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A novel non-platinum group electrocatalyst for PEM fuel cell application

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ABSTRACT

Precious-metal catalysts (predominantly Pt or Pt-based alloys supported on carbon) have traditionally been used to catalyze the electrode reactions in polymer electrolyte membrane (PEM) fuel cells. However as PEM fuel systems begin to approach commercial reality, there is an impending need to replace Pt with a lower cost alternative. The present study investigates the performance of a carbon-supported tantalum oxide material as a potential oxygen reduction reaction (ORR) catalyst for use on the cathode side of the PEM fuel cell membrane electrode assembly. Although bulk tantalum oxide tends to exhibit poor electrochemical performance due to limited electrical conductivity, it displays a high oxygen reduction potential; one that is comparable to Pt. Analysis of the Pourbaix electrochemical equilibrium database also indicates that tantalum oxide (Ta_2O_5) is chemically stable under the pH and applied potential conditions to which the cathode catalyst is typically exposed during stack operation. Nanoscale tantalum oxide catalysts were fabricated using two approaches, by reactive oxidation sputtering and by direct chemical synthesis, each carried out on a carbon support material. Nanoscale tantalum oxide particles measuring approximately 6 nm in size that were sputtered onto carbon paper exhibited a mass-specific current density as high as one-third that of Pt when measured at 0.6 V vs. NHE. However, because of the two-dimensional nature of this particle-on-paper structure, which limits the overall length of the triple-phase boundary junctions where the oxide, carbon paper, and aqueous electrolyte meet, the corresponding area-specific current density was quite low. The second synthesis approach yielded a more extended, three-dimensional structure via chemical deposition of nanoscale tantalum oxide particles on carbon powder. These catalysts exhibited a high ORR onset potential, comparable to that of Pt, and displayed a significant improvement in the area-specific current density. Overall, the highest mass-specific current density of the carbon-powder supported catalyst was 9% of that of Pt.

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1. Introduction

While substantial progress has been made over the past decade in optimizing the anode/cathode structures and the adjacent diffusion media and flow-field designs to reduce the amount of Pt needed in PEM fuel cell stacks, a five-fold

reduction in Pt loading is still needed for large-scale automotive applications [1,2] and little success has been achieved in identifying suitable alternatives. At present over 30% of the stack cost is directly attributable to the cost of the platinum catalysts employed in the electrodes [3], the majority of which is used in the cathode to catalyze the oxygen reduction

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reaction (ORR) shown in Equation (1) below. This reaction is known to be the rate determining step in cell operation and the cause of reduced energy efficiency due to a large associated over potential [4]:



Any viable replacement for Pt must possess the following characteristics: (1) good catalytic activity for the ORR, at least within an order of magnitude of that exhibited by Pt; (2) good electrical conductivity; (3) long-term stability under nominal cell operating conditions in the highly acidic aqueous environment of the stack; and (4) low cost. Arguably, the most restrictive of these requirements is the third. Over the past several decades, the search for non-precious-metal PEMFC cathode catalysts has included numerous candidates, including: transition metal carbides and nitrides (e.g. WC, Mo₂N), chalcogenides (e.g. Mo_{4.2}Ru_{1.8}Se₈ and W–Co–Se), and N₄-chleates (macrocycles such as iron phthalocyanine and cobalt tetramethoxyphenylporphyrin) [5–10]. However, only a few of these alternatives offer ORR onset potential and activities comparable to Pt, and those which come closest to Pt in terms of ORR catalytic activity fail to exhibit sufficient long-term performance stability. Even the most promising and thoroughly developed pyrolyzed metal porphyrins continue to display poor durability under practical fuel cell operating conditions [11–13].

The present study investigates the performance of a carbon-supported nanoscale tantalum oxide catalyst as an alternate ORR catalyst for PEM fuel cells. Although bulk tantalum oxide possesses poor electrochemical performance due to its limited electrical conductivity, it exhibits a high oxygen reduction potential (>0.95 V vs. RHE) that is comparable to Pt. Stability diagrams listed in the Pourbaix electrochemical equilibrium database [14] indicate that tantalum oxide (Ta₂O₅) is chemically stable under the pH and applied potential conditions to which the cathode catalyst is typically exposed during steady-state and transient fuel cell operation. In addition, tantalum oxide is substantially lower in cost than Pt, by over 2 orders of magnitude.

Ta₂O₅, as well as Nb₂O₅, received considerable attention several decades ago as potent alloying additions that enhance activity/selectivity and prolong life for various oxide catalysts employed in the selective oxidation of hydrocarbons [15]. Their use in electrocatalysts has been more limited, with primary interest focused on their corrosion stabilizing properties [16]. For example, Ta₂O₅ additions have shown preliminary synergistic improvements in carbon-supported Pt catalysts (speculated to be due to the preferential adsorption of OH groups to the oxide vs. the Pt surface) [17]. Ribeiro and Andrade [18] reported a significant increase in electrode lifetime when adding Ta₂O₅ to TiO₂/RuO₂-based catalysts used in oxygen evolution reactions (carried out under conditions similar to the PEMFC: 0.5 mol/dm³ H₂SO₄ at 80 °C and voltage sweeps of –0.2–1.2 V vs. RHE). Similarly, Bonakdarpour et al. [19] found that Ta markedly reduces the dissolution of Pt in sputtered Pt_{1–x}Ta_x alloy ORR catalysts by forming a thin Ta₂O₅ passivation layer. Unfortunately, the addition of Ta above ~10 at% also leads to a measurable decrease in ORR activity. The latter finding illustrates the key concern with these compounds and the reason why they have been largely

overlooked for ORR catalysis: they are not electrically conductive (at least in bulk form) at low-to-moderate temperatures [20]. This means that while there may be catalytic sites on the surface of the oxide, the ORR will be kinetically hindered because electronic transport is limited.

An obvious means of rectifying this problem is to mix the oxide with a chemically stable electronic conductor such as graphite. More specifically, the electrochemical performance of tantalum oxide can be enhanced by constructing robust triple-phase boundaries (i.e. regions where oxide, graphite, and aqueous electrolyte meet) that effectively serve as the reaction sites for catalysis. The number and length of these catalytic regions are maximized when the tantalum oxide is finely dispersed as a bonded phase on a high surface area graphitic or carbon support material. To determine the viability of this concept, tantalum oxide was deposited in discrete, nanoscale form on a typical PEM fuel cell grade carbon paper via reactive oxidation sputtering of a tantalum target. Once feasibility was shown with sputtered samples, a more typical powder form of the catalyst was synthesized using a liquid-phase chemical synthesis approach that employs tantalum ethoxide as the tantalum source [21]. The electrochemical properties of the sputtered and chemically synthesized carbon-supported tantalum oxide catalysts were compared with a commercial Pt catalyst.

2. Experimental

To demonstrate the concept of carbon-supported nanoscale tantalum oxide, tantalum oxide was deposited on 25.4 mm diameter discs of teflonized carbon paper (TGPH-090, E-TEK) using reactive oxidation sputtering. In this process, the tantalum metal is DC magnetron sputtered in an atmosphere containing a partial pressure of oxygen that is sufficient to support *in-situ* oxidation during deposition. The carbon substrates were mounted on a stationary water-cooled backing plate in the sputtering chamber, which was subsequently evacuated to 4×10^{-8} Torr. The substrate surfaces were ion cleaned for 5 min in 0.8×10^{-3} Torr argon. Ta sputtering was conducted under an atmosphere of 8 mTorr of Ar/10% O₂ at 0.3 A d.c., 290 V, which corresponds to an approximate deposition rate of 0.4 μm/h. It was found that discrete nanoscale tantalum oxide particles were deposited on the carbon support when sputtering was carried over relatively short time periods (1–5 min). In this way, the average particle size of the deposited tantalum oxide could be controlled in the range between 6–80 nm by adjusting both the time period for each sputtering “burst” and the total number of bursts, or aggregate sputtering time.

The powder form of the catalyst was prepared using a chemical synthesis approach that employed tantalum ethoxide [Ta(OEt)₅, 99.95%; Alfa Aesar] and nanoscale carbon powder (average particle size 30 nm, Asbury Carbons, Grade #: 5345R) that was functionalized with –OH groups using a previously reported procedure [21]. Nanoscale tantalum oxide particles form through direct reaction between the Ta(OEt)₅ and the functional groups on the surface of the carbon particles, a reaction that was carried out by initially dispersing 2.0 g of the functionalized carbon in 20 ml of ethanol (99.995%;

Table 1 – Electrochemical performance of sputtered nanoscale tantalum oxide.

Sample	Temperature (°C)	ORR potential (V)	Current Density (A/cm ²) @ 0.6 V vs. NHE	Current Density (A/g) @ 0.6 V vs. NHE
Pt (10% Pt on activated carbon)	40	1.005	1.41×10^{-2}	2.61
	60	0.968	1.25×10^{-2}	2.29
	80	0.975	1.28×10^{-2}	2.36
Ta ₂ O ₅ (Commercial powder)	40	0.999	4.63×10^{-5}	9.96×10^{-4}
	60	0.924	4.80×10^{-5}	1.03×10^{-3}
	80	0.859	5.45×10^{-5}	1.17×10^{-3}
Sputtered (6.5 nm size)	40	0.687	1.65×10^{-6}	0.309
	60	0.693	4.58×10^{-6}	0.859
	80	0.705	5.17×10^{-6}	0.969
Sputtered (19.4 nm size)	40	0.684	1.83×10^{-7}	0.012
	60	0.693	1.48×10^{-6}	0.093
	80	0.698	1.73×10^{-6}	0.109
Sputtered (77.8 nm size)	40	0.646	1.58×10^{-7}	2.47×10^{-3}
	60	0.672	9.59×10^{-7}	1.50×10^{-2}
	80	0.695	1.51×10^{-6}	2.36×10^{-2}

Alfa Aesar), subsequently adding 4 ml of Ta(OEt)₅, and stirring the resulting slurry overnight at room temperature. The ethanol solvent tends to retard rapid hydrolysis and condensation of Ta(OEt)₅ in forming Ta₂O₅ because it stabilizes the ethoxide, which affords some degree of control over Ta₂O₅ particle size using this process. Once the reaction was complete, the ethanol was removed by evaporation at 60 °C under vacuum overnight. Each sample was subsequently ball-milled for 15 min in a Spex mill.

The electrochemical properties of the sputtered and chemically synthesized samples were measured and compared with those of high-purity Ta₂O₅ powder (-325 mesh, 99.95%; Alfa Aesar) and a commercial carbon-supported Pt catalyst (10 wt% Pt on activated carbon; Alfa Aesar). The measurements were carried out using a typical static 3-electrode half-cell test arrangement that employed 0.1 N sulfuric acid as an electrolyte. Pt mesh and a saturated Calomel electrode were respectively used as the counter and reference electrodes. In the case of the sputtered material, the as-sputtered carbon paper was employed directly as the working electrode. When testing the powder catalyst, working electrodes were prepared by coating teflonized carbon (TGPH-090, E-TEK) discs with a paste consisting of Nafion and catalyst. The active area of these electrodes was 1 cm² and the loading of active catalyst was 50 mg. To measure the electrochemical performance of the catalysts under simulated oxygen reduction reaction conditions, cyclic voltammetry (at a scan rate of 1 mV/s) was performed while slowly bubbling air through the electrolyte. Testing was carried out at 40 °C, 60 °C, and 80 °C. Microstructural analysis of both catalyst forms was conducted by scanning electron microscopy (SEM, JEOL JSM-5900LV) and transmission electron microscopy (TEM, JEOL 2010).

3. Results and discussion

Listed in Table 1 are the comparative results from electrochemical testing of high-purity tantalum oxide powder, a commercial carbon-supported Pt PEM fuel cell catalyst, and

nanoscale tantalum oxide as-sputtered on carbon paper. The Ta₂O₅ sample exhibits a high ORR onset potential (0.999 V vs. NHE at 40 °C and 0.859 V at 80 °C), one that is comparable to the Pt catalyst (1.005 V vs. NHE at 40 °C and 0.975 V at 80 °C). However, both the area-specific and mass-specific current densities measured at 0.6 V vs. NHE were quite low compared to Pt, largely due to the poor electrical conductivity of Ta₂O₅. The values of the area-specific current densities for the sputtered samples were also small (several orders of magnitude below that of Pt at comparable test conditions) because of the low loading of active catalyst, i.e. tantalum oxide, in these samples.

However the mass-specific current densities for the sputtered samples were significantly higher than those of the unsupported Ta₂O₅ powder. In fact, the sputtered sample consisting of the smallest tantalum oxide particles (estimated to be 6–7 nm in diameter on average) displayed values of mass-specific reduction current density well over 1/3 that of the platinum catalyst at 60 and 80 °C. There are two distinct trends in the electrochemical data for the sputtered specimens. First, there is approximately an order of magnitude increase in mass-specific current density as the average oxide particle size is reduced from 77.8 nm to 19.4 nm and again as the particle size is reduced from 19.4 nm to 6.5 nm. Lineal triple-phase boundary density (the overall length of the triple-phase boundaries, or TPB, in the material per unit area of substrate) increases with reducing particle size according to:

$$\ell_{\text{TPB}} = \frac{12m}{d^2 \rho A} \quad (2)$$

assuming that the morphology of the deposited oxide particulate can be represented as a hemispherical lens that makes contact with the carbon substrate along the great circle. In Equation (2), ℓ_{TPB} is the lineal TPB density of the sample, m , d , and ρ are respectively the mass, average diameter, and density of the particulate material deposited, and A is the surface area of the substrate on which the particulate is deposited. Although this is a crude estimate of TPB density, the trend is accurate, indicating that ℓ_{TPB} is inversely proportional to the square of average particle size. That is, the correlation between

current density and tantalum oxide particle size appears to support the hypothesis that an increase in TPB density should lead to greater catalytic activity.

Of course the phenomenon responsible for the observed trend in current density is likely significantly more complex than portrayed above. The reduction in tantalum oxide particle size may increase catalytic activity in other ways, for example via increased oxide surface area or more energetic bonding at the surfaces of the smaller particles. However one might expect that either of these factors should influence the ORR potential, a parameter that is essentially invariant of particle size according to the data in Table 1. The second trend that appears in this data set is the increase in current density with temperature for each of the tantalum oxide samples, including the high-purity powder. This indicates an increase in catalytic activity with temperature, one anticipated by the Arrhenius Law, which is currently under study in an effort to more completely understand the reaction and reaction kinetics occurring with the tantalum oxide catalysts.

Shown in Fig. 1 are typical results from TEM analysis of the sputtered tantalum oxide samples. In this case, the image is that of the sputtered sample with the smallest particle size. The bright-field image shown in Fig. 1(a) shows the

nanocrystalline tantalum oxide particles are not completely discrete, but form agglomerated clusters on the surface of the carbon paper. A corresponding energy dispersive X-ray spectrometry analysis of the tantalum oxide particles indicates that the ratio of oxygen to tantalum in this material is approximately 58:42 when averaged over ten separate measurements, which suggests that the tantalum does not fully oxidized during the sputtering process (the O:Ta ratio in Ta_2O_5 is approximately 71:29). Incomplete oxidation may be responsible for the discrepancy in the ORR onset potentials recorded for the sputtered samples vis-à-vis those measured for the high-purity Ta_2O_5 powder.

To improve the area-specific current density of nanoscale tantalum oxide, we speculated that it would be necessary to extend the “two-dimensional” microstructure of the sputtered heterogeneous catalyst samples into three-dimensions. This is conceptually shown in Fig. 2. In the case of the high-purity Ta_2O_5 powder, the TPB density is particularly low because these catalytic regions are formed only where the relatively large-sized powder particles contact the carbon paper. We believe this is the key reason why the area- and mass-specific current densities of this material were so low. As shown schematically in Fig. 3, the only catalytically active surface

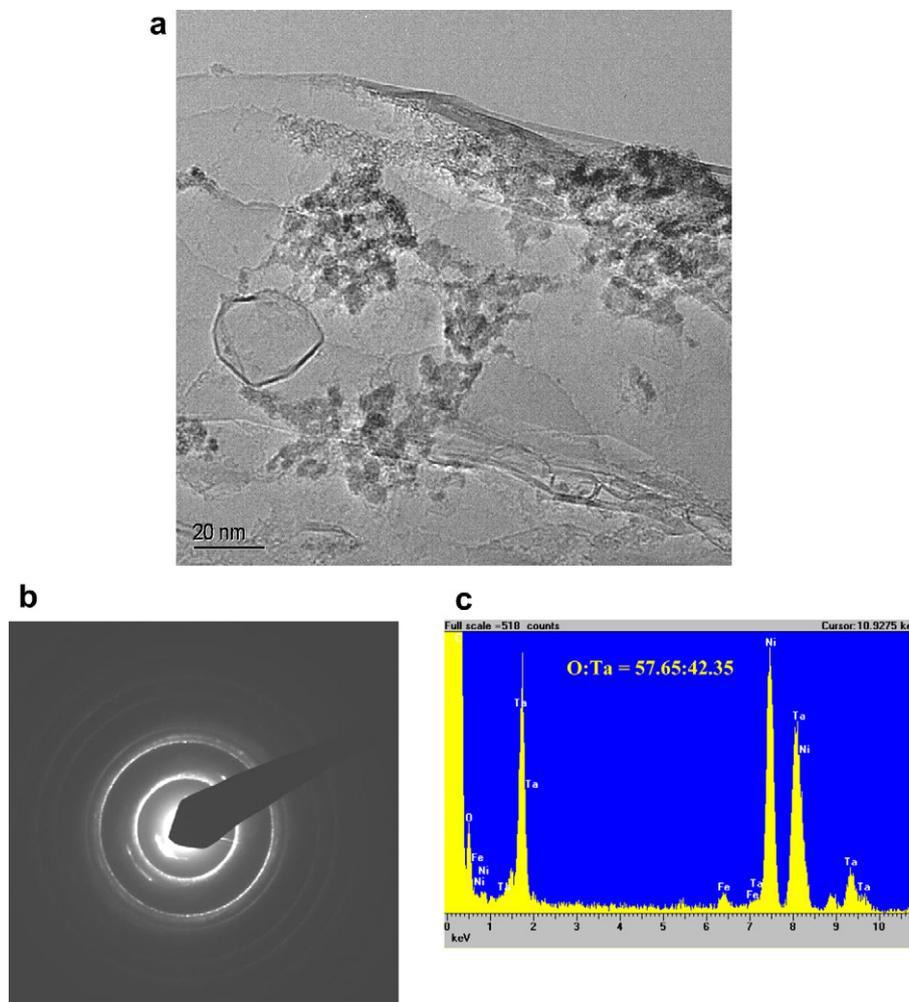


Fig. 1 – TEM analysis results of the 6.5 nm sputtered sample: (a) bright-field image, (b) diffraction pattern, and (c) EDS analysis conducted on representative tantalum oxide particles.

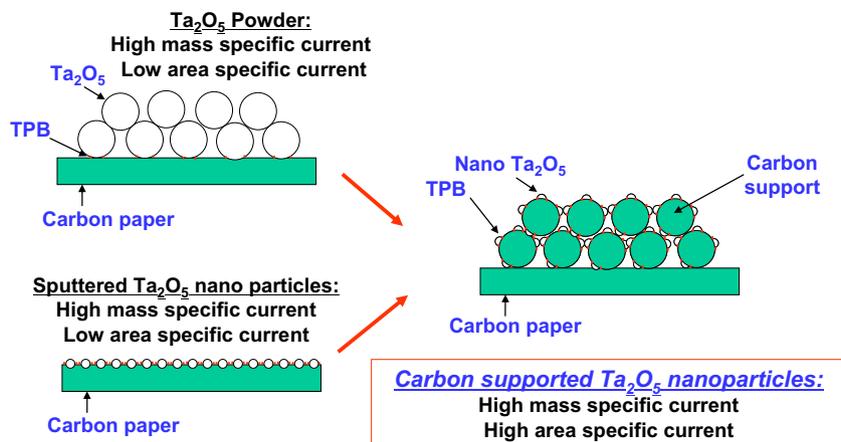


Fig. 2 – A schematic of nanoscale tantalum oxide/carbon composite catalysts.

regions on Ta_2O_5 are those within close enough proximity to the graphite to effect electron transfer (unlike Pt, for example, in which all catalytic surface sites will be active because there is no electron-transport limitation). Oxide surface that lies outside of these interfacial regions may be theoretically capable of catalyzing the ORR but is not active because of poor electronic transport. On the other hand, sputtering of the tantalum oxide as discrete nanosize particles on the surface of the carbon increases the TPB density according to Equation (2). Therefore, the mass-specific current density can be dramatically improved, even though the area-specific current density remains low due to the inherent limitations on oxide loading imposed by the two-dimensional carbon paper substrate. One means of increasing the area-specific current density for nanoscale tantalum oxide is to carry out deposition on a high surface area support material.

Carbon particle supported nanoscale Ta_2O_5 media were synthesized with varying $\text{Ta}(\text{OEt})_5$ -to-carbon ratios using the chemical synthesis approach described above. Shown in Fig. 4

are SEM micrographs collected on the resulting heterogeneous catalysts, which contain 30–77 wt% Ta_2O_5 as determined from wet chemical analysis. Samples containing high tantalum oxide contents, 77 wt% Ta_2O_5 shown in Fig. 4(a) and 63 wt% Ta_2O_5 shown in Fig. 4(b), appear to consist of micron-sized agglomerates of carbon particles that are almost completely coated by Ta_2O_5 . In contrast, samples containing lower amounts of the oxide, for example the 30 wt% Ta_2O_5 sample shown in Figs. 4(d) and 5, are composed of a finer dispersion of nanoscale tantalum oxide that is attached to carbon particles in such a way that the carbon generally remains exposed (i.e. not completely covered by oxide).

The electrochemical performance of these materials is shown in Figs. 6 and 7. To compare the results directly with the commercial Pt catalyst, sample loadings of 50 mg/cm² were employed in all cases. The synthesized composite catalyst exhibits a high ORR onset potential (1.045 V vs. NHE at 40 °C and 0.955 V at 80 °C), comparable to that of Pt as shown by the example in Fig. 6. The data in Fig. 7 indicates that the

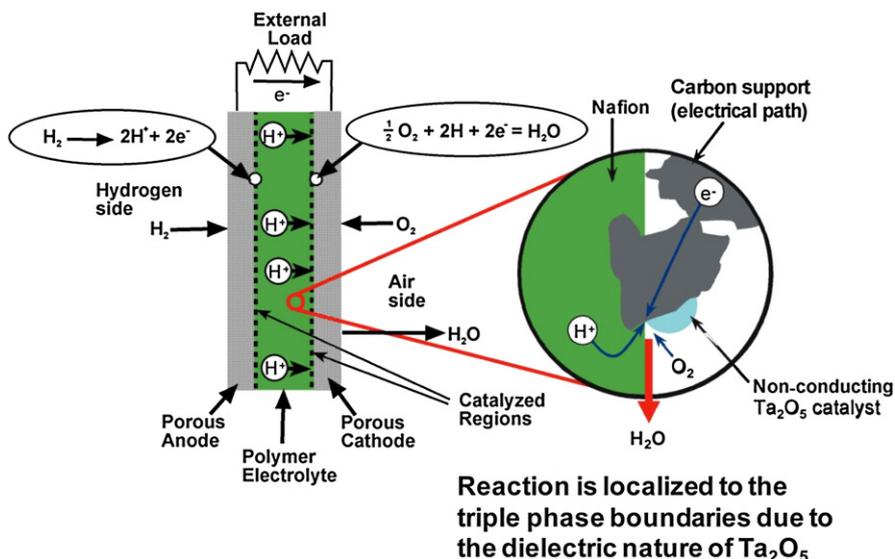


Fig. 3 – A schematic of the nanoscale carbon-support tantalum oxide catalyst system within the cathode side of the membrane electrode assembly (MEA).

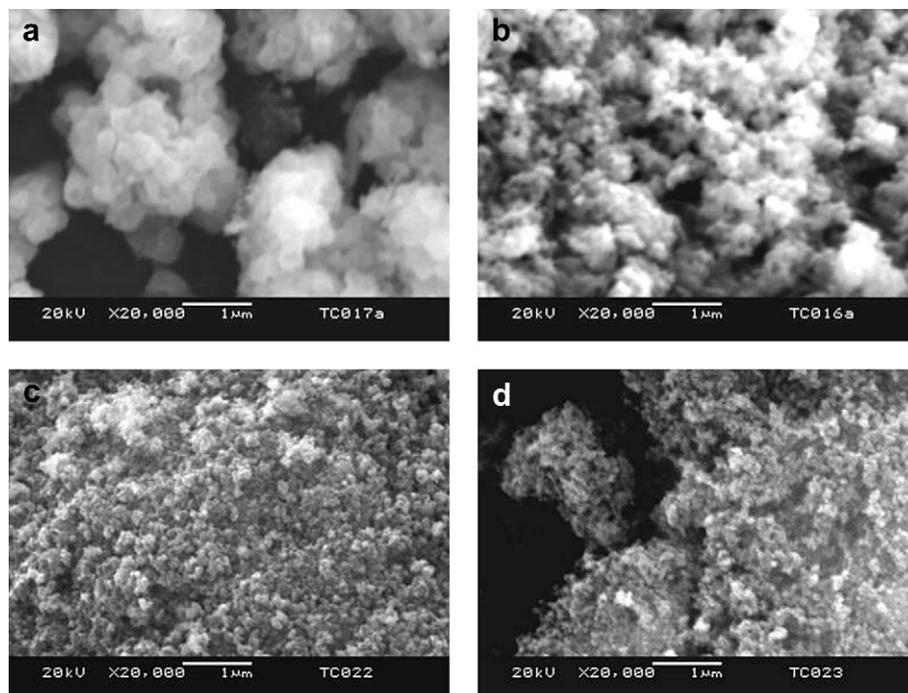


Fig. 4 – SEM micrographs of the carbon particle supported nanoscale Ta_2O_5 catalysts prepared with: (a) 77 wt% Ta_2O_5 , (b) 63 wt% Ta_2O_5 , (c) 46 wt% Ta_2O_5 , and (d) 30 wt% Ta_2O_5 .

mass-specific current densities (measured at 0.7 V vs. NHE) increase with decreasing Ta_2O_5 content. The maximum current density measured for this materials set was recorded for the catalyst containing 30 wt% Ta_2O_5 , which displayed a value that was 9.3% that of the Pt catalyst at 80 °C.

In large part, the results in Fig. 7 can be attributed to the catalyst microstructures observed in Fig. 4(a–d). The agglomerated structure of the high oxide content samples tends to limit electrical connectivity of the nearly completely covered carbon phase, which in turn leads to poor electrical conductivity and results in the comparatively low current densities. Conversely, catalyst structures in which the carbon phase is exposed are more likely to meet or exceed the

percolation limit need for good electrical conductivity and thereby ensure that the TPBs are catalytically active (i.e. electrically connected). This appears to occur for catalysts that contain a lower amount of the Ta_2O_5 phase. Research is currently underway to investigate the limits of this effect in an effort to define the optimal tantalum oxide content, as well as a corresponding optimal average oxide particle size in the heterogeneous catalyst. Although the mass-specific current density for the 30 wt% Ta_2O_5 catalyst is lower than that of the best sputtered sample (9% vs. 30% that of Pt), the results demonstrate some potential of these new nanoscale catalysts and indicate possible options for further improvement.

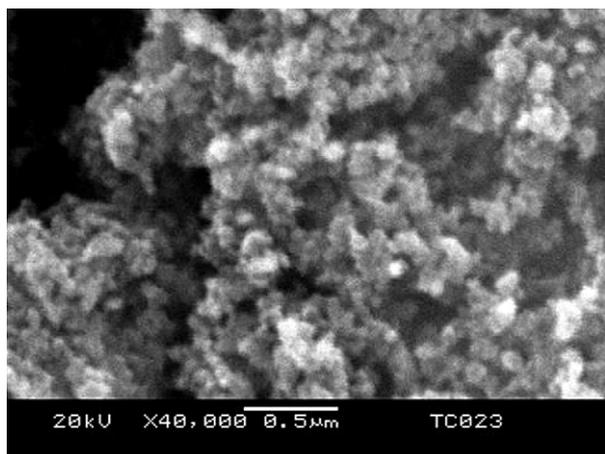


Fig. 5 – High-magnification SEM micrograph of the carbon particle supported nanoscale Ta_2O_5 catalyst prepared with 30 wt% Ta_2O_5 .

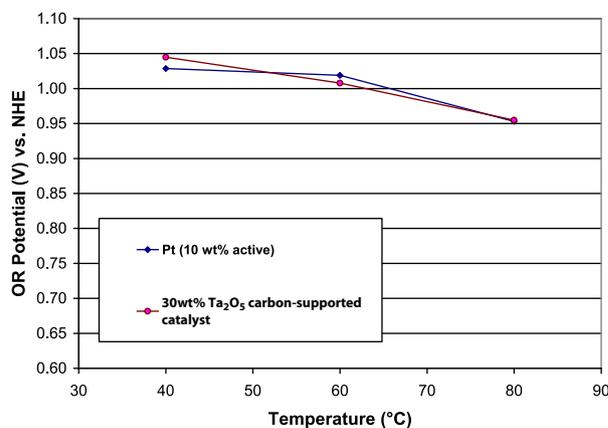


Fig. 6 – ORR onset potentials of a carbon particle supported nanoscale Ta_2O_5 catalyst (containing 30 wt% Ta_2O_5) compared to a commercial Pt catalyst.

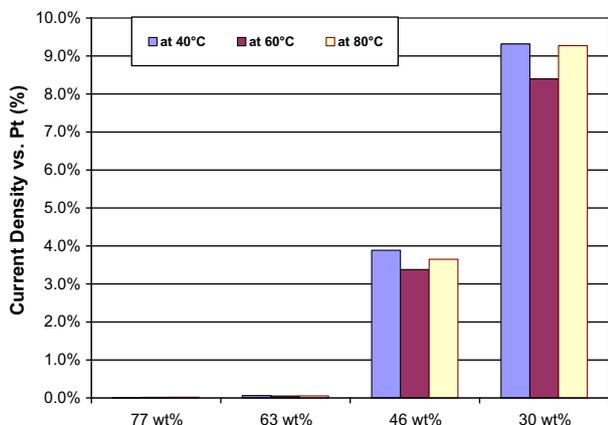


Fig. 7 – Mass-specific current densities of a series of carbon particle supported nanoscale Ta₂O₅ catalysts measured at 0.7 V vs. NHE compared to a commercial Pt catalyst.

4. Summary

Although bulk Ta₂O₅ possesses poor electrochemical properties due to limited electrical conductivity, it displays an oxygen reduction potential comparable to that of Pt. It was speculated that the electrochemical performance of Ta₂O₅ could be improved by supporting the material on an electrochemically stable conductive phase such as carbon, thereby establishing active TPB catalytic reaction sites. To test this concept, carbon-paper supported nanoscale tantalum oxide catalysts were fabricated by a reactive sputtering process. Subsequent half-cell testing demonstrated that the resulting materials exhibited greater catalytic activity for the ORR than Ta₂O₅ powder, with the best materials displaying mass-specific current densities exceeding 1/3 that of a commercial Pt catalyst under the same test conditions. However, because the loadings in the oxide catalysts were so low, the corresponding area-specific current densities were also low. To improve this metric, nanoscale tantalum oxide was deposited on high surface area carbon powder using a solution-based chemical synthesis approach. These resulting heterogeneous catalysts exhibited high ORR onset potential, comparable to Pt, and improvement in area-specific current density. Overall, the highest mass-specific current densities measured in these catalysts were achieved with the lowest Ta₂O₅-containing samples, reaching values as high as 9% that of Pt for a Ta₂O₅ content of 30 wt%. The results demonstrate the some potential of carbon-supported nanoscale Ta₂O₅ catalysts for PEM fuel cell use even though their catalytic performance needs to be improved significantly more to replace Pt.

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