



# Hydrogen Permeation as a Tool for Quantitative Characterization of Oxygen Reduction Kinetics at Buried Metal-Coating Interfaces



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## ABSTRACT

The electrochemical stability of the buried metal-organic coating interface of painted metal is crucially governed by how effectively the oxygen reduction reaction at the interface is inhibited. As this interface is not directly accessible for study by conventional electrochemical techniques, a new non-destructive method has been developed wherein hydrogen permeation is used to quantitatively measure the oxygen reduction kinetics underneath the coatings. Presented here are results obtained with an adaptation of the Devanathan-Stachurski cell where the oxygen reduction reaction kinetics on the coated exit is probed by monitoring the dynamic electrochemical equilibrium potential established as a result of oxygen reduction and hydrogen oxidation reactions. From the hydrogen uptake on the entry side thus a full current-potential relationship curve ( $I(U)$ ) can be constructed. First tested on non-coated Palladium, the results show very good concurrence of the oxygen reduction currents from the permeation experiments and that from standard cyclic-voltammetry (CV) measurements in buffered and non-buffered acidic electrolyte and under alkaline condition. Initial results obtained on coated samples are also presented.

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## 1. Introduction

The role of the oxygen reduction reaction (ORR) in biological processes such as respiration [1], in energy conversion systems, such as proton exchange membrane fuel cells [2], and corrosion of metals [3] makes it one of the most studied reaction. ORR plays also a crucial role in cathodic delamination at a metal/coating interface [4–10]. The mechanisms of delamination originating from a defect in the metal/coating interface are well established [5–10]. At the defect site, there is anodic dissolution of the metal providing electrons for the cathodic oxygen reduction reaction. However, at the intact substrate/coating interface, since oxygen can still diffuse to reach the interface, ORR can still proceed, although at a diminished rate, while metal dissolution is nearly completely inhibited. By galvanic coupling, this then causes the progressive destruction of the intact metal/coating interface.

Since the ORR is the driving force for the electrochemically driven degradation of the metal-coating interface, the quantitative measurement of ORR rate and its further inhibition are the prerequisites when designing coatings for corrosion protection. Protective coatings have demonstrated their ability to provide strong inhibition of the cathodic ORR and decreased anodic

dissolution of the metal. Early reports by the group of Stratmann [8–10] demonstrated the possibility to study the localized electrochemical ORR at the buried interface employing the Scanning Kelvin Probe (SKP) technique. SKP is the only electrochemical technique that is able to provide direct information about the corrosion potentials as a function of time and local position at the buried metal/coating interface. However the SKP is a potentiometric technique and cannot provide direct quantitative information about the interfacial reaction rates at the buried interface.

It would be highly interesting if one could measure the electrochemical ORR at the buried interface, because this would give direct information about reactivity of this interface and advance our understanding of delamination and the correlation with the interfacial properties. Conventional electrochemical techniques rely on polarizing the working electrode in a three electrode setup for studying the ORR, but at the buried interface, this cannot be non-destructively applied. Here, a new robust technique based on an adaptation of the Devanathan-Stachurski cell is introduced where the role of permeating hydrogen is extrapolated as a reducing agent [11] for the oxygen reduction reaction.

The Devanathan-Stachurski permeation technique is well established for measuring the diffusion constant of hydrogen and the characteristics of trap sites in metals [12,13]. The standard Devanathan-Stachurski setup consists of a double

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electrochemical cell, in which hydrogen is electroadsorbed on a material of interest from aqueous solution on one side by galvanostatic or potentiostatic charging (entry side), followed by its absorption and diffusion in the bulk, and final oxidation by anodic polarization on the other side (exit side). The measured exit side current provides direct information about the quantity of hydrogen that has permeated through the sample. In this work a modified Devanathan-Stachurski setup with palladium as the working electrode was made use of, where instead of polarizing the exit cell, oxygen was introduced as an agent for oxidizing the permeating atomic hydrogen. For the first experiments Palladium (Pd) was chosen as sample material because of its high permeability and ready uptake of hydrogen and its favorable catalytic activity for the ORR.

Here, as a first step the oxygen reduction current deduced from such a permeation based potentiometric experiment is proven to indeed follow the current-voltage characteristics of the oxygen reduction reaction on a bare Palladium surface. Thus the hydrogen entry side current is employed to provide direct information regarding the oxygen reduction rate on the exit side at steady-state conditions. Further, this technique is introduced as a reliable method to measure uniquely interfacial oxygen reduction rates underneath coatings. The ability of this potentiometric approach to directly monitor the ORR kinetics underneath coatings non-destructively in a two-electrode setup is shown.

## 2. Experimental

### 2.1. Materials

Pd (99.99%) foil with dimensions of 25 mm × 25 mm × 0.025 mm, used as the working electrode and Au (99.99%) foil with dimensions of 15 mm × 15 mm × 1 mm, used as the counter electrode, were both purchased from Goodfellow Cambridge Limited. Stock solution of 1 M H<sub>2</sub>SO<sub>4</sub> (0.2% accuracy) was purchased from VWR International GmbH. Chemicals NaOH, CH<sub>3</sub>COONa and glacial CH<sub>3</sub>COOH (100%) were purchased from Merck KGaA Darmstadt. Poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate) (PVB) with an average molecular weight 50,000–80,000 and Octane thiol (OT) (98.5%) was purchased from Sigma Aldrich.

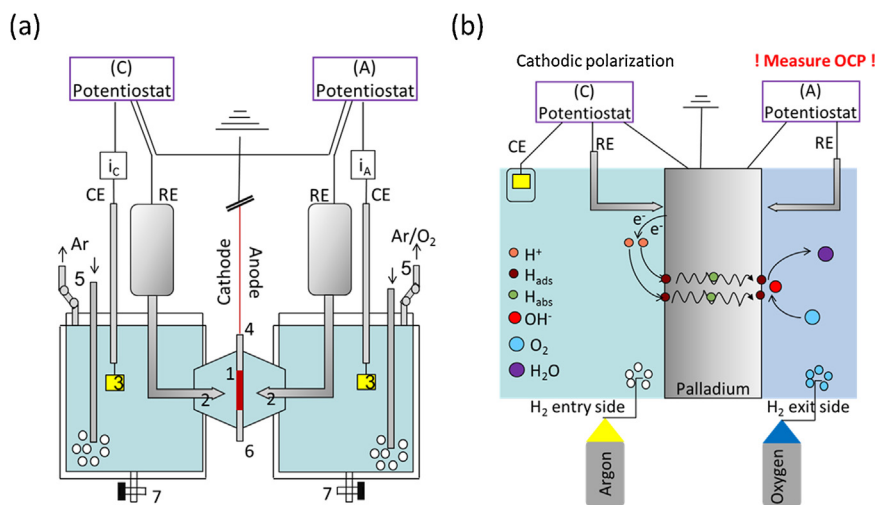
### 2.2. Equipment

Commercial Ag/AgCl reference electrodes (0.23 V vs standard hydrogen electrode (SHE)) from Radiometer Analytical SAS, France

were used in all measurements. All the potentials expressed here are with respect to Ag/AgCl reference electrode. The experiments were conducted with the help of an in-house analog potentiostat (JAISSE Potentiostat-Galvanostat IMP 88) and an Ivium COMPACTSTAT electrochemical interface (B060408) potentiostat.

### 2.3. Methods

The cyclic voltammetry scans were carried out at 1 mV sec<sup>-1</sup>. 0.1 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> solution was prepared by diluting 100 ml of 1 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> with 900 ml of distilled water. The pH of 0.1 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> was in the range of ca. 0.97–1.1. 0.1 mol dm<sup>-3</sup> NaOH solution was made by dissolving 4 g of NaOH pellets in 1000 ml of distilled water. The pH of 0.1 mol dm<sup>-3</sup> NaOH was 12.8. 0.1 mol dm<sup>-3</sup> acetate buffer was prepared by mixing 6 ml of 100% CH<sub>3</sub>COOH, 13.6 g of CH<sub>3</sub>COONa, 3H<sub>2</sub>O and filling up the remaining volume with distilled water to make 1 L of a solution. The pH of 0.1 mol dm<sup>-3</sup> acetate buffer solution was 4.7. PVB coated Pd was prepared by spin coating a 5 wt% PVB solution on the bare Pd surface either twice or 8 times consecutively at 45 rps for 20 seconds per run. The coated sample was then dried in an oven at 75 °C for 1 hour. The thicknesses of the corresponding PVB coatings estimated using ellipsometry were 1.2 μm (in the following referred to as PVB\_1) and 2 μm (referred to as PVB\_2) respectively. An octane thiol (OT) self-assembled monolayer film on one side of the palladium membrane was prepared by immersing the palladium for 24 hours at room temperature in a 10<sup>-3</sup> mol dm<sup>-3</sup> solution of OT in ethanol, followed by rinsing with ethanol, isopropyl alcohol and drying in N<sub>2</sub>. One set of samples was used without further treatment while another set of samples was further spin coated with a thin PVB film (1.2 μm of PVB) to prepare a composite coating (OT+PVB\_1). Fig. 1 shows the Devanathan-Stachurski permeation setup used in this study. The surface area of the working electrode mounted between the two electrochemical cells exposed on both sides to the electrolyte was 0.3286 cm<sup>2</sup>. Each cell contains a Luggin capillary for the Ag/AgCl reference electrode and a thin square gold sheet as the counter electrode. To prevent dissolved gold residues from the counter electrode to deposit on the working electrode under high current density conditions, a protective glass shield with a frit covering the gold counter electrode was made use of. The hydrogen entry side is filled with 0.1 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> and maintained in an Argon atmosphere from which hydrogen is produced by cathodic polarization under potentiostatic conditions. The hydrogen exit side contains either



**Fig. 1.** (a) Schematic representation of experimental setup: 1—Working electrode (Pd membrane); 2—Reference electrode (Ag/AgCl Luggin capillary); 3—Counter electrode (Au foil with glass shield); 4—Copper tape; 5—Ar/O<sub>2</sub> gas inlet and outlet; 6—PTFE joint; 7—Draincock and (b) scheme for measuring oxygen reduction rate.

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