

## Analyses of Kinetic Models for Oxygen Reduction Reaction

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There has been a revival of interest in oxygen reduction reaction of Platinum, in particular regarding the development of kinetic models accounting for multiple elementary reaction steps [1-3]. Wang's multi step double trap mechanism [1] is used as a basis to highlight the importance of developing a consistent framework for describing oxygen reduction in liquid electrolytes. A robust/universal model should be able to reproduce at least the following three experimental characteristics, namely,

1. The oxide coverage in the presence and absence of oxygen
2. Logarithmic growth of oxide during cyclic voltammetry [3,4]
3. Logarithmic growth of oxide during potential step, e.g. experiments wherein mass change is monitored by EQCM [2]

This work examines the ability of some of the existing ORR models in capturing the aforementioned characteristics.

The existing multi-step models of Wang *et al.* [1] and Jinnouchi *et al.* [3] predict that the oxide coverage depends on oxygen concentration. On the other hand, a recent EQCM study [4] and some of recent x-ray absorption measurements indicate that the oxide coverage on platinum is independent of presence or absence of oxygen and solely dependent on water oxidation kinetics.

A characteristic feature of the CV in oxygen-free environment is the presence of a plateau in the anodic sweep. Figure 1 shows that the predicted CV response using Wang's double trap model [1]. It can be seen from the figure that the well established 'plateau' response during the anodic sweep above 0.9 V is missing.

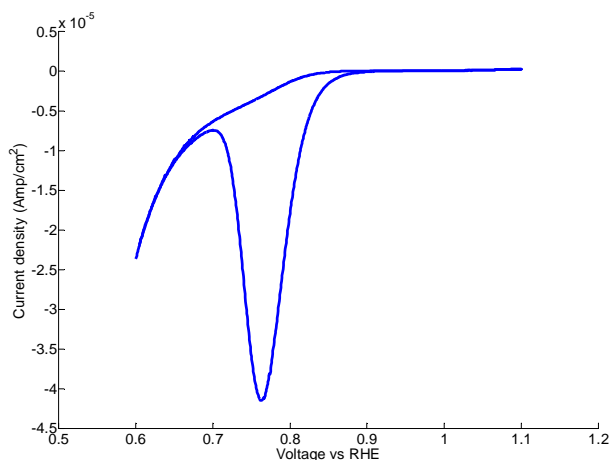


Figure 1: Simulated CV using Wang's double trap model [1]

The plateau is associated with oxide growth from water oxidation. The growth kinetics of these oxide species has been found to be logarithmic in time [5,6]. The mechanism of water oxidation is also found to include a place exchange mechanism, where the oxide and platinum

flip lattice positions to form sub surface oxides [5,6,7]. Similar logarithmic growth of oxide from water oxidation is also found in potential step experiments [4]. Water oxidation reaction is a subset of Wang's double trap kinetics but it does not incorporate the logarithmic growth factor in the model. Similarly, Rai *et al.* [6] proposed a mean field model of water oxidation without considering the log growth factor.

The direct log growth model of Harrington and Heyd [5] adapted by Darling and Meyers [8] captures the essence of CV response as shown in figure 2. But the model is inadequate for predicting ORR rates.

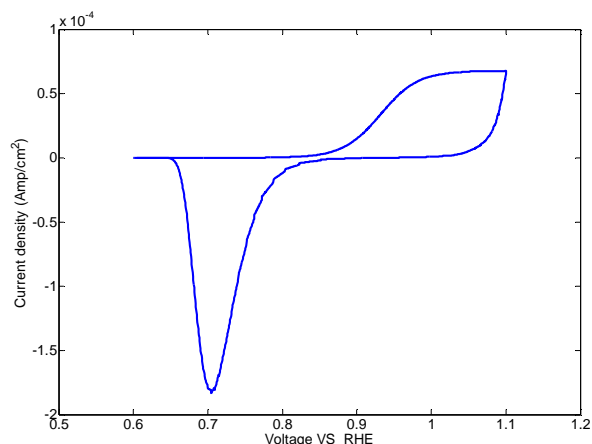


Figure 2: Simulated CV using Darling and Meyers [8] log growth model

In this work, we analyze and present these issues in detail. A comprehensive multi-step mechanism must have the capability within its framework to predict ORR rates as well as experimentally observed oxide coverage, CV and EQCM data.

## References

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