2018

Gortex-Based Gas Diffusion Electrodes with Unprecedented Resistance to Flooding and Leaking

Prema Tiwari  
*University of Wollongong, pt832@uowmail.edu.au*

George Tsekouras  
*University of Wollongong, georget@uow.edu.au*

Gerhard F. Swiegers  
*University of Wollongong, swiegers@uow.edu.au*

Gordon G. Wallace  
*University of Wollongong, gwallace@uow.edu.au*

Publication Details  
Gortex-Based Gas Diffusion Electrodes with Unprecedented Resistance to Flooding and Leaking

Abstract
A significant and long-standing problem in electrochemistry has demanded the need for gas diffusion electrodes that are "flood-proof" and "leak-proof" when operated with a liquid electrolyte. The absence of a solution to this problem has, effectively, made it unviable to use gas diffusion electrodes in many electrochemical manufacturing processes, especially as "gas-depolarized" counter electrodes with significantly decreased energy consumption. In this work, Gortex membranes (also known as expanded PTFE or ePTFE) have been studied as novel, leak-proof substrates for gas diffusion electrodes [PTFE = poly(tetrafluoroethylene)]. We report the fabrication, characterization, and operation of gas diffusion electrodes comprising finely pored Gortex overcoated with 10% Pt on Vulcan XC72, PTFE binder, and a fine Ni mesh as a current carrier. Capillary flow porometry indicated that the electrodes only flooded/leaked when the excess of pressure on their liquid-side over their gas-side was 5.7 atm. This is more than an order of magnitude greater than any previous gas diffusion electrode. The Gortex electrodes were tested as hydrogen- and oxygen-depolarized anodes and cathodes in an alkaline fuel cell in which the liquid electrolyte was pressurized to 0.5–1.5 atm above the gas pressures. Despite the record high electrolyte pressure, the electrodes, which had Pt loadings of only 0.075 mg Pt/cm², exhibited notable activity over 2 d of continuous, leakfree operation. Under the applied liquid pressure, the fuel cell also overcame all of the key technical challenges that have hindered the adoption of alkaline fuel cells to date. The high activity and unprecedented resistance to leaking/flooding exhibited by these electrodes, even when subjected to large liquid electrolyte overpressures under gas depolarization conditions, provide an important advance with far-reaching implications for electrochemical manufacturing.

Disciplines
Engineering | Physical Sciences and Mathematics

Publication Details

This journal article is available at Research Online: https://ro.uow.edu.au/aiimpapers/3232
Gortex-Based Gas Diffusion Electrodes with an Unprecedented Resistance to Flooding and Leaking

Prerna Tiwari, George Tsekouras, Gerhard F. Swiegers,* Gordon G. Wallace

Intelligent Polymer Research Institute, University of Wollongong, Wollongong, NSW 2522, Australia and ARC Centre of Excellence for Electromaterial Science, University of Wollongong, Wollongong, NSW 2522, Australia

KEYWORDS: Gortex, Gore-Tex, gas diffusion electrode, leaking, flooding, capillary flow porometry

ABSTRACT: A significant and long-standing problem in electrochemistry has involved the need for gas diffusion electrodes that are ‘flood-proof’ and ‘leak-proof’ when operated with liquid electrolyte. The absence of a solution to this problem has, effectively, made it unviable to use gas diffusion electrodes in many electrochemical manufacturing processes, especially as “gas-depolarized” counter electrodes with significantly decreased energy consumption. In this work Gortex membranes (also known as expanded PTFE, or ePTFE) have been studied as novel, leak-proof substrates for gas diffusion electrodes (PTFE=poly(tetrafluoroethylene)). We report the fabrication, characterization, and operation of gas diffusion electrodes comprising of finely-pored Gortex overcoated with 10% Pt on Vulcan XC72, PTFE binder and a fine Ni mesh as a current
carrier. Capillary flow porometry indicated that the electrodes only flooded/leaked when the excess of pressure on their liquid-side over their gas-side was 5.7 atm. This is more than an order of magnitude greater than any previous gas diffusion electrode. The Gortex electrodes were tested as hydrogen- and oxygen-depolarized anodes and cathodes in an alkaline fuel cell in which the liquid electrolyte was pressurized to 0.5-1.5 atm above the gas pressures. Despite the record high electrolyte pressure, the electrodes, which had Pt loadings of only 0.075 mg Pt/cm$^2$, exhibited notable activity over 2 d of continuous, leak-free operation. Under the applied liquid pressure, the fuel cell also overcame all of the key technical challenges that have hindered the adoption of alkaline fuel cells to date. The high activity and unprecedented resistance to leaking / flooding exhibited by these electrodes even when subjected to large liquid electrolyte overpressures under gas depolarization conditions, provides an important advance with far-reaching implications for electrochemical manufacturing.

1. INTRODUCTION

The structures and constructions of modern-day gas-diffusion electrodes (GDEs) date back to a series of patents in the early 1960s. Figure 1(a) schematically depicts the cross-sectional arrangement of a typical gas diffusion electrode. On the ‘liquid side’, the electrode is in direct contact with the aqueous electrolyte. On the ‘gas side’, the reaction gas flows into or out of the electrode. The catalyst layer, which lies on the liquid side, normally comprises of carbon particles of small dimensions, fused with catalyst and sufficient poly(tetrafluoroethylene) (PTFE) binder to make this layer partially permeable.
Figure 1. Schematic depiction of the cross-sectional structure of: (a) a typical modern-day gas diffusion electrode, and (b) a Gortex-based gas diffusion electrode of the type studied in this work.
to the liquid electrolyte.\textsuperscript{1-4} The \textit{gas diffusion layer}, which lies on the gas side of the electrode, contains larger and/or more hydrophobic carbon particles, along with higher levels of PTFE.

The intention of this architecture is to create and maintain, within the catalyst layer, a three-way solid-liquid-gas boundary, where the liquid electrolyte interfaces with the reactant/product gas in the presence of the solid catalyst (depicted in Figure 1(a) as an irregular, dashed line). Reaction at the three-phase boundary is driven by electron flow to or from the current carrier, through the conductive catalyst and gas diffusion layers, causing turnover of the catalyst.

While modern-day gas diffusion electrodes have been developed to a high level of technological maturity, they exhibit one seemingly intractable problem: they are prone to “flooding” if their liquid side experiences a pressure that is even marginally more (<0.1 atm) than their gas side. Flooding involves the partial displacement of the solid-liquid-gas interface into the gas diffusion layer. If flooding occurs at any location in a gas diffusion electrode, a pathway is created for liquid electrolyte to constantly leak from the liquid side of the electrode into the gas system of the cell. Present-day gas diffusion electrodes may flood and leak even under the influence of a minor pressure differential, such as that arising from, for example, the hydraulic head of the liquid electrolyte.\textsuperscript{5-7}

This problem is most troublesome in electrochemical manufacturing processes, like chlor-alkali and electrowinning cells, that are strongly influenced by the cost of electricity. Electrical energy, for example, makes up \textasciitilde70\% of the cost of chlorine; the chlor-alkali process is believed to use about 2\% of the USA’s electricity.\textsuperscript{6} A commercially attractive option in such cells is to reduce the energy consumption by using a gas diffusion counter-
electrode that is bathed in a so-called “depolarizing” gas, like oxygen (O2) or hydrogen (H2). This produces a different half-reaction at the counter electrode leading to a drastic decline in the cell voltage (of 1.23 V) and the energy consumption. For example, the minimum energy needed to generate chlorine in a standard chlor-alkali cell is 1.65 kWh/kg Cl2. However, this decreases to 0.73 kWh/kg Cl2 in an “oxygen-depolarized” chlor-alkali cell, which equates to a 56% decline in the consumption of electrical energy. Equations S1-S3 in the Supporting Information explain the half-reactions and electrode/cell potentials for conventional and oxygen-depolarized versions of the chlor-alkali process. Standard and hydrogen-depolarized electrowinning cells are described in equations S4-S6.

Despite the enormous commercial incentive offered by this approach however, very few gas diffusion electrodes are practically employed in electrochemical manufacturing today, including in chlor-alkali plants. This is because the intractable problem of flooding and leaking in modern-day gas diffusion electrodes makes it, effectively, unviable to operate gas diffusion counter electrodes in industrial electrochemical processes.

Over the last 50 years, very extensive and wide-ranging attempts by numerous major chemical companies have been made to overcome this problem. Several hundred patent applications and many publications have described a wide variety of approaches to the problem or its mitigation, including, by way of example only: (i) a clever, but cumbersome “gas pocket” electrode design that, effectively, splits up the hydraulic head (developed by Eltech Systems, Dow Chemical and Bayer, amongst others), (ii) a “falling film” or “percolating”-type gas diffusion electrode, that avoids the problem but creates a large inter-electrode voltage drop (pioneered by Hoechst), (iii) the use of a cell design in which the gas diffusion electrode is located tight against a water-fast ion-exchange membrane (developed, most prominently, by Permelec and DuPont),
and (iv) the use of a horizontally disposed gas diffusion electrode involving a liquid mercury covering.

Despite all of this effort and the truly vast commercial opportunity, the current state-of-the-art involves a sintered and cast electrode with a high elastic modulus developed by De Nora, that is capable of withstanding, without leaking, a 0.2 atm excess of liquid-side pressure over the gas-side pressure during O$_2$-depolarization.\textsuperscript{7} That is, gas diffusion electrode design appears to have advanced only to the point of doubling the liquid electrolyte pressure at which flooding and leaking occurs, from <0.1 atm to 0.2 atm.

The essence of the problem is that, in the current architecture of gas diffusion electrodes (Figure 1(a)), the gas diffusion layer has to be simultaneously optimized for three very different functions. It needs to exhibit: (1) high conductivity (for electron transport), (2) high porosity (for gas transport), and (3) high water-repellence (for flood-resistance). As (1) and (2) are critically important to the performance of the electrode, it should be no surprise that these features are always optimized as fully as possible, which can only be done by inadequately optimizing (3). That is, the impossibility of concurrently optimising three variables means that flood-resistance must always be sacrificed for conductivity and porosity, which are more crucial.

An alternative approach to overcoming the problem of flooding and leaking in gas diffusion electrodes is to employ a different design in which less is asked of the gas diffusion layer. That is, instead of trying to concurrently optimize three functions in the gas diffusion layer, one could optimize two of the functions and provide the third by other means. For example, one could optimize only porosity and water-repellence and provide conductivity to the catalyst layer by
another means. That other means may conceivably involve incorporation of metallic mesh current carriers, as was done in some early alkaline fuel cell electrodes.8-11

A material that has a reputation for displaying near-ideal porosity and water-repellence, is Gortex. Gortex is a common name for a group of membranes that involve a layer of microscopically-small hydrophobic Teflon filaments with overall porosities of up to 90% (referred to as expanded PTFE, or ePTFE) laminated to a fibrous polypropylene backer (PTFE = polytetrafluoroethylene).12-13 Gortex has a structure that is both highly porous and highly hydrophobic, meaning that it allows gases to pass through, but not liquid water, which is repelled. As a textile for example, Gortex permits the exit of water vapor from a wearer’s body, but not the entrance of liquid rainwater.

In this work we report the fabrication, characterization, and testing of novel, leak-proof gas diffusion electrodes comprising of finely-pored Gortex membranes over-coated with conductive layers, including particulate catalyst layers containing 10% Pt on Vulcan XC72 incorporating a metal mesh current carrier. Figure 1(b) schematically depicts the cross-sectional structure of the Gortex-based electrodes.

Capillary flow porometry indicates that the particulate-coated Gortex electrodes only flooded / leaked when the excess of the liquid-side pressure over the gas-side was 5.7 atm. This is more than an order of magnitude greater than the 0.2 atm exhibited by the abovementioned De Nora gas diffusion electrode for O2-depolarization.6 The effectiveness of the Gortex electrodes as hydrogen-depolarized anodes and oxygen-depolarized cathodes was tested in an alkaline fuel cell in which the liquid electrolyte was pressurized to 0.5-1.5 atm above the gas pressures. Despite the record high electrolyte pressure, the electrodes, which had Pt loadings of only 0.075 mg Pt/cm2, exhibited notable activity over 2 d of continuous, leak-free operation. Under the high applied
electrolyte pressure, the fuel cell also overcame all of the key technical challenges that have hindered the adoption of alkaline fuel cells to date. The high activity and unprecedented resistance to leaking / flooding exhibited by these electrodes even when subjected to large liquid electrolyte overpressures under gas depolarization conditions, provides an important advance with far-reaching implications for electrochemical manufacturing.

This work forms part of a series of studies in our laboratory in which Gortex-based gas diffusion electrodes have been shown to display extraordinary interfacial properties.14-15

2. RESULTS AND DISCUSSION

2.1 Gortex as a Potential Gas Diffusion Layer. A key, promising feature of Gortex is that it may be manufactured to reliably exhibit an exceedingly well-defined pore structure of small average size and narrow distribution. The pores are additionally highly hydrophobic. A wide range of different Gortex membranes, each with their own pore structure, are commercially available at low cost and in large scale from the filtration industry. A potential advantage of using Gortex as a gas diffusion layer is therefore that its pore structure can be selected by choosing a particular grade of Gortex membrane. The tight engineering specifications of commercially-available Gortex membranes will then ensure reproducibility in respect of fabricating gas diffusion electrodes in large volumes or dimensions.

The pore structure of Gortex is routinely characterized in the filtration industry using capillary flow porometry.12-13 This technique involves the systematic displacement of a wetting liquid from the pores of a membranous sample by applying a gas with steadily increasing pressures.12-13 The Gortex membrane is first soaked in a liquid, usually i-propanol, that completely fills and “wets” its pores. The wetting liquid is then progressively displaced and pushed out of the
pores by subjecting one side of the wetted membrane to a gas source (typically compressed air) under steadily increasing pressure. In the process, a plot of the gas flow rate (through the membrane) vs. the applied gas pressure is obtained (Figure S1 in the Supporting Information depicts a typical plot). The plot yields the displacement pressures for the largest pores (known as the ‘first bubble point’), the mean pores (known as the ‘mean flow pressure’), and the smallest pores in the membrane. From these measurements, it is possible to determine the dimensions of the largest, smallest, and mean pores, as well as the pore size distribution using the Young-Laplace equation:

\[ P = \frac{4\gamma \cos \theta}{D} \]  

where D is the pore size diameter, P is the measured pressure, \( \gamma \) is the surface tension of the wetting liquid and \( \theta \) is the contact angle of the wetting liquid with the sample.

2.2 Determining the Leak-Resistance of Gortex: Measuring its ‘Liquid-Entry Pressure’.

A similar procedure can be carried out using a “non-wetting” liquid, like water, that does not wet or fill the pores. In this measurement, water is placed on the one side of the dry membrane. The water is then subjected to a systematic increase in pressure until it penetrates and passes through the membrane to the other side. The pressure at which that occurs is known as the “liquid-entry pressure” (or the “water-entry pressure” when water is used). Because Gortex has highly repellent pore structures, it tends to completely halt the passage of water through it until the water-entry pressure is reached, at which point the water literally bursts through the membrane.
When thought of as a potential gas diffusion layer, the water-entry pressure is, effectively, the overpressure on the liquid side relative to the gas side, at which the gas diffusion layer would flood and leak.

Gortex membranes with a wide range of specified water-entry pressures are available from the filtration industry. For the purposes of this study, we selected as our Gortex substrate, a finely pored *Prevail™ expanded PTFE* (ePTFE) membrane supported by a fibrous polypropylene backer, supplied by GE Energy, that had a water-entry pressure of $>4$ atm. That is, the membrane was manufactured to resist penetration by water (flooding / leaking) until the overpressure on the water side of the membrane relative to the gas side, exceeded 4 atm. In choosing this membrane as a substrate for our gas diffusion electrodes, we were therefore aiming to drastically improve upon the leak resistance of modern-day gas diffusion layers.

### 2.3 The Preparation and Physical Properties of Selected, Coated Gortex Membranes.

Other than the present series of studies\(^{14-15}\) and several recent reports in which Gortex membranes were coated with weakly-catalytic conducting polymers and sputtered metals or used in microbial fuel cells,\(^{16-20}\) Gortex does not appear to have been formally considered as an electrode substrate in its own right. Moreover, no attempt has been made to select (based on a commercially-available engineering specification) or study the physical properties of a coated Gortex-based gas diffusion electrode.

To overcome these deficiencies, we prepared and studied the physical properties of Gortex membranes coated with metallic layers and catalysts.
2.3.1. Gortex Coated with Sputtered Pt. In the first set of experiments, we prepared and examined the above **Prevail™** Gortex membrane after sputter-coating with Pt on its ePTFE side. Sputter-coated Gortex electrodes have previously been described, but they had not been physical characterized.\textsuperscript{16-20} It was decided to provide such a characterization in the present study for reference purposes and also to contrast with the particulate coated Gortex electrodes.

![Scanning electron microscopy (SEM) images of the ePTFE surface of Gortex membranes sputter-coated with Pt, with nominal thicknesses (according to the internal thickness monitor of the sputter-coater) of: (a) 50 nm, (b) 200 nm, and (c) 400 nm.](image)

**Figure 2.** Scanning electron microscopy (SEM) images of the ePTFE surface of Gortex membranes sputter-coated with Pt, with nominal thicknesses (according to the internal thickness monitor of the sputter-coater) of: (a) 50 nm, (b) 200 nm, and (c) 400 nm.
Figure 2 shows magnified views of the Gortex membrane after sputter-coating with varying loadings of Pt. Figure 2(a) depicts the membrane after deposition of 0.083 g of Pt per m$^2$ of geometric area. Quartz crystal microbalance (QCM) measurements indicated that this loading was equivalent to a uniform layer of Pt that was ca. 50 nm thick when deposited on a non-porous, solid substrate. As can be seen in Figure 2(a), the fibrous network of the membrane remained relatively unchanged after deposition, with each of the fibers coated with a thin layer of Pt. The metallized membrane was conductive, albeit with a high sheet resistance (~60-80 Ω/square). However, increasing the Pt loading by five-fold, to 0.42 g of Pt per m$^2$ of geometric area, provided a continuous conductive layer of Pt with a lower sheet resistance (in the order of ~10 Ω/square). This loading equated to a nominal thickness of 100 nm on a non-porous, solid substrate, according to the internal thickness monitor of the sputter-coater.

Figure 2(b) depicts the Gortex membrane after deposition of 2.03 g of Pt per m$^2$ of geometric area. This loading equated to a thickness of ca. 200 nm when deposited on a non-porous, solid substrate. As can be seen, in Figure 2(b), the fibres of the membrane were noticeably thickened by the deposition process, with knots of Pt visible. The pore structure, porosity and high internal surface area of the membrane remained essentially intact however.

Because of the thicker Pt coating, the conductance of the membrane surface was enhanced, with a sheet resistance of <3 Ω/square.

Figure 2(c) depicts the Gortex membrane after deposition of 6.47 g of Pt per m$^2$ of geometric area. This loading equated to a thickness of ca. 400 nm when deposited on a non-porous, solid substrate. As can be seen, in Figure 2(c), the fibres in the fibrous network of the membrane
became so thickened by the deposition process that, in many places the surface of the membrane was almost completely covered.

To determine how far the Pt coating penetrated into the Gortex membrane, the Pt-coated membrane in Figure 2(b) was cryogenically frozen, cracked, and the cross-section of the fracture examined using scanning electron microscopy (SEM). Figure 3(a) shows an SEM image of the cross-section, viewed from laterally above the top surface of the exposed edge. As can be seen, the cross-sectional thickness of the expanded PTFE (ePTFE) layer in the membrane was ca. 20 μm, with a thin Pt layer on the top. The cross-section displayed the same complex fibrous network observed in the earlier figures. Below the ePTFE layer, on the opposite side to the Pt coating, could be seen the polypropylene fibers that make up the backing material of the Gortex.

Figure 3. (a) Cross-sectional view and (b) cross-sectional energy-dispersive X-ray (EDX) of the sputter-coated (200 nm nominal thickness) Gortex electrode depicted in Figure 2(b). The Pt layer is shown in red.
Figure 3(b) was generated using Energy-Dispersive X-rays (EDX), tuned to image only specific atoms. The Pt atoms appear as red areas with C atoms colored blue and F atoms green. As can be seen, the sputter-coated Pt was limited to the top ca. 0.85 μm of the Gortex membrane. It could not be ascertained whether the entire 0.85 μm displayed sheet conductivity.

Excluding the polypropylene backer, metallized Gortex electrodes of this type therefore comprised two layers: (i) a porous, metallized, and at least partially conductive Pt layer that penetrated ca. 0.85 μm into the ePTFE layer, and (ii) an underlying layer of virgin, uncoated ePTFE of ca. 19.15 μm thickness. Except for locations where the Pt heavily over-coated the Gortex, the pore structures of the conductive and non-conductive layers appeared very similar. The boundary between them was therefore largely a boundary of electrical conductivity and surface metallization.

2.3.2. Gortex Coated with 10% Pt on Vulcan XC72, Carbon Black, PTFE Binder and Ni Mesh. In a second set of experiments, we prepared and studied gas diffusion electrodes comprising of the Gortex membrane over-coated on its ePTFE side, with a mixture of 10% Pt on Vulcan XC72 commercial catalyst, carbon black (CB), dispersed poly(tetrafluoroethylene) (PTFE) as a binder, and a Ni mesh as current carrier. The weight of the mixture, the type of Ni mesh, and the gap employed between the rollers (of the two-roll mill employed) were all optimized by systematic testing of the resulting Gortex gas diffusion electrodes in desktop alkaline fuel cells (as described in a later section in this work). The optimum electrode contained 0.075 mg Pt/cm² (0.75 g Pt/m²) and 40 wt% PTFE and bound the ePTFE layer of the Gortex strongly (presumably by mechanically interlocking with the upper portion of the PTFE fibres).
Figure 4. Cross-sectional view of a Gortex electrode coated with a precious metal catalyst supported on Vulcan XC72, carbon black, PTFE binder, and a Ni mesh as a current carrier; the dashed line at the top depicts the surface of the catalyst layer.

Figure 4 depicts an optical micrograph of a cross-sectional view of a Gortex electrode of this type. As can be seen, the gas-facing side of the electrode (depicted at the bottom of the Figure) comprised of the ePTFE layer itself (ca. 20 μm thick) backed by the thicker, fibrous polypropylene backing layer of the Gortex. The liquid-facing side (depicted at the top of the Figure) comprised of the catalyst, incorporating carbon black and PTFE binder, enveloping the Ni mesh current carrier.

A transmission electron micrograph of the 10% Pt on Vulcan XC72 catalyst used in this study (Figure S2) indicated that the catalyst exhibited a rather ideal morphology, comprising of 2-4 nm Pt nanoparticles evenly dispersed over the carbon support.
<table>
<thead>
<tr>
<th>Gas Diffusion Electrode</th>
<th>Nominal thickness of coating on Gortex (nm/μm)</th>
<th>Mean flow pressure (IPA)(^a) (atm)</th>
<th>Mean flow pore diameter (IPA)(^a) (μm)</th>
<th>Bubble point pressure (IPA)(^a) (atm)</th>
<th>Bubble point pore diameter (IPA)(^a) (μm)</th>
<th>Liquid-entry pressure (H(_2)O) (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt sputter-coated on Gortex</td>
<td>0 nm</td>
<td>1.1204</td>
<td>0.5695</td>
<td>1.0331</td>
<td>0.6176</td>
<td>4.2558</td>
</tr>
<tr>
<td></td>
<td>50 nm</td>
<td>1.9474</td>
<td>0.3276</td>
<td>1.8948</td>
<td>0.3367</td>
<td>4.7047</td>
</tr>
<tr>
<td></td>
<td>100 nm</td>
<td>1.9323</td>
<td>0.3302</td>
<td>1.8945</td>
<td>0.3368</td>
<td>4.4852</td>
</tr>
<tr>
<td></td>
<td>150 nm</td>
<td>1.8638</td>
<td>0.3423</td>
<td>1.8193</td>
<td>0.3507</td>
<td>4.2939</td>
</tr>
<tr>
<td></td>
<td>200 nm</td>
<td>1.2556</td>
<td>0.5082</td>
<td>1.2025</td>
<td>0.5306</td>
<td>3.991</td>
</tr>
<tr>
<td></td>
<td>400 nm</td>
<td>1.1822</td>
<td>0.5397</td>
<td>1.1345</td>
<td>0.5624</td>
<td>3.508</td>
</tr>
<tr>
<td>10% Pt on Vulcan XC72, carbon black, PTFE and Ni mesh on Gortex</td>
<td>~200 μm</td>
<td>1.1708</td>
<td>0.5450</td>
<td>1.0969</td>
<td>0.5817</td>
<td>5.702</td>
</tr>
</tbody>
</table>

\(^a\)wetting liquid was IPA (\(=\)-propanol)

Table 1. Capillary flow analysis of Gortex-based gas diffusion electrodes.\(^{12-13}\)

2.4 Physical Characterization of the Coated Gortex Using Capillary Flow Porometry. To the best of our knowledge, capillary flow porometry has never before been used to characterize gas diffusion electrodes. Such structures are normally examined with mercury intrusion porosimetry\(^{21}\) and/or BET nitrogen sorption (to measure macroscopic (>10 μm) and microscopic (<10 μm) pores respectively).\(^{22}\) Capillary flow porometry differs from these techniques in that it is skewed towards smaller pores of the type that would be present in gas diffusion layers that were optimized for porosity and water-repellence.\(^{22-25}\) Because of the compressibility of the pores in Gortex, mercury intrusion porometry cannot be reliably used.\(^{23}\) The fact that modern-day gas diffusion electrodes flood and leak aqueous electrolyte at low liquid overpressures (<0.2 atm),\(^{5-7}\) indicates that their pore structures and/or hydrophobicities are likely too large, too ill-defined or
too broadly distributed for measurement using capillary flow porometry. They may, additionally, be insufficiently robust, leading them to be damaged by the technique.

Table 1 summarizes the data obtained for the above coated Gortex membranes. The most significant data is the liquid (water) entry pressure, which was measured to be $>4$ atm for all electrodes that had been sputter-coated with a Pt layer of $<200$ nm nominal thickness, as well as for the electrode coated with 10% Pt on Vulcan XC72, carbon black, PTFE and Ni mesh. The latter was found to be a remarkable 5.702 atm, which is more than an order of magnitude larger than the 0.2 atm reported for the De Nora O$_2$-depolarizing gas diffusion electrode.\(^7\)

The mean flow pore and the bubble point pore diameters of the electrodes generally followed the respective trends in those pressures that are evident in Table 1. It is noticeable however, that for the electrode coated with the particulate, 10% Pt on Vulcan catalyst layer, these quantities were similar to those of the uncoated Gortex membrane, suggesting that they were set by the Gortex gas diffusion layer, with the catalyst layer having little influence.

Figure 5 depicts the computed distribution (by number) of the average pore diameter of the Gortex electrodes. As can be seen, 90% of the pores of the control, uncoated Gortex fell in the range 0.5-0.6 $\mu$m (Figure 5(a)). However, sputter-coating with Pt at 50-150 nm nominal thickness caused the average pores to decrease to 0.3-0.4 $\mu$m size (Figure 5(a)). Thicker sputter-coating of the membranes (200 and 400 nm nominal thickness) saw 65%-95% of their pores in the 0.5-0.6 $\mu$m diameter range. This was likely due to the surface pores becoming largely blocked, meaning that the average pore reverted to the size found in the uncoated Gortex. The Gortex electrode coated with 10% Pt on Vulcan XC72, incorporating carbon black, PTFE and Ni mesh, had 65% of its pores in the range 0.5-0.6 $\mu$m diameter, with declining numbers of pores at lower diameters.
Figure 5. Pore size distribution (by number) of the Gortex electrodes: (I) of the uncoated and Pt-coated ePTFE electrodes according to porometry: (©) uncoated, (5) 50 nm, (Δ) 100 nm, (⊙) 150 nm, (★) 200 nm, (●) 400 nm Pt. (II) Bar-graph of the pore size frequency (by number) of (a) uncoated Gortex (control), (b)-(f) sputter-coated with Pt of 50-400 nm nominal thickness, and (g) over-coated with 10% Pt on Vulcan XC75 incorporating carbon black, PTFE binder, and Ni mesh current carrier.

Figure 6 shows porometric air permeability data for the Gortex electrodes. To make these measurements, air was passed through 1 cm$^2$ of the dry electrodes and the flow rate was measured as a function of the applied pressure. As can be seen, the electrodes displayed highly porous structures that each exhibited approximately linearly increasing flow rates with applied pressure. The almost parallel slopes of their air permeability data relative to and below the control, uncoated
Gortex membrane, indicated that their overall porosity decreased as a result of the coating. The porosity of the sputter-coated electrodes generally declined with an increase in the loading of Pt. The Gortex electrode that had been sputter-coated with Pt of nominal 400 nm thickness displayed the lowest porosity as shown by the filled circles (●) in Figure 6. By contrast, the electrodes coated with 10%Pt/carbon black/PTFE/Ni mesh (＋” symbols in Figure 6) displayed an intermediate flow rate, indicating an intermediate porosity in the catalytic layer.

**Figure 6.** Air permeability measurements per 1 cm² area of the uncoated and coated gas diffusion electrodes obtained by porometry: (○) uncoated Gortex control, Gortex sputter-coated with Pt to nominal thicknesses of: (□) 50 nm, (Δ) 100 nm, (○) 150 nm, (▲) 200 nm, (●) 400 nm, and (+) Gortex over-coated with particulate 10% Pt on Vulcan XC72, incorporating carbon black, PTFE binder, and Ni mesh.

It should be noted however that, even for the poorest performing of the above electrodes, a very substantial flow of air, equal to ca. 2 L per min, passed through a 1 cm² area of electrode at
a 0.5 atm pressure differential. Clearly there was no significant hindrance to gas transport into or out of the Gortex gas diffusion electrodes. This confirmed previous findings in this respect.\textsuperscript{14-15}

<table>
<thead>
<tr>
<th>Nominal thickness of sputtered Pt on Gortex membrane (nm)</th>
<th>Contact angle (water 5(\mu)L @ 0.5(\mu)L/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>117.2</td>
</tr>
<tr>
<td>50</td>
<td>106.7</td>
</tr>
<tr>
<td>100</td>
<td>98.8</td>
</tr>
<tr>
<td>150</td>
<td>92.5</td>
</tr>
<tr>
<td>200</td>
<td>78.2</td>
</tr>
<tr>
<td>400</td>
<td>74.5</td>
</tr>
</tbody>
</table>

Table 2. Contact angles of the coated Gortex membranes

2.5 **Hydrophobicity of the Gortex-based Gas Diffusion Electrodes.** The contact angles of the coated surfaces of the above electrodes were measured and compared to that of the uncoated, control Gortex membrane. The catalyst surface of electrodes coated with 10\%Pt/carbon black/PTFE/Ni mesh wetted completely when a droplet of water was placed on it, meaning that they were strongly hydrophobic. No contact angle could be measured. However, water droplets beaded on the catalyst surface of the Gortex electrodes that had been sputter-coated with Pt.

Clearly, the thick layer of 10\%Pt/carbon black/PTFE/Ni mesh lay on top of the ePTFE layer of the Gortex and was therefore hydrophilic, while, by contrast, the Pt layer, being thinner and fully penetrated into the body of the ePTFE layer of the Gortex, was hydrophobic.

Table 2 summarizes the contact angles of these samples. As can be seen, the surface of the control, uncoated membrane was strongly hydrophobic, with a contact angle of ca. 117°. However, when sputter-coated with increasing loadings of Pt, the contact angle and the hydrophobicity of
the surface progressively declined, to 98.8° at 100 nm nominal thickness, 78.2° at 200 nm, and 74.5° at 400 nm. The coating of 10%Pt/carbon black/PTFE/Ni mesh was too hydrophilic to obtain a contact angle.

2.6 Electrochemical Testing of the Gortex Electrodes as Gas-Depolarized Gas Diffusion Electrodes. In order to test the Gortex electrodes in hydrogen- and oxygen-gas depolarization, we required cells in which they would be required to facilitate such half-reactions. The simplest cell in which to perform such tests is a hydrogen-oxygen fuel cell, which, effectively, involves a

![Figure 7. Schematic depiction of the alkaline fuel cell used to test the gas diffusion electrodes of this study.](image)

hydrogen-depolarized anode paired with an oxygen-depolarized cathode, employing the following reactions (in the case of an alkaline fuel cell):
Anode: \[ 2 \text{H}_2 + 4 \text{OH}^- \rightarrow 4 \text{H}_2\text{O} + 4 \text{e}^- \] 
\[ E^\circ_{\text{ox}} = 0.83 \text{ V} \] \( \cdots (2) \)

Cathode: \[ \text{O}_2 + 2 \text{H}_2\text{O} + 4 \text{e}^- \rightarrow 4 \text{OH}^- \] 
\[ E^\circ_{\text{red}} = 0.40 \text{ V} \] \( \cdots (3) \)

Alkaline fuel cell 
\[ E^\circ_{\text{cell}} = 1.23 \text{ V} \]

We therefore assessed the performance of the Gortex electrodes in a bench-scale alkaline fuel cell of the type schematically depicted in Figure 7. To confirm their resistance to flooding and leaking under gas-depolarized conditions, the liquid electrolyte in the cell was pressurized to 0.5-1.5 atm above the pressures of the feedstock gases. The Gortex electrodes sputter-coated with Pt proved to perform very poorly in such a cell, due most likely to their high hydrophobicity (which would have pushed their liquid-gas interface away from the Gortex and the Pt layer). However, the Gortex electrodes coated with particulate 10%Pt/carbon black/PTFE/Ni mesh performed well.

In the tests, two 1 cm\(^2\) electrodes were placed in facing dispositions, 3 mm apart, within a custom-built cell that contained gas chambers behind each of the anode and the cathode electrodes (Figure 7). The central cavity of the cell, between the electrodes, was filled with aqueous 6 M KOH electrolyte. The headspace above the aqueous electrolyte was filled with nitrogen, which was either maintained at atmospheric pressure (1 atm) or overpressured by 0.5-1.5 atm (to 1.5-2.5 atm in total) during the tests. The feedstock gases (high purity oxygen and hydrogen) were, in all cases, provided at 1 atm pressure. Because of their high water-entry pressures, the aqueous electrolyte was unable to pass through the Gortex gas diffusion electrodes and the central cavity of the cell was liquid-fast and leak-free. Gortex electrodes coated with particulate 10%Pt/carbon black/PTFE/Ni mesh were used at both the anode and the cathode in the cell.

In general, the measured data was not noticeably affected by the pressure of the electrolyte. That is, very similar data was obtained regardless of whether the aqueous 6 M KOH
was at a pressure of 1.0 atm (0 atm overpressure), 1.5 atm (0.5 atm overpressure), 2.0 atm (1 atm overpressure), or 2.5 atm (1.5 atm overpressure). For consistency, the data reported below was collected with the electrolyte at 1.5 atm.

Alkaline Fuel Cells (AFCs) were, until the 1990’s, regarded as the most promising of the fuel cell technologies.\textsuperscript{8-10} During that decade however, Proton Exchange Membrane (PEM) Fuel Cells came to dominate the field. Several of the technical challenges associated with AFCs contributed to that change. According to authoritative reviews at the time, key amongst these were:\textsuperscript{8-10} (i) the difficulty of producing a well-defined, uniform pore system and evenly distributed catalyst in AFC gas diffusion electrodes, (ii) the excessive cost of the gas diffusion electrodes and the difficulty of fabricating them reproducibly in large scale, (iii) the non-availability, due to the phasing out of asbestos, of ion-permeable, gas-impermeable inter-electrode diaphragms that were alkaline-stable, and (iv) the problem of CO\textsubscript{2} intolerance in air-breathing AFCs, which saw insoluble carbonate crystallites forming within, and blocking the pores of the gas diffusion electrodes.

The Gortex electrodes coated with particulate 10\%Pt/carbon black/PTFE/Ni mesh, overcame all of these limitations. Challenges (i) and (ii) above were surmounted by the fact that the Gortex substrate was available in large scale and dimension with a reproducibly well-defined and uniform pore system. An even layer of catalyst could be easily applied. An ion-permeable, gas-impermeable inter-electrode diaphragm (challenge (iii) above) also proved unnecessary in the AFC because the high bubble points (>1 atm) of the particulate-coated Gortex electrodes (Table 1) essentially eliminated the likelihood of gas bubbles forming in the aqueous electrolyte during operation. Without gas bubbles to keep separate, there was no need for a diaphragm. To assess the susceptibility of the cell to CO\textsubscript{2} poisoning ((iv) above), we also operated it in open air with air
oxygen passing through the cathode gas chamber. No difficulties arising from CO$_2$ uptake with accompanying carbonate precipitation were observed in the Gortex electrodes. This was likely due to the small size and strongly hydrophobic nature of the Gortex pores combined with the overpressure of the electrolyte. Carbonate crystallite formation would likely have had to occur in a confined, very hydrophobic environment (the Gortex pores) to which such crystallites could not easily adhere. For this reason, the instead crystallites remained in the aqueous 6 M KOH electrolyte, which slowly became progressively cloudy.

2.7 Fuel Cell Performance with Gortex Gas Diffusion Electrodes Coated with 10%Pt/carbon black/PTFE/Ni mesh. The Gortex gas diffusion electrodes coated with 10% Pt on Vulcan XC72, carbon black, PTFE binder and a Ni mesh were systematically optimized by testing them in the above AFC. The Supporting Information describes these optimization experiments (Figure S3). The optimum electrodes proved to contain catalyst loadings of 0.075 mg/cm$^2$ Pt. This loading was substantially lower than that of, for example, PEM fuel cells, which typically employ >0.3 mg Pt/cm$^2$.

Figure 8(a) depicts polarization (left axis) and power density (right axis) curves for the cell incorporating the optimized electrodes. Figure 8(b) depicts the equivalent circuit used to model the corresponding two-electrode electrochemical impedance spectrum in the form of a Nyquist plot (Figure 8(c)) and Bode plot (Figure 8(d)), measured galvanostatically at 10 mA/cm$^2$.26
Figure 8. (a) Polarization curve (left axis) and power density curve (right axis) at 20 °C for alkaline fuel cells containing Gortex electrodes coated with 10% Pt on Vulcan XC72, carbon black, PTFE, and woven Ni mesh. Electrolyte: 6 M KOH. (b) Equivalent circuit. (c) Nyquist and (d) Bode plots at 10 mA/cm², showing measured data (individual data points) and modelled data (solid line). The modelled data used the equivalent circuit shown in (b).
As can be seen, the above gas diffusion electrodes generated 230 mA/cm\(^2\) and 84 mW/cm\(^2\) at 0.35 V at room temperature. At 0.7 V, the cell produced 75 mA/cm\(^2\). When operated at a fixed 10 mA/cm\(^2\), the cell produced a constant 0.857-0.860 V over 2 d of continuous operation (Figure S4). The minor fluctuations in the voltage observed during that period appeared to be associated with temperature variations in the external environment, including when the fume hood was opened and closed.

Because of the paucity of research on liquid electrolyte alkaline fuel cells, only a few reports of comparable AFC polarisation curves are available. The above results compare favourably, however, with those previously reported for liquid electrolyte alkaline fuel cells, especially when considering their low Pt loading, room temperature operation, the atmospheric pressures of the feedstock gases, and the overpressure of the liquid electrolyte. For example, Strasser and co-workers recently described a high performing Pt-based liquid electrolyte alkaline fuel cell that generated ca. 58 mA/cm\(^2\) at 0.7 V at room temperature using 0.2 mg Pt/cm\(^2\), which is about triple the Pt loading of the present study\(^{27}\). Gouérec and co-workers at Eident Energy built liquid electrolyte alkaline fuel cells employing a 9-fold higher Pt loading than the present work (0.6-0.7 mg Pt/cm\(^2\) at both the anode and cathode), that yielded ca. 55 mA/cm\(^2\) at 0.7 V when operated at 65 °C\(^{28}\). Kiros and colleagues\(^ {29}\) and Kordesch and colleagues\(^ {30}\) reported liquid electrolyte alkaline fuel cells that delivered 88-125 mA/cm\(^2\) and 125-160 mA/cm\(^2\), respectively, at 0.7 V when operated at 80 °C with gases applied at high pressures\(^ {2-4}\). The Pt loadings were not given in these works however Tomantschger and co-workers have shown that increases in temperature and gas pressures amplify current and power densities in liquid electrolyte alkaline fuel cells\(^ {3}\).
It should be noted that alkaline exchange membrane (AEM) fuel cells with much smaller inter-electrode gaps, are capable of producing much higher current and power densities than liquid electrolyte alkaline fuel cells.\textsuperscript{31,32} For example, AEM fuel cells exhibiting $>1.0$ A/cm\textsuperscript{2} at 0.7 V have recently been reported.\textsuperscript{31,32} PEM fuel cells are capable of even higher current and power densities, in the range of $>1.5$ A/cm\textsuperscript{2} at 0.7 V.\textsuperscript{33} These performances are typically achieved with higher Pt loadings (typically $>0.25$ mg/cm\textsuperscript{2}) and much smaller inter-electrode gaps (typically $<0.25$ mm).\textsuperscript{31-33}

The EIS data of the above fuel cell was modelled using the equivalent circuit depicted in Figure 8(b).\textsuperscript{34-37} The individual data points in Figure 8(c) show the data as measured, while the solid lines in Figure 8(c) show the modelled data. As can be seen, an excellent fit of the modelled and the measured data was achieved. The modelling results are listed in Table 3.

<table>
<thead>
<tr>
<th>Catalyst Layer</th>
<th>Activation overpotential (V)</th>
<th>Voltage at 10 mA/cm\textsuperscript{2} (V)</th>
<th>$R_o$ ($\Omega$ cm\textsuperscript{2})</th>
<th>$R_t$ ($\Omega$ cm\textsuperscript{2})</th>
<th>$C_t$ (F)</th>
<th>$Z_d$ ($\Omega$ cm\textsuperscript{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>10% Pt on Vulcan, carbon black, PTFE, weaved Ni mesh</td>
<td>0.375</td>
<td>0.857-0.860</td>
<td>0.79</td>
<td>0.31</td>
<td>0.000098</td>
<td>3.4</td>
</tr>
</tbody>
</table>

Table 3. Electrochemical Impedance Spectroscopy modelling data for ohmic resistance ($R_o$), charge transfer resistance ($R_t$), charge transfer capacitance ($C_t$) and diffusion resistance ($Z_d$) of the alkaline fuel cell containing Gortex electrodes coated with 10% Pt on Vulcan XC72, carbon black, PTFE, and Ni mesh. Electrolyte: 6 M KOH. The equivalent circuit in Figure 8(b) was used to model the EIS data.

The data in Table 3 demonstrate notable performance. The charge transfer resistance ($R_t$ 0.3 $\Omega$ cm\textsuperscript{2}) and diffusion resistance ($Z_d$ 3.4 $\Omega$ cm\textsuperscript{2}) are low. The ohmic resistance ($R_o$ 0.79 $\Omega$ cm\textsuperscript{2})
was also close to the expected resistance of 0.5266 Ω cm² for a 6 M KOH solution at 20 °C over a 3 mm inter-electrode gap. The activation overpotential, which corresponds to the hypothetical y-axis intercept of the ohmic region of the polarisation curve, was 0.375 V. The hydrophilicity of the particulate coating on the Gortex was clearly essential to the performance of the cell.

Most significantly, the coated Gortex proved to be efficient, leak-free gas diffusion electrodes for both hydrogen and oxygen-depolarization under conditions where the liquid electrolyte was subjected to a substantial overpressure of 0.5-1.5 atm. The liquid overpressure had a negligible effect on their catalytic activity, as evidenced by the fact that their performance was, essentially, unaffected by the size or presence of the liquid overpressure. These results are notable in light of the impediment that flooding and leaking has been to the deployment of gas diffusion electrodes in industrial electrochemistry.5-7

It is also significant insofar as the half-reaction at the cathode of the above fuel cell (equation (3)) is identical to the half-reaction at an O₂-depolarized cathode in a chlor-alkali cell (equation (S3)) as previously described. Both systems moreover employ strongly basic liquid electrolytes (26.8 wt% KOH vs. 25-35 wt% NaOH), meaning that the above Gortex-based electrodes may be expected to have practical utility as the cathode in a chlor-alkali cell. We will report on this matter in greater detail in future work. Present-day industrial chlor-alkali cells typically operate at relatively low current densities.

3. CONCLUSIONS

This work has sought to address the hitherto intractable challenge of flooding and leaking that has hindered the widespread adoption of gas diffusion electrodes in many
electrochemical manufacturing cells. A new approach has been developed in which the gas diffusion layer of such electrodes has been optimized in terms of water-repellence (for leak-resistance) and porosity (for gas transport) but not electrical conductance (for electron transport), which has, instead, been provided by other means.

*Gortex* membranes are known to be near-ideal in respect of water-repellence and porosity. In this work, they were studied, in finely-pored form, as gas diffusion layers within novel gas diffusion electrodes. Gortex electrodes coated with 10% Pt on Vulcan/PTFE/Ni mesh were found to display hitherto unprecedented water-entry pressures, demonstrating a remarkable resistance to flooding and leaking. Capillary flow porometry showed them to leak only when the excess of pressure on their liquid-sides over their gas-sides was an astonishing 5.7 atm. When deployed in a desktop alkaline fuel cell charged with aqueous 6 M KOH electrolyte pressurised to 0.5-1.5 atm above the gas reactants, they generated notable current and power densities (230 mA/cm$^2$ and 84 mW/cm$^2$, respectively, at 0.35 V) in line with, or exceeding those achieved by alkaline fuel cells in general, as a class of fuel cell. This was accomplished with unusually low Pt loadings (0.075 mg/cm$^2$) during room temperature operation and with the gases at atmospheric pressure. The fuel cell, moreover, appeared to overcome all of the key technical challenges that have hindered the adoption of alkaline fuel cells to date.

4. **EXPERIMENTAL**

4.1 **Materials.** The following materials were employed (supplier): Carbon black (AkzoNobel) (washed with ascorbic acid before use), 10% Pt on Vulcan XC72 (Premetek Co. # P10A100),
Poly(tetrafluoroethylene) (PTFE) (60 wt.% dispersion in alcohols/H$_2$O; Sigma-Aldrich #665800), KOH 90%, flakes (Sigma-Aldrich #484016), woven Ni mesh, 200 LPI, supplied by Century Woven (Beijing) (cleaned using isopropyl alcohol prior to use), and conductive, adhesive copper tape (6.35 mm wide) (3M). Polypropylene-backed Preveil Gortex membranes with specified water-entry pressures of >4 atm, produced by General Electric Energy were used in all experiments. Cross-sections for optical microscopy were prepared by sectioning and polishing samples fixed in Epo-fix resin using the cold mounting technique of Struers, Ballerup, Denmark.

4.2 Preparation of Gortex Sputter-Coated with Pt. Pt nanolayers of different loadings were sputter-coated onto the membranes under argon atmosphere, using suitable targets. The rate of deposition of the metal coating was controlled by a thickness monitor, which used a QCM crystal to determine the build-up of material within the sputter chamber. Sputter conditions were 40 W, with argon flow maintained at ~100 kPa.

4.3 Preparation of Gortex Coated with Particulate Catalyst. The particulate catalyst layers were prepared as a slurry, by weighing out catalyst (10% Pt on Vulcan XC72) and carbon black into a 20 mL vial, purging with N$_2$ for ca. 2 min to remove air, then adding isopropyl alcohol (IPA) and water. The mixture was sheared using a homogeniser (IKA T25) with dispersing element (IKA S 25 N – 18 G) at 10,000 rpm for 5 min. PTFE aqueous dispersion was then added dropwise with continuous shearing. After all of the PTFE was added, shearing at 10,000 rpm was continued for another 5 min.

The resulting catalyst slurry was drop-cast onto the ePTFE side of the Gortex membranes (24 mm x 24 mm membrane pieces) and spread out into a square shape measuring ca. 12 mm x 12
mm as depicted in Figure S5 in the Supporting Information. Nickel mesh, which had been laser cut to dimensions 12 mm x 12 mm for the square part with an attached 4 mm x 34 mm neck, was laid on top of the wet slurry and pushed down gently using tweezers to ensure even wetting. Membrane/slurry/mesh assemblies were allowed to dry under ambient conditions.

The dried membrane/slurry/mesh assemblies were compacted using a double-roll mill, having metal rollers. After drying, membrane/slurry/mesh assemblies were rolled three-times through a gap equal to 0.1 mm plus the mesh thickness. For the woven mesh used, a roller gap of 0.1 mm + 0.15 mm = 0.25 mm was set. As the membrane was ca. 0.2 mm thick, the membrane/slurry/mesh assemblies were compressed by 0.1 mm during rolling.

After rolling, the membrane/slurry/mesh assemblies were weighed. These values were used, together with the weight of the membrane (pre-measured before applying catalyst) and the weight of the mesh (pre-measured before use) to calculate the catalyst loading and the PTFE loading. In the optimum electrode, the catalyst loading was, on average, 0.075 mg/cm² Pt and the PTFE loading was 40% by weight.

4.4 SEM Microscopy, Porometry and Contact Angle of the Coated Gortex Membranes.

The coated membranes were imaged using a JSM-7500F scanning electron microscope (SEM). A CFP-1200-AEXL Capillary Flow Porometer from PMI Porous Materials Inc, integrated with PMI Capwin software, was used to characterize the coated membranes. The hydrophobicity of the membrane electrodes were characterized using a contact angle system from Data Physics. A drop of water was carefully placed on the surface of the membrane and the contact angle was measured with the help of an optical scope.
4.5 Electrode Preparation. Electrodes were prepared by mounting the coated Gorex membranes, with associated Ni mesh, in a plastic (PET) laminate that became rigid after hot lamination by passing through a stationery-store laminator.

After weighing, each dried electrode was mounted in a pre-cut, folded PET laminate of the type available in stationery stores. The laminate was first cut, using a laser cutter, to a design depicted in Figure S6, which included a 1 cm x 1 cm window in each side.

Membranes that had been coated with particulate catalyst, binder and Ni mesh, were placed inside the folded-over laminate such that the membrane/catalyst/mesh was located in the middle of the window (as depicted in Figure S6). The resulting assembly was then fixed in place by carefully passing it through a commercial hot laminator of the type found in stationery stores.

Using the above technique, both sides of the catalyst-coated Gorex membrane remained open and exposed, within the window in the laminate. A small piece of conductive copper tape was attached over the terminus of the neck of the Ni as an electrode contact (see Figure S6).

The 10 mm x 10 mm window in the laminate limited the geometric area of the electrode to 1 cm².

4.6 Cell Construction. Stainless steel and polymeric test cells were custom-built to match the dimensions of the laminated electrodes. Figure S7 depicts a photograph and a cross-sectional schematic of one such cell, showing how the laminate-mounted electrodes were placed between the three components of the cell, which were then bolted together using twelve, edge-arrayed screws / bolts. Each laminate-mounted electrode was placed in the cell such that the exposed, windowed catalyst-mesh side faced inwards, toward the opposing electrode, and the uncoated back of the Gorex faced outwards. The cell was assembled using a 3 mm spacer between the electrodes.
The gas connections were made using gas-tight fittings. The central cavity of the cell was filled with 6 M KOH. The cell was tested in a fume hood to ensure that hydrogen and oxygen were safely released from the cell.

4.7 Cell Polarization Measurements and Electrochemical Impedance Spectroscopy. On either sides of the central reservoir in the above test cell, behind the Gortex-based electrodes, were liquid- and gas-tight chambers, through which hydrogen (ultra-high purity grade, compressed, supplied by BOC) and oxygen (high purity grade, compressed, supplied by BOC) were slowly passed at atmospheric pressure. Fuel cell polarization measurements were conducted at room temperature (20 °C). Electrochemical measurements were carried out as a two-electrode system in which the anode (hydrogen side) was connected as the working electrode and the cathode (oxygen side) was connected as a combined auxiliary/reference electrode. All reported voltages are therefore against O₂.

Tests of each cell commenced with a measurement of its Open Circuit Voltage (OCV). Thereafter, the cells were characterized by Linear Sweep Voltammetry (LSV), and Potentiostatic-Electrochemical Impedance Spectroscopy (PEIS) and/or Galvano-Electrochemical Impedance Spectroscopy (GEIS). Fuel cell polarization curves were obtained by the LSV technique, with voltage typically scanned from a lower to an upper limit at scan rates of 10 mV/s. To eliminate the effects of capacitive charging, chronoamperometry experiments were also conducted and compared to the LSVs. These provided the steady-state current at particular voltages over time and, when plotted as a polarization curve, proved to match the LSV-based polarization curves. EIS was used to analyze frequency-dependent losses in the tested fuel cells. For the PEIS experiments (fuel cells utilizing Gortex membranes sputter-coated with Pt), an AC perturbation of 10 mV
amplitude was applied from 1 MHz to 0.2 Hz at 0.8 V DC bias. For the GEIS experiments (fuel cells utilizing particulate-coated Gortex membranes), the same perturbation was applied at 10 mA/cm².

ASSOCIATED CONTENT

Supporting Information

The supporting information is available free of charge on the ACS publications website at …

Description of and half-reactions for the phenomenon of gas depolarisation, as used in electrochemical manufacturing. Schematic depiction of the output of a capillary flow porometry experiment. TEM image of the catalyst employed. Graphs depicting optimization experiments for the 10%Pt on Vulcan XC72 electrodes. Chronopotentiogram over 2 d of the test fuel cell. Schematics depicting the preparation, mounting, and use of Gortex electrodes in the test fuel cell.

AUTHOR INFORMATION

Corresponding Author

*Email: Swiegers@uow.edu.au

ORCID

G. F. Swiegers 0000-0002-4713-6090

Notes
Portions of this work are drawn from the PhD thesis of PT.

GT and GFS declare part-time work with the industry partner for the grant that funded this work.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge support under Australian Research Council (ARC) Linkage Grant LP130101135 and from industry partner, AquaHydrex Pty Ltd. PT gratefully acknowledges an ARC Post-Graduate Award (APA). Support from the ARC Centre of Excellence Scheme (Project Number CE140100012) is gratefully acknowledged. The authors acknowledge use of facilities and the assistance of Tony Romeo and Gilberto Casillas-Garcia within the University of Wollongong Electron Microscopy Centre. This research used equipment funded by ARC – Linkage, Infrastructure, Equipment and Facilities (LIEF) grant LE160100063 located at the University of Wollongong Electron Microscopy Centre. The authors thank the Australian National Fabrication Facility (ANFF) Materials Node for equipment use and for design and printing of custom-built parts.

REFERENCES


(2)  For alkaline fuel cell gas diffusion electrodes, see: (a) Liu, J.; Yang, C.; Liu, C.; Wang, F.; Song, Y. Design of Pore Structure in Gas Diffusion Layers for Oxygen Depolarised


