

45d The Behavior of Porous Rotating Disk Electrodes

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An experimental and theoretical study combining the attributes of porous electrodes and the rotating disk arrangement is presented. The porous rotating disk electrode (PRDE) offers several potential benefits over the classic rotating disk electrode (RDE) as an analytical electrochemistry tool. The high specific surface area of the porous disk increases the current density and the sensitivity of the PRDE compared to the RDE. Because the porous disk can be formed from materials used in industrial electrochemical processes, a PRDE provides a means for their rapid evaluation and quantitative determination of reaction rates and mass-transfer rates. In many circumstances agents are bound to the porous medium to catalyze or promote electrochemical reactions, and the PRDE would be a convenient tool for evaluation of the agents and binding methods.

Measurements of the current as function of rotation rate for a PRDE exhibit a much richer behavior than the flat RDE. At low rotation rates, the measured current is similar to that for a flat disk. However, at a critical rotation rate, which depends on the radius, thickness and porosity of the porous disk, the current increases at a greater rate, but still scaling with the square root of the rotation rate. At a larger, upper critical rotation rate, the current approaches saturation with a current density more than 20 times greater than that for a flat electrode. Based on simulations the critical rotation rates are shown to correspond to variations in the flux and penetration of fluid into the porous rotating disk. The behavior of the current is explained in terms of the ratio of the residence time in the reacting porous media and the reaction time. At low rotation rates the flow rate is low and hence the residence time is long compared to the reaction time; the reactant is primarily consumed near the surface of the PRDE, and so it appears similar to a RDE. At very high rotation rates, the flow rate is high and residence time in the porous disk is short compared to the residence time, and the reactant concentration and current density is maximized. From these results we develop practical models to use a PRDE as a tool to measure kinetics and mass-transfer rates and evaluate catalysts bound to the surface of porous media for electrochemical reactions.