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Study on the effect of platinum micro- and mesoporous structures on the electrocatalytic reaction kinetics

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Electrocatalytic reactions are essential to effectively utilize electrical energy from renewables by converting it into chemical energy and vice versa. Fuel cells employ electrocatalytic reactions and represent themselves as a promising energy conversion device. However, their widespread use is impeded by the high overpotentials of their electrode reactions, such as oxygen reduction and alcohol oxidation reactions. Reducing the overpotentials currently relies on high-cost platinum-based electrocatalysts. Previous studies have attempted to decrease platinum electrocatalyst loading by increasing their surface area and specific activity. In the meantime, little attention has been paid to the specific activity modification of platinum porous electrocatalysts due to the difficulty of the structural control. It would be possible to further reduce the novel metal usage if the specific activity can be enhanced in porous electrocatalysts. Therefore, this study aims to elucidate the effect of platinum micro- and mesopores on the reaction kinetics. The analysis was aided by employing platinum porous electrodes containing one-dimensional pores with regulated diameters of 1.3, 1.8, and 3.0 nm, and varied lengths. The kinetics of the oxygen reduction and alcohol (methanol, ethanol, and ethylene glycol) oxidation reactions are correlated with the structures of the porous and planar electrodes, and the origin of the resultant kinetic change is discussed. The doctoral dissertation comprises the following five chapters.

Chapter 1 is the introduction, including fundamental descriptions of fuel cells and the oxygen reduction and alcohol oxidation reactions. The emphasis is placed on strategies to reduce their reaction overpotentials by modifying the interfacial structure between electrocatalysts and electrolytes. This section also describes the previously reported effect of nanoporous structures on their surface catalytic sites, related electronic structures, and electrolyte states.

Chapter 2 describes experimental procedures, such as fabricating the porous electrodes using surfactant templates coupled with electrodeposition. It also describes the characterization methods for electrocatalytic measurement, structural analysis, and electronic structure analysis of the electrodes. In addition, it includes a numerical simulation method for calculating the oxygen concentration profiles in the nanopores.

Chapter 3 describes the results and discussions for the oxygen reduction activity. Firstly, the effect of the pore length was investigated. A longer pore length increased the apparent current due to its enhanced electrochemical surface area. However, a longer pore increases the mass transport resistance and decreases the utilization ratio of Pt surface atoms. Then, the pore length was reduced to mitigate the mass transport resistance, and the reaction kinetics of the porous electrodes with different pore diameters were evaluated in 0.1 mol dm⁻³ KOH and HClO₄ solutions. The kinetic enhancement for the porous electrodes relative to the planar electrode in the acidic medium is more significant than that in the alkaline medium. This is because the porous electrodes likely possess concave stepped sites, which show high oxygen reduction kinetics in the acidic medium. Moreover, the oxygen reduction kinetics follow a volcano relationship with a kinetic maximum at a pore diameter of 1.8 nm in both solutions. The catalytic trend is ascribed to the d-band center downshift caused by the compressive strain along with a decrease in the pore size. The d-band center downshift lowers the bond strength between the platinum surface and the reaction species. When the nanopore is introduced, the adsorption of reaction inhibitors, *i.e.*, *OH, is less likely to occur, thus enhancing the kinetics. However, the adsorption of the reactants is not favorable when the pore size is too small, which lowers the kinetics. Furthermore, the effect of alkali metal cations on the oxygen reduction kinetics was investigated in 0.1 mol dm⁻³ MOH (M = Li, Na, K, Cs) solutions. While the oxygen reduction kinetics show volcano relationships in K⁺- and Cs⁺-containing solutions, clear kinetic trends are not obtained in Na⁺- and Li⁺-containing solutions due to the strong modification of adsorption energy by the hydrated cations at the catalytic interface.

Chapter 4 describes the results and discussions for the alcohol oxidation activity in 1 mol dm⁻³ alcohol-containing 1 mol dm⁻³ KOH. The apparent reaction currents increased for the porous electrodes in comparison to the planar electrode due to their enhanced electrochemical surface area. In methanol oxidation reactions, the reaction kinetics decreased with a decrease in the pore size. This is consistent with the d-band center downshift, which is unfavorable for the dehydrogenation reaction. The porous electrodes exhibited more tolerance toward surface poisoning due to the faster oxidation kinetics of carbon monoxide. In ethanol and ethylene glycol oxidation reactions, the kinetics and stabilities were enhanced with the porous model electrodes compared to the planar surface. However, the kinetics decreased when the pore size was too small. These origins were correlated with the change in the adsorption energy of the reaction species caused by the nanoporous structure.

Chapter 5 describes the conclusions and outlook. The above results show that the porous electrodes with specific pore sizes enhance the kinetics for the oxygen reduction and alcohol oxidation reactions. The increase in the stability against poisoning was also observed for the latter. These findings emphasize the importance of tuning the electrocatalyst porous structure not only to obtain high surface area but also to enhance the electrocatalytic activity and stability. Furthermore, since the electronic structure dictates the kinetics of other electrocatalytic reactions, such as oxygen evolution, hydrogen evolution/oxidation, CO₂ reduction, and nitrogen reduction reactions, tuning pore structure is a promising approach for improving the kinetics of various electrocatalytic reactions.