

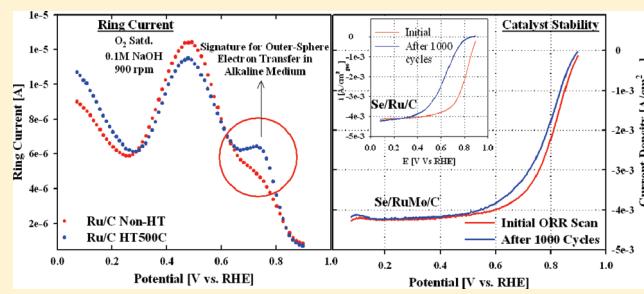
# Electrochemical Kinetics and X-ray Absorption Spectroscopic Investigations of Oxygen Reduction on Chalcogen-Modified Ruthenium Catalysts in Alkaline Media

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**ABSTRACT:** The oxygen reduction reaction (ORR) in alkaline media has been investigated on chalcogen-modified ruthenium nanoparticles (Ru/C, Se/Ru/C, Se/RuMo/C, S/Ru/C, S/RuMo/C) synthesized in-house via aqueous routes. In acidic medium, it is well known that modification by a chalcogen prevents the oxidation of the underlying transition-metal (Ru) surface, thereby promoting direct molecular O<sub>2</sub> adsorption on the Ru metal. On an unmodified Ru catalyst in alkaline media, the surface oxides on Ru mediate the 2e<sup>-</sup> reduction of molecular O<sub>2</sub> to a stable peroxide anion (HO<sub>2</sub><sup>-</sup>) intermediate via an outer-sphere electron-transfer mechanism.

This increases the activity of HO<sub>2</sub><sup>-</sup> near the electrode surface and decreases the overpotential for ORR by effectively carrying out the reduction of HO<sub>2</sub><sup>-</sup> to OH<sup>-</sup> at the oxide-free ruthenium metal site. An increase in ORR activity of Ru is observed by modification with a chalcogen; however, the increase is not as significant as observed in acidic media. Ternary additives, such as Mo, were found to significantly improve the stability of the chalcogen-modified catalysts. Detailed investigations of the ORR activity of this class of catalyst have been carried out in alkaline media along with comparisons to acidic media wherever necessary. A combination of electrochemical and X-ray absorption spectroscopic (EXAFS, XANES,  $\Delta\mu$ ) studies has been performed in order to understand the structure/property relationships of these catalysts within the context of ORR in alkaline electrolytes.



## 1. INTRODUCTION

Development of non-noble metal electrocatalysts and reduction in overpotential and loading on the existing class of Pt-based materials for the oxygen reduction reaction (ORR) have both significant fundamental and technological implications. Acidic electrolyte-based fuel cells narrow down the choice of catalyst materials due to stringent requirements based on the "acid-stability" criterion. On the other hand, alkaline electrolyte-based fuel cells provide the much required window of opportunity to develop non-noble metal-based catalyst materials. Alkaline fuel cells (AFCs), once a very promising renewable energy source, failed to attract continued research interest primarily due to issues, such as the effect of carbonate precipitation and electrolyte leakage.<sup>1</sup> Fortunately, the recent research efforts in developing alkaline anion-exchange membranes (AAEMs) for hydroxide anion conductivity brings promise to this technology of AFCs.<sup>2,3</sup>

The ORR pathway on Pt-based catalysts in both acid and alkaline media is understood to be similar based on extensive electrochemical kinetic studies on polycrystalline and single-crystal electrodes.<sup>3,4</sup> The first electron-transfer step to the adsorbed molecular O<sub>2</sub> is widely agreed to be the rate-determining step in the overall 4e<sup>-</sup> multistep process,<sup>4,5</sup> although Yeager et al<sup>6</sup> suggested that the initial molecular adsorption of oxygen as the rate-determining step. Parallel routes consisting of predominantly the 4e<sup>-</sup> transfer via either a "direct" or a "series" pathway and a minor 2e<sup>-</sup> pathway leading to peroxide is

typically observed based on rotating ring-disk electrode (RRDE) studies. We recently showed that, on metal surfaces, such as Pt, contrary to acidic media, certain important changes in the ORR mechanism and double-layer structure take place in alkaline media.<sup>7</sup> These mechanistic changes involve the possibility of outer-sphere electron transfer at oxide-covered metal sites at the higher pH. O<sub>2</sub> reduction by one-electron transfer to superoxide (O<sub>2</sub><sup>•-</sup>) is observed at  $E^\circ = -0.3 \pm 0.03$  V vs SHE, corresponding to  $\Delta G^\circ = 3.0 \pm 2$  kJ mol<sup>-1</sup> with both O<sub>2</sub> and O<sub>2</sub><sup>•-</sup> remaining in the aqueous phase.<sup>8,9</sup> Given the pH independence of this redox couple (O<sub>2</sub>/O<sub>2</sub><sup>•-</sup>), the potential of this reaction does not change as the pH is varied from 0 to 14.<sup>10</sup> However, due to the occurrence of four proton-transfer steps in oxygen reduction, its standard reduction potential changes by 0.828 V from 1.229 to 0.401 V vs SHE as the pH value changes from 0 to 14. This causes the overpotential for the first electron-transfer step (O<sub>2</sub>/O<sub>2</sub><sup>•-</sup>) to decrease from 1.53 V at pH = 0 to 0.7 V at pH = 14, indicating a sharp decrease at alkaline pH conditions.<sup>10</sup> We showed recently<sup>7</sup> that, in alkaline media, the specifically adsorbed hydroxyl species (OH<sub>ads</sub>) on the catalyst surface mediates an outer-sphere electron transfer to solvated molecular O<sub>2</sub> species to form a superoxide radical anion. This superoxide

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