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# *Supplementary Information*

# Kinetics for CO2 Electrolysis on Composite Electrode Consisting of Cu and Samaria Doped Ceria

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## Butler-Volmer Equation for $CO_2$ Electrolysis

The electrolytic reaction on the electrode is show as

$$CO_{2(g)} + V_O^{\bullet\bullet} + 2e' \leftrightarrow CO_{(g)} + O_O^{\times} \quad (1)$$

Based on the report in the literature[1], elementary reaction processes are proposed for $CO_2$ electrolysis on Cu-SDC electrode as shown in Table 1.

Table 1 Elementary steps for the $CO_2$ electrolysis reaction at the three phase boundary (TPB) of Cu-SDC composite cathodes.

| Step code | Elementary process |
|---|---|
| (1) $CO_2$ adsorption | $CO_{2(g)} \leftrightarrow CO_{2(TPB)}$ |
| (2) Charge transfer | $CO_{2(TPB)} + O^{\times}_{O(TPB)} + e^- \leftrightarrow (CO_3)_{O(TPB)}$ |
| (3) Charge transfer | $(CO_3)_{O(TPB)} + V^{\bullet\bullet}_{O(TPB)} + e^- \leftrightarrow CO_{(TPB)} + 2O^{\times}_{O(TPB)}$ |
| (4) Desorption | $CO_{(TPB)} \leftrightarrow CO_{(g)}$ |

The derivation of the Butler-Volmer (B-V) equation for the kinetics of reaction (1) comes from the literature reports for the multielectron reaction process[2]. If the elementary step (2) is the rate limiting step, regardless of the mass-transfer effects, B-V equation derived from the elementary step is shown as

$$j = j_0 \left\{ \exp\left[ -\frac{\alpha_1 F\eta}{RT} \right] - \exp\left[ \frac{(2-\alpha_1)F\eta}{RT} \right] \right\} \quad (2)$$

where $\alpha_1$ is the charge transfer coefficient ($0 < \alpha_1 < 1$), $j_0$ the exchange current density, $j$ the net current density, $\eta$ the overpotential, $T$ the temperature, $R$ the gas constant (8.314 J mol$^{-1}$ K$^{-1}$) and $F$ the Faraday constant (96485 A s mol$^{-1}$). If the elementary step (3) is the rate limiting process, B-V equation is

$$j = j_0 \left\{ \exp\left[ -\frac{(1+\alpha_2)F\eta}{RT} \right] - \exp\left[ \frac{(1-\alpha_2)F\eta}{RT} \right] \right\} \quad (3)$$

where $\alpha_2$ is the charge transfer coefficient ($0 < \alpha_2 < 1$). Comparing eqn (2) and (3), it can be seen that the charge transfer coefficient of the forward current term of the B–V equation of the $CO_2$ electrolysis reaction is different due to different rate determining step, *i.e.* the former is less than 1, and the latter greater than 1.

Eqn (4) can be used to represent either Eqn (2) or Eqn (3), shown as

$$j = j_0 \left\{ \exp\left[ -\frac{\alpha F\eta}{RT} \right] - \exp\left[ \frac{(2-\alpha)F\eta}{RT} \right] \right\} \quad (4)$$

where $\alpha$ is the transfer coefficient ($0 < \alpha < 2$). The value of the charge transfer coefficient derived from experiment data can be used to determine which, step (2) or (3) in Table 1, is rate-determining step.

## References


1. M. Zheng, S. Wang, M. Li and C. Xia, *Journal of Power Sources*, 2017, **345**, 165-175.
2. A. J. Bard, L. R. Faulkner, J. Leddy and C. G. Zoski, *Electrochemical methods: fundamentals and applications*, wiley New York, 1980.