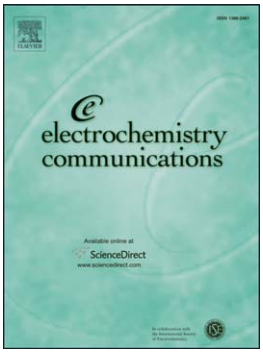

Surface spectators and their role in relationships between activity and selectivity of the oxygen reduction reaction in acid environments

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Surface spectators and their role in relationships between activity and selectivity of the oxygen reduction reaction in acid environments

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Abstract

We use the rotating ring disk (RRDE) method to study activity-selectivity relationships for the oxygen reduction reaction (ORR) on Pt(111) modified by various surface coverages of adsorbed CN_{ad} (Θ_{CNad}). The results demonstrate that small variations in Θ_{CNad} have dramatic effect on the ORR activity and peroxide production, resulting in "volcano-like" dependence with an optimal surface coverage of Θ_{CNad} = 0.3 ML. These relationships can be simply explained by balancing electronic and ensemble effects of co-adsorbed CN_{ad} and adsorbed spectator species from the supporting electrolytes, without the need for intermediate adsorption energy arguments. Although this study has focused on the Pt(111)-CN_{ad}/H_2SO_4 interface, the results and insight gained here are invaluable for controlling another dimension in the properties of electrochemical interfaces.

1. Introduction

The oxygen reduction reaction (ORR), the cathodic half-cell reaction in fuel cells [1,2], is one class of electrocatalytic reaction exhibiting strong relationships between interfacial properties and reactivity, due its multi-electron reaction nature that includes a number of elementary steps involving different reaction intermediates (e.g., O_2*, H_2O_2*, and OH*)[3–5]. From studying the ORR on well-characterized metal single crystal surfaces it was found that the reaction kinetics varies with the crystal face differently according to the electrolyte used [6], strongly suggesting that structure sensitivity arises mainly from the geometry dependent