential, also called applied electrode potential (E), should be applied to the working electrode, which has to be more negative than E_0 of CO_2RR. The η is defined as the difference between E and E_0 at a given current density (equation 1), which thus reflects the extra amount of energy required to overcome the energy barrier for the reaction.

$$\eta = E - E_0 \qquad (1)$$

2) Faradaic efficiency (FE): The FE describes the percentage of the charge participated in the generation of a given product over the total charge consumed. The FE can be calculated by equation (2):

$$FE = \frac{anF}{Q} \qquad (2)$$

where α is the electron transfer number, for example, α = 2 for the reduction of CO_2 to CO. n is the mole of the product generated. F is the Faraday constant (96 485 C mol^{-1}). Q is the total charge passed.

3) Current density (J): The J is the current normalized by the geometric area of the working electrode. The J is directly associated with the density of active sites and reaction kinetics, presenting the product generation rate (productivity). Because the electrode area is related to the electrolyzer size, J is an important descriptor to evaluate the system cost for practical application. The partial current density for a specific product can be calculated by total J multiplied by FE of the product.

4) Energy efficiency (EE): The EE refers to the ratio between the output energy from CO_2RR and the input energy, standing for the energy utilization efficiency toward the desired product. The EE can be calculated by equation (3):

$$EE = \frac{E_0}{E} * FE = \frac{E_0}{E_0 + \eta} * FE \tag{3}$$

It can be inferred that a high EE can be obtained by increasing FE while lowering η. Note that the anodic OER should be considered when calculating the cell EE. The E_0 can be calculated by the difference between the E_0 of anodic OER (1.23 V) and the E_0 of cathodic CO_2RR, for example, E_0 = 1.23 V – (– 0.11 V) = 1.34 V for CO generation.

5) Stability: Stability is another key factor determining the feasibility for practical application. An ideal catalyst should be designed to retain both J and FE while without the increase in η during long-term continuous operation.

Note 2. The effects of electrolyte, temperature, and pressure on CO_2RR

The role of the electrolyte is of particular interest in CO_2 reduction since the interplay between the electrode surface and electrolyte composition plays an important role in determining the outcome of CO_2RR.[2, 3] CO_2 is known to have a low solubility in aqueous solution. To overcome this drawback, adding non-aqueous organic additives in aqueous media or using organic electrolyte (acetonitrile, N, N-dimethylformamide, and ionic-liquid) have been employed to increase CO_2 concentration due to the strong interaction between N-containing groups of organic electrolytes and CO_2.[3] Moreover, the organic solvents have low proton concentrations, which could help to suppress the unwanted HER. However, it should be noted that carbon source in the final product may come from the organic electrolyte, thus the ^{13}C isotope labeling is recommended for the organic electrolyte system. On the other hand, increasing the cation size of alkali metal has been reported to be able to reduce the FEs for H_2 and C_1 product but increase C_{2+} selectivity on Cu surface due to enhanced CO_2 adsorption and local concentration of dissolved CO_2.[4] Besides cations, anions also have significant effects on the outcome of CO_2RR. Varela et al.[5] studied the effect of halide anions on CO_2 reduction and found that adding Cl^- and Br^- in $KHCO_3$ electrolyte can increase CO selectivity while incorporating I^- lead to the enhanced CH_4 formation. The observed changes in selectivity were attributed to the adsorption of the anions on the catalytic surface that changes the charge density and stabilizes positively charged catalysts species.[5] Future research on developing multiscale modeling is also highly required to understand the ion distribution across the electrode interface and its effects on CO_2 reduction.

The temperature of CO_2RR electrolyzer influences CO_2RR because many parameters, including the concentration of dissolved CO_2, pH, solution resistance, viscosity, and diffusion rate of CO_2 and intermediates, are highly temperature-dependent.[6] Mizuno et al. investigated the temperature effects on indium, tin, and lead electrodes for HCOOH formation in the range of 20-100 °C.[7] They found that indium electrode can achieve about 100% FE at 20-60 °C, while the FE decreases to 44.5% at 100° C. For tin and lead, they performed the best at 20 °C and 60 °C, respectively. Ahn et al.[8] studied the effects of electrolyte temperature on polycrystalline copper. It was found that 2 °C is the optimal condition for converting CO_2 to CH_4 with an FE of 50% while FE of C_2H_4 decreases to 10%. Above room temperature, the production of H_2 dominates the reaction (>50% FE) because of the decrease in CO_2 concentration. Note that the effects of temperature on CO_2RR vary among catalysts, extensive works are still needed to explore influences of reaction temperature on newly developed catalysts.

The partial pressure in electrolyzer considerably affects CO_2 concentration and rate of CO_2 mass transport to the electrode surface because CO_2 solubility in aqueous electrolytes typically shows a linear increase with pressure according to Henry's law.[6, 9] A large number of studies reporting the effects of pressure on product selectivity and reaction rate of CO_2RR have been done. Hara et al.[10] found that there is no change in product distribution on Ag for CO generation and Sn for HCOOH production under a higher pressure but results in the enhanced FEs and current density. Over Cu catalysts, they reported a shift from hydrocarbon production at 1 atm to CO and HCOOH at 30 atm. Generally, high pressure is considered to be beneficial for CO_2 reduction due to enhanced CO_2 concentration, however, it will change the product distribution and increase the complexity and cost of the electrolyzer. Besides, arising pressure also requires balancing the pressure in the anode and cathode chambers to prevent damage to the separator.[6]

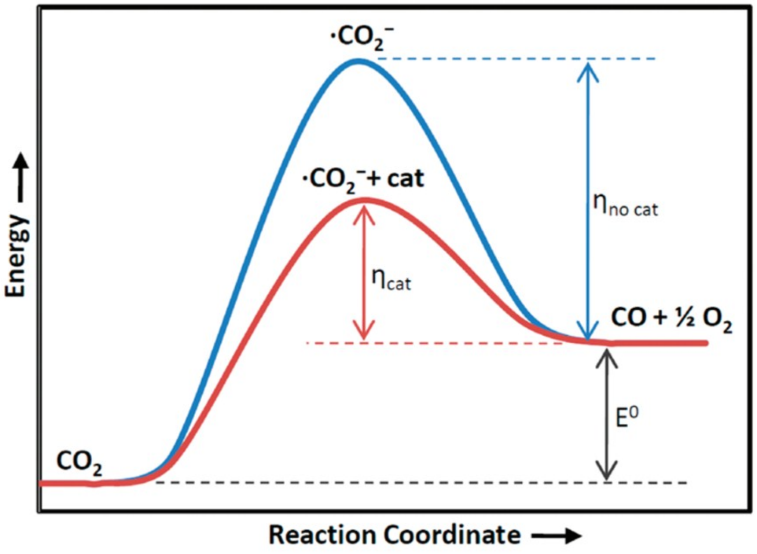

Figure S1. A qualitative reaction scheme for the reduction of CO_2 to CO. Catalysts and electrolytes acting as cocatalysts can lower the energy for the formation of $*CO_2^{\bullet-}$ intermediate. Adapted with permission from Ref. [11]. Copyright 2010 American Chemical Society.

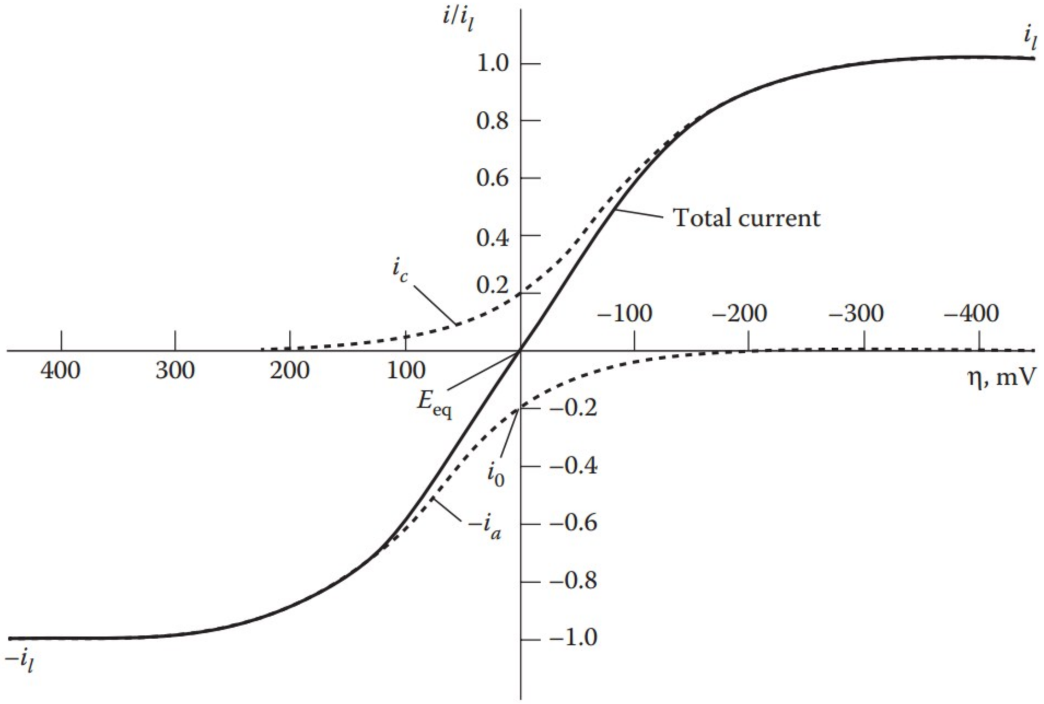

Figure S2. Current-overpotential curves for the system with a transfer coefficient of 0.5. The dashed lines show the component of i_c and i_a. Adapted with permission from Ref.[12]. Copyright 2001 Wiley.

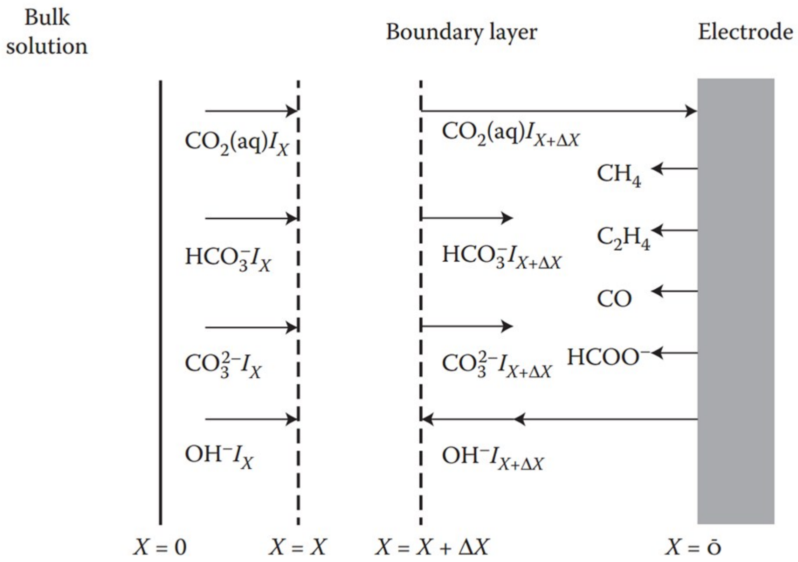

Figure S3. Mass transfer across the electrode-electrolyte boundary layer. Adapted with permission from Ref.[13]. Copyright 2006 Springer.

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