Catalyst supports for polymer electrolyte fuel cells

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A major challenge in obtaining long-term durability in fuel cells is to discover catalyst supports that do not corrode, or corrode much more slowly than the current carbon blacks used in today’s polymer electrolyte membrane fuel cells. Such materials must be sufficiently stable at low pH (acidic conditions) and high potential, in contact with the polymer membrane and under exposure to hydrogen gas and oxygen at temperatures up to perhaps 120°C. Here, we report the initial discovery of a promising class of doped oxide materials for this purpose: Ti1−xMxO2, where M = a variety of transition metals. Specifically, we show that Ti0.7W0.3O2 is electrochemically inert over the appropriate potential range. Although the process is not yet optimized, when Pt nanoparticles are deposited on this oxide, electrochemical experiments show that hydrogen is oxidized and oxygen reduced at rates comparable to those seen using a commercial Pt on carbon black support.

Keywords: fuel cells; oxides; catalyst supports; nanoparticles; conductivity

1. Introduction

Fuel cells were invented about 170 years ago by Sir William Grove (Grove 1839). Nonetheless, the promise of generating electricity at high efficiency from the electrochemical reaction of a fuel and oxygen has remained elusive. Widely used technologies, such as combustion of fossil fuels or heat from nuclear reactors, rely on thermal cycles to generate steam to power turbines and connected generators. Because the efficiency of these systems is limited by the second law of thermodynamics to the Carnot limit (max. efficiency = (T_hot − T_cold)/T_hot), current power plants are about 35 per cent efficient, rejecting about 65 per cent of the heat to the environment. This efficiency is limited by the materials available that can reliably withstand T_hot and last for many years of operation. Technologists believe that even the most advanced materials possible can only extend the efficiency of thermal power plants to 50 per cent at best. However, while not a common practice, the overall efficiency can be increased by using the waste heat in co-generation systems.

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One contribution of 13 to a Discussion Meeting Issue ‘Energy materials to combat climate change’.

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In contrast, fuel cells are the only known method of potentially converting fuels to electricity at nearly 100 per cent efficiency. The free energy of any redox reaction could theoretically be completely converted to electrical energy. In thermal systems, efficiency is determined from the fraction of the enthalpy of the reaction that is converted, as limited by Carnot considerations and inefficiencies in the process. A direct comparison of the efficiencies of the two different systems (thermal and fuel cell) must include the difference between the free energy and the enthalpy: namely $T\Delta S$ ($T$ is the absolute temperature and $\Delta S$ the change in entropy).

Because of the promise of high efficiency, many potential fuel cell technologies have been explored and are under development. These technologies are characterized by the temperature of operation and also by the fuels that can be used in that technology. We focus here on so-called polymer electrolyte membrane fuel cells (PEMFC) that operate at or near room temperature. These fuel cells are currently being developed for possible use in automobiles and for a variety of portable applications. There are still many challenges to be overcome if any of the fuel cell technologies are to be widely deployed, including PEMFCs. This work concerns the development of more durable catalyst supports for PEMFCs.

Current PEMFC technology uses carbon black as a catalyst support. The particular blacks used have been optimized to bind 3–5 nm platinum catalyst nanoparticles and are conducting enough to transport charge to and from the catalyst. The carbon morphology is also important in supporting open porosity in the electrodes, so that fuel or oxidant can enter and product gases can escape. Typically the carbon black forms an open interconnected network of 50–100 nm particles.

However, the carbon black catalyst support corrodes too rapidly, especially under transient load and on/off operation conditions (Mathias et al. 2005; Borup et al. 2007; Cheng et al. 2007; Gasteiger et al. 2007; Bagotsky 2009). Carbon, in any form, is thermodynamically stable below about 0.2 V, but only kinetically stable above that potential ($C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^-$, $E^\circ = 0.207$ V). However, under fuel starvation conditions in a fuel cell stack, even the anode of a single cell can be forced to a high potential (up to +1.5 V), as oxidation of the carbon is the only process that can support the imposed stack current (Bagotsky 2009). In fact, no single metal is thermodynamically stable at such potentials in acidic aqueous media (Pourbaix 1974). Gold has the highest reduction potential at 1.5 V versus SHE (standard hydrogen electrode) and will dissolve at lower potentials if the concentration of gold cations in solution is low—as it would be in a PEMFC. Of course, the expense of gold precludes it being used as a catalyst support if fuel cells are to be widely used. Other metals either dissolve as cations or less frequently form chemically passivating and electrically insulating oxide coatings at high potentials. Under alkaline conditions, soluble metal-containing oxo-anions or passivating oxide/hydroxide layers usually result. Since the free energy of formation of intermetallic compounds is usually small compared with that of the respective oxides of the same metals, the result is not much different when intermetallic compounds are exposed to such highly oxidizing conditions. The mechanisms of oxidation will probably be more complex for intermetallics—e.g. leaching and oxidation of the more electropositive element is likely to occur first (Sieradzki 1993;
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Wagner et al. 1997; Dimitrov et al. 1999, 2000; Erlebacher et al. 2001; Sieradzki et al. 2002; Erlebacher & Sieradzki 2003; Hayes et al. 2006; Rugolo et al. 2006; Salgueirino-Maceira et al. 2006; Thorp et al. 2006)—but the end result is expected corrosion.

If stability (or sufficient metastability) in air/water is desired, then one should look to oxides in which metals are already near or in their highest oxidation state. Materials based on other anions, such as sulphides, carbides and nitrides, will thermodynamically prefer to oxidize or hydrolyse to oxides, at least at the surface. Depending on the material and conditions (pH, temperature, other ions in solution, etc.), the oxidation or hydrolysis of these other classes of materials will form surface reaction layers from a few nanometres thick to completely consuming the material. Since we are considering support materials that are randomly or periodically ‘structured’ on the nano- or mesoscale, the design and control of the surface layer will determine whether these materials can be used in fuel cells. In any case, it is clear that, at least in the cathode, the essential catalyst and catalyst support surface are some form of oxide/hydroxide.

The key issues in considering oxides for cathode catalyst supports are: (i) structural and electronic (meta)stability of the bulk as well as the surface at the potentials and pH of use, and (ii) bulk and surface electronic conductivity. There are so few binary oxides that are insoluble at low pH and high potential that they can be listed: TiO$_2$, Nb$_2$O$_5$, Ta$_2$O$_5$ and WO$_3$ (Pourbaix 1974). Hydrated forms of these oxides, prepared from aqueous solution, may be less stable at certain pH or potentials, but we consider here the more stable structures, such as the rutile form of TiO$_2$. However, none of the above oxides is electronically conducting. A conductivity of 0.1 S cm$^{-1}$ is all that is needed for catalyst supports (Gasteiger 2007; Wagner et al. 2009).

We also anticipate that oxide supports could interact synergistically with the catalyst to improve catalyst performance, as has been observed for NbO$_2$ (Sasaki et al. 2008).

Based on the high stability of TiO$_2$ in water over a broad range of pH (−1 to 14) and from low to high potential (the actual range is pH-dependent), as indicated by the Pourbaix diagrams (Pourbaix 1974), and as observed in devices such as Graetzel photovoltaic cells (O’Regan & Graetzel 1991; Burke et al. 2008), it seemed likely that some form of doped TiO$_2$ materials might be both electrically conducting and quite resistant to corrosion under fuel cell conditions, especially in fuel cells operating near ‘room temperature’ (Gerstner 1979).

It is known that rutile (TiO$_2$) can be doped with other cations to prepare Ti$_{1-x}$M$_x$O$_2$, where M = Zr, Hf, V, Nb, Ta, Cr, Mo, W, Ru, Os, Ir and Sn, and some of these oxides have been evaluated in electrochemical environments (Chang 1968; Sakata et al. 1969; Horkans & Shafer 1977; Pejryd 1986; Smith et al. 1998; Murata et al. 2000; Roy et al. 2000; Chen et al. 2003; Colomer & Velasco 2007; Garcia et al. 2007; Sasaki et al. 2008). In this paper, we discuss the preparation and properties of W-doped TiO$_2$ (rutile phase: Ti$_{1-x}$W$_x$O$_2$) and explore the preparation and use of 50 nm nanoparticles suitable for catalyst supports. The preparation of Ti$_{0.53}$W$_{0.47}$O$_2$ by high-temperature methods has been previously reported (Peters & Mueller-Buschbaum 1996), so we had some confidence that we could prepare a variety of compositions and produce nanoparticles with sufficient porosity for our purposes. While we are also examining Nb$_2$O$_5$, Ta$_2$O$_5$ and WO$_3$ as doping hosts for catalyst supports, they are more difficult to dope to the metallic
state while keeping the host structure (at least at high temperatures) and they have more open structures, perhaps allowing easier access to water or $H^+$, as in $H_xWO_3$. While we will explore all these systems, for discussion purposes, we focus here only on the TiO$_2$ host.

2. Synthesis

While we have prepared nearly single-phase powder of Ti$_{1-x}$W$_x$O$_2$ by hot pressing stoichiometric reactants under an argon atmosphere in a graphite furnace at 1400–1500°C, we have found a lower-temperature method to be more convenient. Sealing the appropriate ratio of precursors in a silica tube is sufficient to fix the oxygen stoichiometry during synthesis, e.g. at 1100°C with a halide transport agent such as chlorine: $(1 - x)TiO_2 + (2x/3)(0.5W +WO_3) \rightarrow Ti_{1-x}W_xO_2$. Typically 8–10 g of product can be prepared in a 16 mm internal diameter sealed silica tube (about 20 cm in length) containing only about 10 mg of hexachlorobenzene. The hexachlorobenzene decomposes at elevated temperatures to release chlorine, which is a suitable chemical transport agent under these conditions (Schafer 1964). The powder produced by this method is largely agglomerates of small single crystals with dimensions between 1 and 20 μm. We have determined that the maximum doping ($x_{\text{max}}$) that retains the single-phase rutile structure is greater than 50 per cent for W.

For use as catalyst supports in fuel cells, this preparation method produces particles that are much too large. In order to produce 50–100 nm nanoparticles of the desired composition, a multi-step process has been developed. Titanium tetra-isopropoxide and tungsten hexa-ethoxide are weighed out in an argon atmosphere glove box and dissolved in diglyme, and added to a solution of citric acid and glycol. After mixing without exposure to air, the solution is poured into a Petri dish and put into an oven in air and heated to 160°C for several hours. The resulting dark, pliable mass is transferred to an alumina container and calcined at 450°C for up to 12 h. The product at this point is a free-flowing, white to light tan powder. The X-ray diffraction pattern is weak and nearly amorphous with maxima near the peaks expected for the anatase form of TiO$_2$.

At this point, the W is fully oxidized (6+), and needs to be reduced. This is accomplished by sealing the degassed calcined product in a silica tube with a thin foil of Zr metal contained in a small silica capsule. Stoichiometric amounts of Zr are used to form ZrO$_2$ and reduce the W to 4+ when heated to 700–800°C (Marezio et al. 1989). The particle size is determined by the time and temperature of heating, while particle morphology and connectivity can be changed by varying the solvents and coordinating ligands used in the first step of the procedure.

Pt nanoparticles were deposited on the nanoscale Ti$_{1-x}$W$_x$O$_2$ powders by two different methods. The first was accomplished by suspending the oxide in a degassed methanol solution of H$_2$PtCl$_6$ and then reducing the solution with an excess NaBH$_4$, all under an N$_2$ purge. The powder was dried and then annealed under N$_2$ gas flow at 300°C for several hours. In the second approach, Dr Michael Carpenter at GM Research Laboratories deposited Pt from an aqueous solution of 1.54 g Pt(NH$_3$)$_2$(NO$_2$)$_2$ in 222 ml water by reduction with hydrazine (0.49 g in water) at pH 3.0 (adjusted by adding acetic acid) and under continuous diffuse
sparging with CO for 120 min (Tsurumi et al. 1996). While neither process has been optimized for deposition on oxide supports, Pt was clearly deposited as seen by the electrochemical behaviour (see below).

3. Characterization

Figure 1 shows a powder X-ray diffraction pattern of a sample at $x = 0.30$ that was heated for 10 days at 1100°C. The pattern can be completely indexed with a tetragonal unit cell: $a = 4.682(1)$ Å, $c = 2.903(1)$ Å, vol. = 63.66 Å$^3$. The lattice parameters of pure TiO$_2$ are $a = 4.593$ Å, $c = 2.956$ Å, with $Z = 2$ and vol. = 62.42 Å$^3$ (Cromer & Herrington 1955), while WO$_2$ has a distorted rutile structure (monoclinic) that shows pronounced W–W pair formation with a volume of 65.43 Å$^3$ for two formula units (Palmer & Dickens 1979). The lattice parameters vary linearly with $x$: the $a$-axis expands while the $c$-axis contracts due to W–W pair formation that occurs even in the doped TiO$_2$ (Aryanpour et al. 2009). However, the unit-cell volume increases linearly with the W content.

The Ti$_{1-x}$W$_x$O$_2$ produced by the low-temperature citric acid method is also single phase, as determined by X-ray powder diffraction (figure 2). The X-ray peaks are broad, due either to the nanoscale size of the oxide crystallite domains or possibly to small compositional inhomogeneity. Assuming uniform composition, the domain size calculated by the Scherer equation for this pattern is $20 \pm 2$ nm. An SEM picture (figure 3) of the particles prepared at $x = 0.3$ shows the desired particle size and an open network of interconnected particles. The smallest particles visible are consistent with the domain size determined by X-ray diffraction.

An electrical conductivity of approximately $10^2$ S cm$^{-1}$ is observed in pressed powders of Ti$_{1-x}$W$_x$O$_2$ prepared by the high-temperature method at $x = 0.3$, even though the expected percolation limit for near-neighbour W–O–W connectivity is near $x = 0.5$ (Zallen 1983). Density functional theory calculations by Hoffmann and co-workers predict metallic conductivity owing to the overlap of occupied W 5d orbitals with neighbouring O and Ti (Aryanpour et al. 2009).

The stability of the Ti$_{1-x}$W$_x$O$_2$ powders to oxidation or dissolution was first tested on the large-grain materials prepared at high temperature by adding a few millilitres of 1–2 M nitric acid to a small amount (50–100 mg) of powder in a capped vial. While TiO$_2$ powder does not dissolve, as expected from the Pourbaix diagram, purplish black WO$_2$ powder is oxidized in several days to a light green powder of WO$_3$ under the same conditions. On the other hand, even at $x = 0.5$, the black Ti$_{1-x}$W$_x$O$_2$ powders do not change colour after more than one year in acid. We surmise that the TiO$_2$ framework imparts kinetic stability to the ‘trapped’ W(4+) oxide. It is probable that W at the particle surface is oxidized even by exposure to air, but this oxidized layer is apparently very thin.

We have also tested the stability of the nanosized Ti$_{1-x}$W$_x$O$_2$ powders in a variety of acids and in a solution containing Nafion, the acidic membrane material. In contrast to the results obtained with micrometre-sized crystals, we found some corrosion in a variety of acids, especially in H$_2$SO$_4$, but not in the Nafion solution. While the latter observation is encouraging, detailed electrochemical testing is needed. Our initial results from such testing are presented next.

Phil. Trans. R. Soc. A (2010)
Figure 1. The X-ray diffraction pattern of Ti$_{0.7}$W$_{0.3}$O$_2$ produced by the high-temperature (1100$^\circ$C) method described in the text. The peaks are indexed to a tetragonal unit cell, but are shifted slightly from that of rutile (Powder Diffraction File, PDF no. 001-072-4812) due to the substitution of W for Ti.

Figure 2. The X-ray diffraction pattern of Ti$_{0.7}$W$_{0.3}$O$_2$ produced by the low-temperature citric acid method shows a single-phase product. The broad lines indicate small crystallite domain sizes of the order of 20nm in size.

The Ti$_{1-x}$W$_x$O$_2$ nanopowders were sonicated in a 5wt% ethanol solution of Nafton (added as a binder) and then a drop of the solution was put on a glassy carbon electrode and dried in air prior to rotating disc electrochemical (RDE) studies. The important electrochemical window for a fuel cell is from 0 to 1.2V versus the standard hydrogen electrode (SHE). As shown in figure 4, when the sulphuric acid solution (pH = 1) is degassed with argon, the oxide is not electrochemically active from $-0.25$V to above 1.2V versus an Ag/AgCl reference electrode ($+0.20$V relative to SHE). The reduction of H$^+$ begins below $-0.5$V versus Ag/AgCl, implying a 0.30V overpotential for that process. The
Figure 3. An SEM image of Ti$_{0.7}$W$_{0.3}$O$_2$ prepared using the low-temperature citric acid method shows the desired open network of small particles ranging from 20 to 100 nm in size. Scale bar, 200 nm.

Figure 4. The electrochemical behaviour of Ti$_{0.7}$W$_{0.3}$O$_2$ prepared using the low-temperature citric acid method and deposited on a glassy carbon (GC) electrode shows no electrochemical activity in oxygen-free 0.1 M H$_2$SO$_4$ between $-0.5$ and $+1.5$ V (versus Ag/AgCl, which is $+0.2$ V positive of the standard hydrogen electrode). Below $-0.5$ V small reduction currents suggest the reduction of W, perhaps accompanied by the intercalation of H$^+$. When the solution is saturated with oxygen, the oxygen is reduced at potentials below 0 V. This potential is far below that for reversible oxygen reduction (by 1.0 V). The observed electrochemical behaviour poses no problems for the use of this oxide as a catalyst support at either the anode or the cathode potentials expected in fuel cells. Curves: dotted line, bare GC, Ar saturated; solid line, Ti$_{0.7}$W$_{0.3}$O$_2$ coated GC, Ar saturated; dashed line, Ti$_{0.7}$W$_{0.3}$O$_2$ coated GC, O$_2$ saturated.

small oxidation current seen above 1.2 V is due to the oxidation of the glassy carbon electrode. When oxygen is present in the solution, it is apparent that the O$_2$ is reduced at potentials below $-0.20$ V versus Ag/AgCl. Given that this potential is above the reduction potential of H$^+$, the probable product is peroxide.
or water. This potential is much too low to be of interest for a fuel cell and occurs at potentials below those expected even at the anode. These data show at least short-term (meta)stability of Ti$_{0.7}$W$_{0.3}$O$_2$ in the potential range of fuel cell operation.

Next, Pt nanoparticles were deposited on the oxide and both hydrogen oxidation and oxygen reduction were studied. Figure 5 shows the oxidation of hydrogen (H$_2$ saturated solution) on the oxide-supported Pt prepared by borohydride reduction in comparison to that obtained from commercial Pt on a Vulcan substrate. The curves are essentially identical. The reduction of oxygen (O$_2$ saturated solution) on two different oxide-supported Pt catalysts was carried out. The sample prepared by borohydride reduction showed poor performance, while the sample prepared by the above hydrazine reduction scheme showed activity that was very similar to the commercial Pt on Vulcan. We have yet to optimize the Pt deposition process, so these results are very encouraging.

4. Discussion

The long-term testing of Ti$_{1-x}$W$_x$O$_2$ in Nafion solutions suggests that these materials may have the desired durability to be a useful catalyst support in PEMFCs. Electrochemical testing of these oxides, both with and without deposited catalyst, further support this conclusion. However, more work needs to be done to show long-term stability under realistic fuel cell operating conditions. Further, the process for depositing the catalyst nanoparticles as well as the design of open porosity in the oxide network needs to be optimized.
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Of course, one would expect that mixed doping with two or more different metals (say M and M′) will be possible if the dioxides of the metals are separately soluble in TiO$_2$. For example, Ti$_{1-(x+y)}$Nb$_x$W$_y$O$_2$ should readily form since both individual dopants can be included in TiO$_2$ at a very high level. Indeed, such multiply doped materials may have a superior combination of oxidation/corrosion resistance and conductivity; this is an obvious hypothesis that we will explore.

Finally, we have found that TiO$_2$ cannot be appreciably doped with transition metals that normally exhibit oxidation states of 3+ or below, as have others (Fleischhammer et al. 2009). However, Ti$_{1-x}$W$_x$O$_2$ can be doped with such elements. We find that the maximum content of such substitution occurs when the W is oxidized to 5+. For example, we have prepared single-phase rutile-structure materials such as Ti$_{0.7}$W$_{0.15}$Cr$_{0.15}$O$_2$ and Ti$_{0.7}$W$_{0.2}$Fe$_{0.1}$O$_2$, which contain Cr$^{3+}$ and Fe$^{2+}$, respectively. The preparation and properties of these materials will be the subject of another publication.

This work was supported by the Department of Energy through grant DE-FG02-87ER45298 and by a collaborative grant with General Motors Fuel Cell Division in Honeoye Falls, NY, through the New York State Energy and Research Development Authority (NYSERDA). Dr Fred Wagner and Dr Michael Carpenter of GM Research participated in very helpful discussions, platinized a sample of Ti$_{0.7}$W$_{0.3}$O$_2$ by the hydrazine method, and tested it for oxygen reduction using the rotating disc electrode method.

### References


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