Study on Elementary Charge Transfer Reactions in SOCs

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Abstract:

Charge transfer reaction is generally present as the rate-determining step in solid oxide cells (SOCs). It is known that, under extremely low current density, reaction rate is inversely proportional to the corresponded polarization resistance R_p.[1] The R_p values can be obtained though the deconvolution of impedance spectra based on the distribution function of relaxation times and the extended equivalent circuit model.[2] Here we study the dependence of the reaction rate on partial pressure of reactant and product and the electrode reaction mechanisms.

The first example is about the electroreduction of CO_2 to CO on manganese doped ceria in an electrolysis cell. The R_p values are deconvoluted from the impedance spectra measured on the cell under open circuit conditions. We find that the electroreduction of CO_2 to CO passes through two elementary charge transfer reactions. The first one is associated with $(CO_3)_{O,S}^{\cdot\cdot}$ to $(CO_3)_{O,S}^{\cdot}$ and has an activation energy of 178.7 kJ mol^{-1} and a pressure dependence of $P_{CO_2}^{0.76} P_{CO}^{0.24}$. The second one, associated with $(CO_3)_{O,S}^{\cdot}$ to CO, is the rate determining step for CO_2 electroreduction and has an activation energy of 100.6 kJ mol^{-1} and a pressure dependence of $P_{CO_2}^{0.27} P_{CO}^{0.73}$.

Another example is about oxygen reduction reaction on $Gd_{0.1}Ce_{0.9}O_{2-\delta}$ (GDC) films with preferential orientation of [100] and [111] in a solid oxide fuel cell. The R_p values are deconvoluted from the impedance spectra measured under both open circuit conditions and negative DC bias. On GDC (100), the reaction rate of the rate-determining step exhibits oxygen pressure dependent exponent of 0.439 under OCV conditions and 0.379 under 0.15 V negative bias, whereas on GDC (111), reaction rate of the rate-determining step exhibits oxygen pressure dependent exponent of 0.397 under open circuit conditions and 0.177 under 0.15 V negative bias. Different oxygen reduction reaction mechanisms are proposed.

Key words: Solid oxide cells, charge transfer reaction, reaction kinetics, electrode reaction mechanism

References

[1] K.J. Vetter, Electrochemical Kinetics (Academic Press, New York, 1967) p. 339.
[2] H. Schichlein, E. Ivers-Tiffée, et. al., J. Appl. Electrochem., 32(2002)875–882.