

Supplementary Information

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

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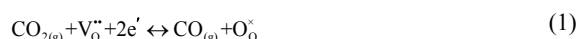
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Butler-Volmer Equation for CO₂ Electrolysis

The electrolytic reaction on the electrode is show as



Based on the report in the literature¹, elementary reaction processes are proposed for CO₂ electrolysis on Cu-SDC electrode as shown in Table 1.

Table 1 Elementary steps for the CO₂ electrolysis reaction at the three phase boundary (TPB) of Cu-SDC composite cathodes.

Step code	Elementary process
(1) CO ₂ adsorption	$\text{CO}_{2(g)} \leftrightarrow \text{CO}_{2(TPB)}$
(2) Charge transfer	$\text{CO}_{2(TPB)} + \text{O}_{0(TPB)}^* + \text{e}^- \leftrightarrow (\text{CO}_3)_{0(TPB)}$
(3) Charge transfer	$(\text{CO}_3)_{0(TPB)} + \text{V}_{0(TPB)}^{**} + \text{e}^- \leftrightarrow \text{CO}_{(TPB)} + 2\text{O}_{0(TPB)}^*$
(4) Desorption	$\text{CO}_{(TPB)} \leftrightarrow \text{CO}_{(g)}$

The derivation of the Butler-Volmer (B-V) equation for the kinetics of reaction (1) comes from the literature reports for the multielectron reaction process². 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 α_1 is the charge transfer coefficient ($0 < \alpha_1 < 1$), j_0 the exchange current density, j the net current density, η 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 α_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 CO₂ 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 α 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.