



Short communication

Thin solid state reference electrodes for use in solid polymer electrolytes

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ABSTRACT

This paper reports two low-profile (~10 μm thick) solid state reference electrodes for use in solid polymer electrolytes. The thin, open geometry of the electrodes enables close positioning between the working and counter electrodes. The first electrode uses the palladium hydride (Pd|PdH_x) couple (PHRE), and the second utilises the hydrous iridium oxide (IrO_x·yH₂O|IrO₂·bH₂O) couple (IORE). To our knowledge this is the first use of the latter as a reference electrode. The PHRE had a stable potential of +70 mV vs RHE with a 4 mV h⁻¹ drift and two hour lifetime, whilst the IORE gave a potential of +847 mV vs RHE with a drift of 0.3 mV h⁻¹ and no deterioration after 24 h of use. The use of these reference electrodes in a three-electrode solid state cell and a fuel cell is demonstrated.

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1. Introduction

Solid polymer electrolytes (SPEs) find widespread use in electrochemical devices such as fuel cells, electrolysers and redox flow batteries. For commercial success of these devices, it is critical to have a good understanding of the kinetic processes occurring at the electrode/SPE interface. For this, in-situ analysis using a reference electrode (RE) is highly desirable. However, placement of a RE for accurate analysis, whilst not perturbing the measurement has proven challenging due to the use of thin SPEs in bipolar electrode geometries. This has led to a number of different approaches using either external or internal REs:

External REs include the popular DHE [1–3] and other bulky REs, placed in contact with the SPE, laterally offset from the electrodes and are by far the easiest setup. However, this geometry is prone to a large ohmic resistance through the electrolyte (especially at low humidity) and edge effects [4]. Alternatively, a salt bridge can be placed through the backing plates to contact the SPE perpendicularly within the electrode under study; removing edge effects or potential drop errors [5]. However, this requires modification of the

backing plates and electrode, this is not always practical and may alter reactant distribution at precisely the point where the measurement is made, and hence perturb the potential.

Internal REs, placed between the electrodes in the SPE, avoid edge effects and if placed close to the electrode under study, minimise potential drops through the electrolyte. However, having an RE in the SPE can disrupt the current distribution across the membrane. For a 25 μm thick wire, as used in [6], the RE would have to be 125 μm away from each electrode, to follow the 5d/3 requirement to prevent shielding [7] – this goes against the general trend for thinner SPEs.

In this communication, we report a thin and robust RE design which can be incorporated into a thin (50 μm) SPE, directly between electrodes, with minimal disruption. This involves a fine gold mesh with a thin (8 μm) and open (40% porosity) profile and a high surface area (22.6 mm² for the 7.3 mm² geometric area i.e. roughness factor of ~3). Two active materials were deposited on the mesh which exhibit stable potentials; palladium hydride (PdH) and hydrous iridium oxide (IrO_x). To our knowledge this is the first use of IrO_x as a RE material.

In both cases, the potential is controlled by a single solid state material resulting in miniature, liquid free, easy to fabricate, robust electrodes. Potentials of the REs are dependent upon proton activity, similar to a reversible hydrogen electrode (RHE); which is beneficial when studying proton activity dependent reactions such as the oxygen reduction or hydrogen oxidation reactions.

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2. Materials and methods

Tabbed gold TEM grids (300 mesh, G2930A, Agar Scientific) were joined using gold dag (78% Au, Agar Scientific) to 10 μm thick porous polycarbonate (15% porosity, PCTF0447100, Sterlitech) previously sputtered with 40 nm gold (Emitech K575X Sputter Coater), Fig. 1. This provides a low profile, yet flexible, robust and porous electrical connection to the RE. Analytical grade water ($>18\text{ M}\Omega\text{ cm}$, Millipore Milli-Q) and gasses (Air Products, BIP+, $>99.999\%$) were used throughout.

2.1. Preparation

Palladium was deposited using a hydrazine based electroless bath as previously reported [8]. Deposition resulted in a silvery grid exhibiting typical palladium voltammetry. The palladium deposits were 1.5 μm thick on the basis of exhaustive coulometric oxidation of the charged electrodes assuming a stoichiometry of $\text{PdH}_{0.80}$ [9]. Prior to measurements the palladium-hydrogen reference electrodes (PHRE) were galvanostatically charged with hydrogen.

IrO_x was deposited using a previously reported anodic electrochemical deposition [10,11] followed by boiling in sulphuric acid (0.5 M) for 1 h, and then stored in water. The electrodes showed a uniform dark purple colour with the characteristic redox behaviour of hydrous iridium oxide [11,12].

2.2. Characterisation

The stability of the electrodes was investigated by monitoring the open circuit potential in N_2 purged 0.5 M H_2SO_4 for 3 and 24 h, PHRE and IORE respectively. The pH response of the IORE was investigated by measuring potentials vs. SCE in buffer solutions of pH 4.01, 7.01, 10.01 (Hanna instruments) and in 0.1 M H_2SO_4 and NaOH.

Prior to lamination between two Nafion sheets as described below, REs were submerged in Nafion solution (5 wt.% in 45% H_2O , Sigma-Aldrich) and then dried in air. This was repeated three times to ensure good ionic contact throughout the RE structure.

For use in a previously reported [2] three electrode cell, REs were sealed between two Nafion 115 sheets by hot-pressing (3 min, 150 $^\circ\text{C}$, 1.2 MPa). The voltammetry of Pt black (Johnson Matthey, Batch CE0177) abrasively deposited on an Au microelectrode (50 μm diameter) was recorded against the REs whilst in contact with the Nafion|RE|Nafion assemblies.

For use in a polymer electrolyte fuel cell (PEFC) IOREs were trimmed to $\sim 0.75\text{ mm} \times 2\text{ mm}$, removing the thick outer-ring (Fig. 1). The IORE was sealed between two Nafion 212 sheets whilst electrodes (Alfa Aesar, 45372) were hot-pressed to both sides (3 min, 150 $^\circ\text{C}$, 1.2 MPa). REs were aligned such that the RE overlapped a single channel of the cell flow field with the polycarbonate electrical connection, approximately 2 mm wide, completely outside the active area of the cell. A polarisation

curve of the cell containing a RE was within $\pm 10\text{ mV}$ for a cell constructed in the same way (i.e. two sheets of Nafion) without the RE.

Fuel cell startup was replicated by flooding both anode and cathode sides of the fuel cell with air. Next, H_2 was fed into the air filled anode whilst both the potential differences between anode and cathode, and anode and RE were monitored. All gasses were supplied at 40 scfm, 85% RH and 80 $^\circ\text{C}$ to the 4 cm^2 cell heated to 80 $^\circ\text{C}$.

3. Results & discussion

3.1. Electrode geometry

The mesh is an excellent geometry for an in-situ RE. Its large surface area and thin profile (8 μm), when compared to single a wire, ensure that enough material is present for a stable potential while causing minimal disruption to the electrolyte. The gold mesh used here can also be easily cut so that the RE measures only a small region.

Using gold sputtered polycarbonate as a current collector ensures a flexible and thin (10 μm) electrical connection. The gold sputtered polycarbonate connection to the reference electrode used here is expected to be ionically insulating. However, the width of this electrical connection can be made quite small ($<1\text{ mm}$) as negligible current flows to the RE. In our case the polycarbonate connection did not appreciably obscure the anode and cathode. However, if this was to prove an issue, the porous polycarbonate may be rendered ionically conducting by imbibing Nafion into the porous structure. Such electrolyte sheets may have surprisingly high conductivity given their moderate porosity [13].

Considering only one bar of the mesh as a flat electrode width (d) 31 μm , the electrode must be placed $5d/3$ from the WE to avoid shielding [7]. This is 51 μm , the thickness of hydrated Nafion 212; allowing it to be placed inside the electrolyte of a typical PEFC ($\sim 100\text{ }\mu\text{m}$), between the anode and cathode. We have made electrodes using grids with 5 μm bars and 5 μm spaces, which could be used with electrolytes down to $\sim 8\text{ }\mu\text{m}$ thickness.

In hydrated Nafion at 80 $^\circ\text{C}$ we calculate that this separation contributes an uncompensated resistance of approximately 5 $\text{m}\Omega\text{ cm}^2$. Having such a low uncompensated resistance is crucial for making measurements in functioning devices where high current densities are common and changes in hydration reduce conductivity.

3.2. Characteristics of reference electrodes

3.2.1. Palladium hydride

Before use the palladium electrode must be cathodically charged with hydrogen. Fig. 2 shows the potential of the electrode during treatment at -0.9 mA cm^{-2} for 1.3 h, though we have found that a good PHRE can be obtained with higher current densities over shorter periods ($<5\text{ min}$ at -6.67 mA cm^{-2}).

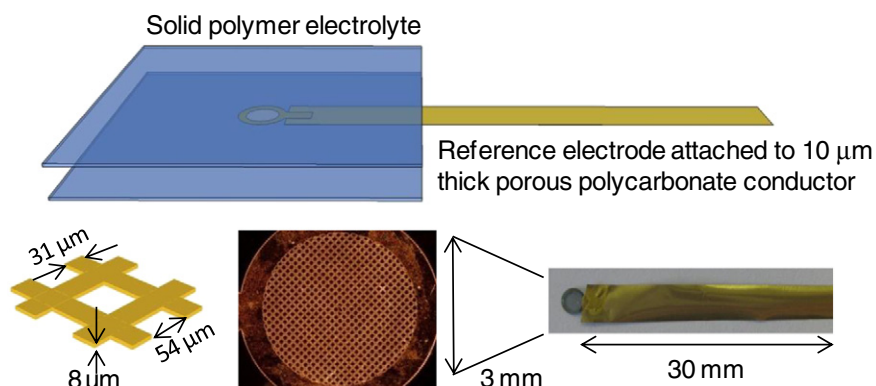


Fig. 1. Geometry of the reference electrodes.

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