

Review Article

Fundamental Mechanistic Understanding of Electrocatalysis of Oxygen Reduction on Pt and Non-Pt Surfaces: Acid versus Alkaline Media

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Complex electrochemical reactions such as Oxygen Reduction Reaction (ORR) involving multi-electron transfer is an electrocatalytic inner-sphere electron transfer process that exhibit strong dependence on the nature of the electrode surface. This criterion (along with required stability in acidic electrolytes) has largely limited ORR catalysts to the platinum-based surfaces. New evidence in alkaline media, discussed here, throws light on the involvement of surface-independent outer-sphere electron transfer component in the overall electrocatalytic process. This surface non-specificity gives rise to the possibility of using a wide-range of non-noble metal surfaces as electrode materials for ORR in alkaline media. However, this outer-sphere process predominantly leads only to peroxide intermediate as the final product. The importance of promoting the electrocatalytic inner-sphere electron transfer by facilitation of direct adsorption of molecular oxygen on the active site is emphasized by using pyrolyzed metal porphyrins as electrocatalysts. A comparison of ORR reaction mechanisms between acidic and alkaline conditions is elucidated here. The primary advantage of performing ORR in alkaline media is found to be the enhanced activation of the peroxide intermediate on the active site that enables the complete four-electron transfer. ORR reaction schemes involving both outer- and inner-sphere electron transfer mechanisms are proposed.

1. Introduction

Oxygen reduction reaction (ORR) on noble and nonnoble metal surfaces remains as one of the well-investigated electrochemical processes. While under acidic conditions Pt-based systems remain the mainstay as catalyst materials for ORR, in alkaline electrolyte a wide range of nonnoble metals and their oxides are stable enough for practical applications [1, 2]. *ORR pathway rather than ORR mechanism* has typically been addressed in the literature due to the easy accessibility of the former from rotating ring-disk electrode (RRDE) studies, and the complexity in understanding the latter [3]. ORR pathway is found to be similar in both acid and alkaline media on Pt-based materials [3, 4]. Based on the initial propositions by Damjanovic et al. [4–6], rate determining step (*rds*) on Pt electrodes is widely agreed to

be the first electron transfer step to the adsorbed molecular O₂ with or without rapid proton transfer [4–6]. A major alternative viewpoint to *rds* in ORR was proposed by Yeager et al. [7], wherein it was proposed that ORR on Pt surfaces is likely to involve dissociative chemisorption of molecular O₂ with the initial adsorption of O₂ (with or without an electron transfer) as the *rds*. ORR on Pt-based catalysts is understood to proceed via “parallel” routes with the 4e⁻ “direct” or “series” pathway as the predominant route and a minor route involving 2e⁻ pathway to peroxide. Various kinetic models for ORR have been developed to understand the reaction pathways. The first model was developed by Damjanovic et al. [8] following which Wroblowa et al. [9], and Anastasijević et al. [10, 11], proposed extensive models.

For electrocatalytic reactions proceeding via inner-sphere electron transfer mechanism, it is typically assumed that