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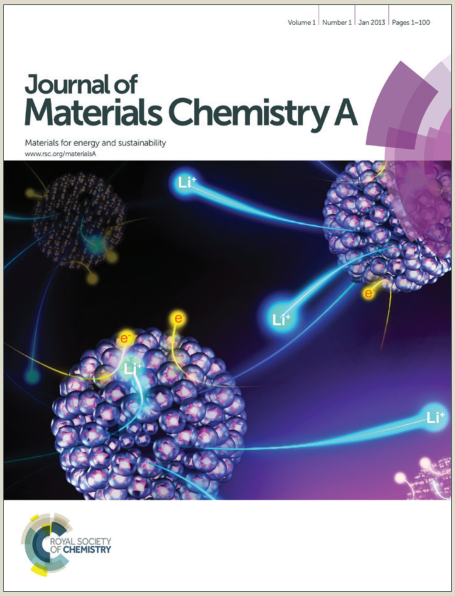

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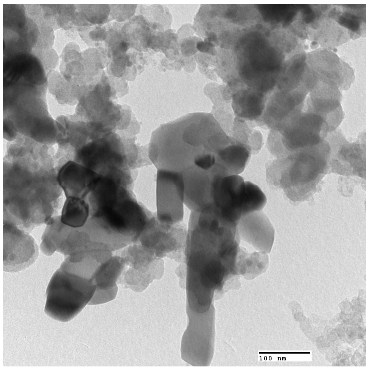
1. Colour graphic (maximum size 8cm × 4cm):



2. Text (one sentence, of maximum 20 words, highlighting the novelty of the work)

"The addition of $Ta_{0.01}Nb_{0.03}Ti_{0.96}O_2$ improves the electrocatalytic activity and stability of carbon for oxygen reduction reaction."

COMMUNICATION

Ta and Nb co-doped TiO_2, and Its Carbon-Hybrid Materials for Supporting Pt-Pd Alloy Electrocatalysts for PEM Fuel Cells Oxygen Reduction Reaction

Yan-Jie Wang,[a,b] David P. Wilkinson,*[b] Vladimir Neburchilov, *[a] Chaojie Song,[a] Alan Guest,[a] and Jiujun Zhang*[a]

To explore possible substitutes for carbon support in PEM fuel cell catalysts, both Ta and Nb co-doped TiO_2 (TaNbTiO$_2$) and carbon-TaNbTiO$_2$ (C-TaNbTiO$_2$) hybrid support materials are successfully synthesized by a modified thermal hydrolysis method. These materials are employed as support candidates for Pt-Pd alloy catalysts for oxygen reduction reaction. Among several supported catalysts, $20wt\%Pt_{0.62}Pd_{0.38}\ /C_{75wt\%}\text{-}Ta_{0.01}Nb_{0.03}Ti_{0.96}O_2)_{25wt\%}$ is found to have an oxygen reduction reaction (ORR) mass activity of 260 mA/mgPt and an ORR loss of 30%, which are slightly better than the commercially available Pt/C baseline catalyst which has a mass activity of 110 mA/mgPt and an ORR loss of 40% probably because of a strong physicochemical interaction among Pt-Pd alloy catalyst particle, carbon-TaNbTiO$_2$ support and carbon, as well as the stability of oxide to protect carbon from corrosion by the distribution of oxide onto carbon, respectively.

In order to achieve commercialization of polymer electrolyte membrane (PEM) fuel cells, great efforts have been made to reduce their cost and further improve their performance and durability [1-3]. Regarding the contributors to both high cost and insufficient durability, the major limitation has been identified as the PEM fuel cell catalyst (Pt-based). To address these challenges of catalysts, among several other approaches, two thrusts have been developed recently, one aimed at reducing the Pt loading for cost reduction, and the other aimed to replacing carbon support of the catalysts using some materials such as carbides, nitrides, transition metal oxides, and metal oxide-carbon composites for improving catalyst stability [4-6]. However, compared to carbon support, some drawbacks such as low electronic conductivity, large solubility, insufficient chemical/electrochemical and thermal stability, as well as low surface area have been found to hinder their application as catalyst support.

Recently, titanium dioxide (TiO_2)-based materials have been explored as a promising catalyst support due to their low cost, commercial availability, the ability to control their size and structure, as well as the high chemical/electrochemical and thermal stability [4, 7, 8]. However, their electronic conductivity is the major concern. To improve the electronic conductivity of conventional TiO_2 material, various approaches such as heat treatment [9], transition metal doping [10, 11], and compositing [9, 12-14] have been explored with attention to make them highly conductive and durable TiO_2-based catalyst support. Among these approaches, doping strategies using metal or nonmetal elements are considered as an efficient way to obtain conductive TiO_2-based noncarbon support materials for fuel cell electrocatalyst application [10, 11]. As an example, Nb-doped TiO_2 shows higher conductivity than other traditional TiO2-based materials [15, 16].

To further improve the physicochemical properties of Nb-doped TiO_2, an additional doping with Ta was explored to co-dope the TiO_2 with Nb to form Ta and Nb co-doped TiO_2 in this paper. As one of promising support materials, TaNbTiO$_2$ is found to play an important role in the modification of carbon and the protection of carbon from corrosion, improving the durability of the C-TaNbTiO$_2$ hybrid support. Furthermore, the doping by two transition metals might produce more conductive and stable TiO_2, which then improve the electrochemical stability of carbon and enhance the Pt ORR mass activity of their supported electrocatalysts as well. However, compared to carbon material, the electronic conductivity of TaNbTiO$_2$ seems still not to be sufficient. In the effort to increase the conductivity, this TaNbTiO$_2$ was distributed in carbon powder to form a C-TaNbTiO$_2$ hybrid material. Then this hybrid material was used to support Pt-Pd alloy nanoparticles, and tested for ORR. In this work, C-TaNbTiO$_2$ supported Pt-Pd electrocatalysts were synthesized by a two-step procedure. In the first step, the TaNbTiO$_2$ was distributed into carbon via a hydrothermal reaction at 120 ^{o}C for 12 hours and a subsequent reduction treatment was done to obtain the TaNbTiO$_2$ support material. In the second step, this TaNbTiO$_2$ was mixed with carbon to form supported 20wt% Pt-Pd catalyst by a microwave assisted polyol method. The experimental details can be seen in the supplementary information. Our measured results show that this C-TaNbTiO$_2$ supported Pt-Pd alloy catalysts have a higher ORR activity as well as a better stability compared to those of commercially available Pt/C catalysts.

To investigate the TaNbTiO$_2$ support structure, the XRD spectra were recorded for carbon, TaNbTiO$_2$ and its carbon-hybrid support materials, as shown in Figure 1. It can be seen that when the total molar content of Ta and Nb is less than 20 at%, only TiO_2 rutile phase (Dark circles in Figure 1) can be detected in $Ta_xNb_yTi_{1-x-y}O_2$ support materials without detect-

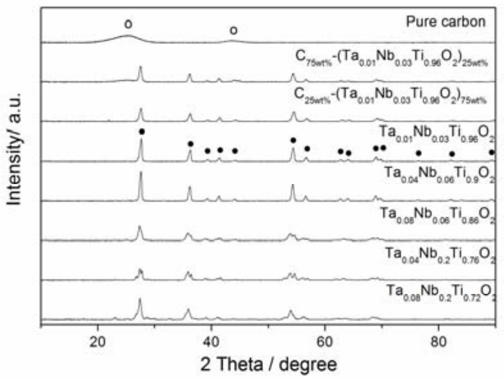


Figure 1. XRD for pure carbon, $Ta_xNb_yTi_{1-x-y}O_2$, and $C_{75wt\%}$-$(Ta_{0.01}Nb_{0.03}Ti_{0.96}O_2)_{25wt\%}$ and $C_{25wt\%}$-$(Ta_{0.01}Nb_{0.03}Ti_{0.96}O_2)_{75wt\%}$ support materials.

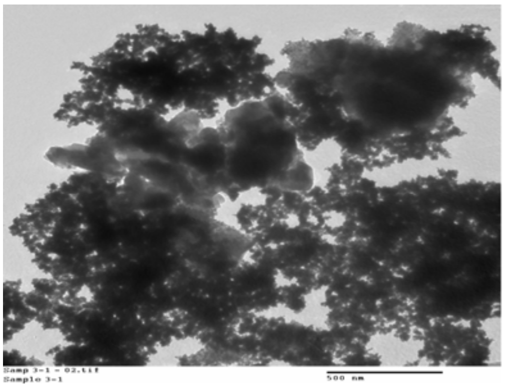
able Ta or/and Nb oxide phases. This may suggest an easy doping of rutile TiO_2 by metal Nb or Ta at this doping level, forming a complete solid solution with the bimetals (Ta and Nb) into TiO_2 [17, 18]. However, when the doping level is beyond 14 at% (i.e. Nb: 6 at%; Ta: 8 at%), some additional phases such as TaO_2 and Nb_2O_5 can be detected. This probably results from the evaporation of HCl and the thermal hydrolysis of hydroscopic Ta and Nb's precursors at their high concentrations. It is clear that at this high doping level (> 14 at%), an incomplete co-doping of Ta and Nb into TiO_2 can be done. In addition, compared to two characteristic peaks (Open circle in Figure 1) of pure carbon black (TKKE) at 25.6° and 43.7° respectively, the $C_{75wt\%}$-$(Ta_{0.01}Nb_{0.03}Ti_{0.96}O_2)_{25wt\%}$ hybrid support has the clear carbon peak at 25.6° and the rutile peaks of TiO_2 while the $C_{25wt\%}$-$(Ta_{0.01}Nb_{0.03}Ti_{0.96}O_2)_{75wt\%}$ hybrid support only shows two insignificant TKKE peaks and the characteristic peaks for TiO_2 in rutile phase. In our previous work, the rutile TiO2 has already proven to enhance the electronic conductivity of Nb doped TiO_2 support material and improve the synergetic interaction between Nb doped TiO_2 and Pt-Pd alloy particles, favoring the improvement of electrochemical properties [9]. Here, the rutile TiO_2 is expected to have a positive effect on C-$Ta_{0.01}Nb_{0.03}Ti_{0.96}O_2$ hybrid support material in the electrochemistry.

Table 1. Room temperature conductivities and specific surface areas of pure carbon, C-$TaNbTiO_2$ and various $TaNbTiO_2$.

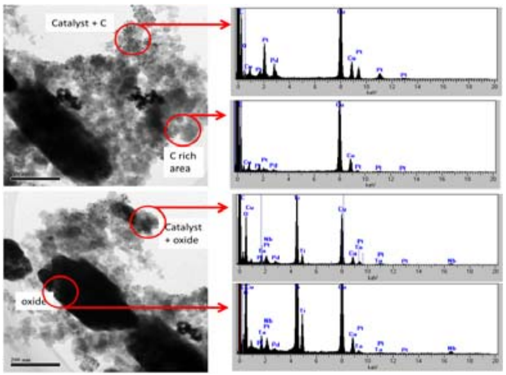
Sample	Total content of Ta and Nb (at%)	Ta content (at%)	Nb content (at%)	Room temperature conductivity (S/cm)	Room temperature conductivity (Log, S/cm)	Specific surface area (m^2/g)
Carbon	-	-	-	7.8	-	866
$C_{75wt\%}$-$(Ta_{0.01}Nb_{0.03}Ti_{0.96}O_2)_{25wt\%}$	4	1	3	4.88	-	683
$C_{25wt\%}$-$(Ta_{0.01}Nb_{0.03}Ti_{0.96}O_2)_{75wt\%}$	4	1	3	0.23	-	45
$Ta_{0.01}Nb_{0.03}Ti_{0.96}O_2$	4	1	3	1.56×10^{-6}	-5.808	3.5
$Ta_{0.04}Nb_{0.06}Ti_{0.9}O_2$	10	4	6	4.12×10^{-6}	-5.385	4.3
$Ta_{0.08}Nb_{0.06}Ti_{0.9}O_2$	14	8	6	9.77×10^{-6}	-5.010	6.3
$Ta_{0.04}Nb_{0.2}Ti_{0.76}O_2$	24	4	20	9.60×10^{-5}	-4.018	11.7
$Ta_{0.08}Nb_{0.2}Ti_{0.72}O_2$	28	8	20	8.73×10^{-4}	-3.059	8.6

Table 1 shows the room temperature conductivities and specific surface areas of pure carbon, $TaNbTiO_2$ and two C-$Ta_{0.01}Nb_{0.03}Ti_{0.96}O_2$ hybrid supports at various doping levels of Nb and Ta. It can be seen that with an increase in total doping level of Ta and Nb, the conductivity increases, especially, at the total content of Ta and Nb from 24 at% to 28 at%. Compared to the total doping level of 4 at%, the conductivity of 28 at% sample could have an increase up to 560 times. This result suggests that the increasing the total doping level of Ta and Nb in the support can enhance the electronic conduction of the $TaNbTiO_2$ support. However, all of $TaNbTiO_2$ supports have low conductivity below 10^{-3} S/cm, which is much lower than that of pure carbon. After the addition of carbon, the combination of carbon with $Ta_{0.01}Nb_{0.03}Ti_{0.96}O_2$ in the C-$Ta_{0.01}Nb_{0.03}Ti_{0.96}O_2$ hybrid supports show higher electronic conductivity than 0.1 S/cm. Especially at 75wt% carbon, the conductivity of the hybrid support was increased up to 4 S/cm, which was close to the conductivity of pure carbon, probably because high carbon content could contribute to the ionic conduction of the C-$Ta_{0.01}Nb_{0.03}Ti_{0.96}O_2$ hybrid support. This high electronic conductivity might favor the electron transfer from Pt catalyst clusters to/through the support during the ORR in PEM fuel cells [19, 20].

Unfortunately, all pure $TaNbTiO_2$ support's specific surface area values are low in the range of less than 12 m^2/g. Although its area is slightly increased by increasing total Ta/Nb doping level, there is no significant difference at different doping level. After the support is hybridized with carbon, the produced $C_{75wt\%}$-$(Ta_{0.01}Nb_{0.03}Ti_{0.96}O_2)_{25wt\%}$ can give a BET surface as high as ~683.63 m^2/g, which is much higher than 100 m^2/g from the commercial requirement of electrocatalysts in PEM fuel cell [4]. Even with a small amount of carbon addition such as 25 wt% (i.e. $C_{25wt\%}$-$(Ta_{0.01}Nb_{0.03}Ti_{0.96}O_2)_{75wt\%}$), the specific surface area can increases significantly from 3.5 to 45 m^2/g. It is expected that this significant specific surface are increase can help improve distribution of the reduced Pt-Pd alloy particles on support surface and thus enhance the ORR mass activity.



(a)



(b)

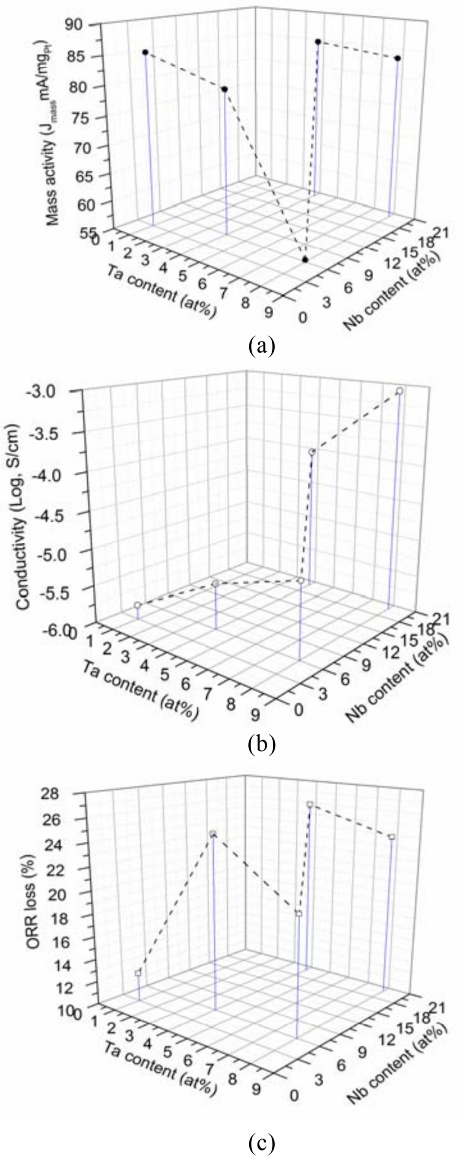
Figure 2. TEM-EDX data for two catalysts: (a) $20wt\%Pt_{0.62}Pd_{0.38}/Ta_{0.01}Nb_{0.03}Ti_{0.96}O_2$, and (b) $20wt\%Pt_{0.62}Pd_{0.38}/C_{75wt\%}$-$(Ta_{0.01}Nb_{0.03}Ti_{0.96}O_2)_{25wt\%}$

Two Pt-Pd alloy catalysts supported on $Ta_{0.01}Nb_{0.03}Ti_{0.}96O_2$ and $C_{75wt\%}$-$(Ta_{0.01}Nb_{0.03}Ti_{0.96}O_2)_{25wt\%}$ supports, respectively, synthesized in this paper, were characterized using TEM-EDX technique. Figure 2 shows their micrographs of $20wt\%Pt_{0.62}Pd_{0.38}/Ta_{0.01}Nb_{0.03}Ti_{0.96}O_2$ and $20wt\%Pt_{0.62}Pd_{0.38}/C_{75wt\%}$-$(Ta_{0.01}Nb_{0.03}Ti_{0.96}O_2)_{25wt\%}$. It can be seen that both catalysts show some big clusters with the sizes varying from 200 nm to 500 nm. Since the $Ta_{0.01}Nb_{0.03}Ti_{0.96}O_2$ with a low specific surface area (~3.5 m^2/g) cannot provide enough surfaces for the uniform distribution of Pt-Pd alloy particles, the micrographs show that most of Pt-Pd alloy particles were separated from the oxide and agglomerated. Compared to the agglomeration of Pt-Pd alloy particles in the $20wt\%Pt_{0.62}Pd_{0.38}/Ta_{0.01}Nb_{0.03}Ti_{0.96}O_2$ catalyst shown in Figure 2 (a), Pt-Pd alloy particles appear as more uniformly distributed on the both surfaces of the $Ta_{0.01}Nb_{0.03}Ti_{0.96}O_2$ oxide and TKKE carbon in the $20wt\%Pt_{0.62}Pd_{0.38}/C_{75wt\%}$-$(Ta_{0.01}Nb_{0.03}Ti_{0.96}O_2)_{25wt\%}$ catalyst according to EDXS analysis shown in Figure 2 (b). The Pt-Pd alloy particles have an average size of ~7 nm. Interestingly, most of Pt-Pd catalyst particles stay on the TKKE carbon surface even the metal oxide particles have a high hydrophilicity. That suggests that the interaction between Pt-Pd alloy particles and carbon is stronger than the one between Pt-Pd alloy particles and $Ta_{0.01}Nb_{0.03}Ti_{0.96}O_2$. Additionally, as discussed above, the addition of TKKE carbon can give $C_{75wt\%}$-$(Ta_{0.01}Nb_{0.03}Ti_{0.96}O_2)_{25wt\%}$ a much higher BET surface area as compared to $Ta_{0.01}Nb_{0.03}Ti_{0.96}O_2$, offering an improved distribution area to the Pt-Pd alloy particles in the catalyst preparation. This kind of high distribution of Pt-Pd alloy particles should favor the electronic transfer between the support and alloy catalyst particles.

For $Ta_xNb_yTi_{1-x-y}O_2$ supported Pt-Pd catalysts, their ORR mass activities were measured using RDE technique at an electrode rotating rate of 1600 rpm. The current at 0.9V vs. RHE and the catalyst loading was used to calculate the mass activity, and expressed as mA per mg of Pt (mA/mgPt). For the series of $20wt\%Pt_{0.62}Pd_{0.38}/Ta_xNb_yTi_{1-x-y}O_2$ catalysts (x = 0.01 to 0.08, and y = 0.03 to 0.20, respectively) in Figure 3 (a), the measured ORR mass activities drop in the range of 80 - 90 mA/mgPt, except that the activity is 55 mA/mgPt at x= 0.08 and y=0.06 (see Table S1 in the supplementary information). It can also be found that at the Ta content of 0.04, the increasing content of Nb can result in a slight improvement forthe ORR activity. However, when the Nb content is fixed at 0.08, the ORR activity significantly can be decreased from 80 mA/mgPt to 55 mA/mgPt with increasing the content of Ta probably because the impurity oxide phases seen in XRD, coupled with low conductivity (~10^{-6} cm), can result in a poor interaction between support and PtPd alloy, and thus low activity. For these supported Pt-Pd catalysts, their ORR mass activity firstly decreases and then goes up with increasing total doping level of Ta and Nb (see Figure S2 in the supplementary information). At the total doping of 0.14, the activity is the lowest. This might be attributed to the support's small conductivity (<10^{-4} S/cm) dependence on the doping level, as shown in Table 1 and Figure 3 (a). The further reason needs to be found out in the future work.

The ORR catalytic durability of these TaxNbyTi1-x-yO2 supported Pt-Pd catalysts were also tested using cyclic voltammetry technique. Compared to that of $20wt\%Pt_{0.62}Pd_{0.38}/Nb_{0.06}Ti_{0.94}O_2$ (note this catalyst support has no Ta co-doping) which had an ORR loss of 31% (see Figure S3 (c)) after 1000 cycles of potential step from 0 to 1.2 V vs.

RHE, the 20wt%$Pt_{0.62}Pd_{0.38}/Ta_xNb_yTi_{1-x-y}O_2$ catalysts had a lower loss from 13 to 26% in Figure 3 (c), depending on the loading level. The corresponding calculated values of ORR loss are given in Table S1 in the supplementary information. For example, the 20wt%$Pt_{0.62}Pd_{0.38}/Ta_{0.01}Nb_{0.03}Ti_{0.96}O_2$ catalyst has a low loss of less than 13%, and the 20wt%$Pt_{0.62}Pd_{0.38}/Ta_{0.04}Nb_{0.2}Ti_{0.96}O_2$ catalyst has 26% of ORR activity loss. It is still not fully understood why increasing doping level could lead to a less stable catalyst and thus further work is required. To obtain reliable data, the electrochemical test was repeated three times at least with an experimental error in the range of 3%.



(a)

(b)

(c)

Figure 3. (a) Pt ORR mass activity for 20wt%$Pt_{0.62}Pd_{0.38}/Ta_xNb_yTi_{1-x-y}O_2$, (b) Electronic conductivity of $Ta_xNb_yTi_{1-x-y}O_2$ (x = 0.01 to 0.08, and y = 0.03 to 0.20) support materials, and (c) ORR loss for various 20wt%$Pt_{0.62}Pd_{0.38}/Ta_xNb_yTi_{1-x-y}O_2$ catalysts after 1000 potential step.

Compared to the commercially available catalyst such as 47wt%Pt/C which has a loss of 40%, and Nb doped TiO2 support which has a loss of 31%, all Pt-Pd catalysts supported on Ta and Nb co-doped TiO_2 support have a higher electrochemical stability. It can be inferred that $TaNbTiO_2$ should be more durable than $NbTiO_2$ and carbon, and that the possible physicochemical interaction between bimetals (i.e. Ta and Nb) and Pt-Pd alloy may facilitate the improvement of electrochemical properties more efficiently than the interaction between Nb and Pt-Pd alloy. Further work with spectroscopic methods such as XANES would also help elucidate such effects.

Although the $TaNbTiO_2$ supported Pt-Pd catalysts has a low ORR activity loss, all of $TaNbTiO_2$ supports were measured to have low specific surface area less than 100 m2/g and poor conductivity below 0.1 S/cm. According to the commercial requirement for electrocatalysts in PEM fuel cell [4, 21, 22], these supports would not be able to provide enough surfaces for the uniform distribution of Pt-Pd catalyst particles, and support enough electron transfer between Pt-Pd catalyst clusters and support materials for oxygen reduction reaction. To enhance the electronic conduction and increase specific surface area of $TaNbTiO_2$ supports, carbon was used to form a composite structure with $TaNbTiO_2$ so that the final conductivity and specific surface area could reach 7.8 S/cm and 866 m^2/g, respectively, as shown in Table 1. With the addition of TKKE carbon material, it was found that at the carbon content of 75wt%, the C-$TaNbTiO_2$ hybrid support materials exhibited some excellent electrochemical properties, as shown in Figure 4. To study the effect of carbon content on a hybrid support physicochemical properties, 25wt% C and 75wt% C were used to form the C-$TaNbTiO_2$ hybrid support materials by acidic catalyzed thermal hydrolysis process, respectively.

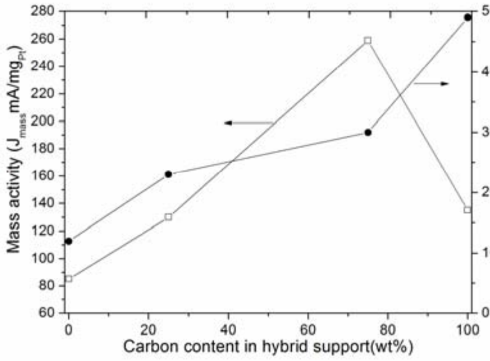


Figure 4. Pt mass activity and ORR loss for four catalysts: 20wt%$Pt_{0.62}Pd_{0.38}/Ta_{0.01}Nb_{0.03}Ti_{0.96}O_2$, 20wt%$Pt_{0.62}Pd_{0.38}/C_{75wt\%}\text{-}(Ta_{0.01}Nb_{0.03}Ti_{0.96}O_2)_{25wt\%}$, 20wt%$Pt_{0.62}Pd_{0.38}/C_{25wt\%}\text{-}(Ta_{0.01}Nb_{0.03}Ti_{0.96}O_2)_{75wt\%}$, and 20wt%$Pt_{0.62}Pd_{0.38}$/C(TKKE), respectively.

In Figure 4, the Pt ORR mass activity of the C-$Ta_{0.01}Nb_{0.03}Ti_{0.96}O_2$ supported Pt-Pd electrocatalysts increases with increasing carbon content. The measurement was repeated three times at least with an experimental error in the range of 3%. At 75wt% carbon in the hybrid support, the Pt

ORR mass activity of 20wt%$Pt_{0.62}Pd_{0.38}/C_{75wt\%}$-$(Ta_{0.01}Nb_{0.03}Ti_{0.96}O_2)_{25wt\%}$ catalyst has the highest ORR activity of 260 mA/mgPt among all results, which is much higher than that (110 mA/mgPt) of the commercial 47wt%Pt/C baseline catalyst. Moreover, the Pt ORR loss of 20wt%$Pt_{0.62}Pd_{0.38}/C_{75wt\%}$-$(Ta_{0.01}Nb_{0.03}Ti_{0.96}O_2)_{25wt\%}$ is about 30%, lower than those 40% of the commercial 47wt%Pt/C(TKKE) baseline catalyst, 49% of the 20wt%$Pt_{0.62}Pd_{0.38}$/C(TKKE) catalyst [23], as well as 31% of the 20wt%$Pt_{0.62}Pd_{0.38}/Ta_{0.01}Nb_{0.03}Ti_{0.96}O_2$. It is indicated that at 75wt% carbon, significant increases in both conductivity and specific surface area may favor the physicochemical interaction among carbon, oxide, and Pt-Pd alloy particles, and thus enhance the catalytic activity and electrochemical durability of the C-$Ta_{0.01}Nb_{0.03}Ti_{0.96}O_2$ supported Pt-Pd catalysts.

Therefore, after the addition of $TaNbTiO_2$ into carbon, its supported Pt-Pd catalyst exhibited better mass activity and durability than the pure carbon supported Pt-Pd catalyst although the hybrid support has a lower conductivity. The higher ORR activity of hybrid supported Pt-Pd catalyst is probably due to the interaction between Pt-Pd catalyst particle and hybrid support while the electrochemical stability of $TaNbTiO_2$ results in a lower corrosion of carbon in the hybrid support than pure carbon. This means that the $TaNbTiO_2$ material play an important role in the protection of carbon from corrosion and the improvement of catalyst performance, which is promising as support materials in the application of fuel cell cathode.

In conclusion, both $TaNbTiO_2$ and C-$TaNbTiO_2$ support materials were successfully synthesized by a modified thermal hydrolysis method and these materials were em-ployed as carbon substitute support for Pt-Pd alloy catalysts for oxygen reduction reaction. Compared to pure carbon and/or $TaNbTiO_2$ supports, C-$TaNbTiO_2$ hybrid support provides high specific surface area (>100 m^2/g), favoring the uniform distribution of Pt-Pd alloy particles, and enough electronic conductivity for the electronic transfer between the Pt-Pd alloy particle clusters and the support in oxygen reduction reaction. Using a composition of 75wt% carbon black (TKKE) and 25wt% of $TaNbTiO_2$ to form a hybrid support, the obtained catalyst, 20wt%$Pt_{0.62}Pd_{0.38}/C_{75wt\%}$-$(Ta_{0.01}Nb_{0.03}Ti_{0.96}O_2)_{25wt\%}$, was found to have a ORR mass activity of 260 mA/mgPt which is much higher than the commercially available baseline catalyst (47wt%Pt/C(TKKE)) which has a mass activity of 110 mA/mgPt. This catalyst also exhibits better ORR durability, and ORR loss of 30%, which is lower than that of 40% of 47wt%Pt/C(TKKE). The ORR mass activity and durability improvement may be attributed to a strong physicochemical interaction among Pt-Pd alloy catalyst particle, carbon-$TaNbTiO_2$ support and carbon, as well as the stability of oxide to protect carbon from corrosion by the distribution of oxide onto carbon.

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Notes and references

[a] *National Research Council Canada Energy, Mining & Environment (NRC-EME),, Vancouver, BC, Canada, V6T 1W5. E-mail address: Jiujun.Zhang@nrc-cnrc.gc.ca, Vladimir.Neburchilov@nrc-cnrc.gc.ca*

[b] *Department of Chemical and Biological Engineering (UBC), University of British Columbia, Vancouver, BC, Canada, V6T 1Z3. E-mail: dwilkinson@chbe.ubc.ca*

1 R. Bashyam, P. Zelenay, *Nature* 2006, **443**, 63-66.
2 C. Wang, M. Waje, X. Wang, J. M. Tang, R. C. Haddon, Y. Yan, *Nano Lett.* 2004, **4**, 345-348.
3 V. R. Stamenkovic, B. Fowler, B. S. Mun, G. Wang, P. N. Ross, C. A. Lucas, N. M. Markovic, *Science* 2007, **315**, 493-497.
4 Y. –J. Wang, D. P. Wilkinson, J. Zhang, *Chem. Rev.* 2011, **111**, 7625-7651.
5 H. A. Gasteiger, S. S. Kocha, B. Sompalli, F. T. Wagner, *Appl. Catal. B-Environ*. 2005, **56**, 9-35.
6 Y. Y. Shao, J. Liu, Y. Wang, Y. H. Lin, *J. Mater. Chem.* 2009, **19**, 46-59.
7 T. Matsui, K. Fujiwara, T. Okanishi, R. Kikuchi, T. Takeguchi, K. Eguchi, *J. Power sources* 2006, **155**, 152-156.
8 N. F. Zheng, G. D. Stucky, *J. Am. Chem. Soc.* 2006, **128**, 14278-14280.
9 Y. –J. Wang, D. P. Wilkinson, J. Zhang, *Dalton Trans.* 2012, **41**, 1187-1194.
10 X. Chen, S. S. Mao, *Chem. Rev.* 2007, **107**, 2891-2959.
11 Y. –C. Nah, I. Paramasivam, P. Schmuki, *ChemPhysChem* 2010, **11**, 2698-2713.
12 Z. Sun, X. Zhang, B. Han, Y. Wu, G. An, Z. Liu, S. Miao, Z. Miao, *Carbon* 2007, **45**, 2589-2596.
13 J. –M. Lee, S. –B. Han, J. –Y. Kim, Y. –W. Lee, A. –R. Ko, B. Roh, I. Hwang, K. –W. Park, *Carbon* 2010, **48**, 2290-2296.
14 Y. –F. Lee, K. –H. Chang, C. –C. Hu, K. –M. Lin, *J. Mater. Chem.* 2010, **20**, 5682-5688.
15 N. R. Elezović, B. M. Babić, Lj. Gajić-Krstajić, V. Radmilović, N. V. Krstajić, L. J. Vračar, *J. Power Sources* 2010, **195**, 3961-3968.
16 S. –Y. Huang, P. Ganesan, B. N. Popov, *Appl. Catal. B Environ.* 2010, **96**, 224-231.
17 B. L. García, R. Fuentes, J. W. Weidner, *Electrochem. Solid-State Lett.* 2007, **10**, B108-B110.
18 H. Chhina, D. Susac, S. Campbell, O. Kesler, *Electrochem. Solid-State Lett.* 2009, **12**, B97-B100.
19 A. S. Fialkov, *Russ. J. Electrochem.* 2000, **36**, 389-413.
20 A. S. Fialkov, C. Leclerc, J. P. Contour, *J. Catal.* 1973, **29**, 31-40.
21 H. A. Gasteiger, *Electrochemistry*, 2007, **75**, 103-103.
22 F. T. Wagner, S. G. Yan, P. T. Yu, Catalyst and catalyst-support durability. In Handbook of fuel cells: fundamentals, tech-nology and applications, vol. 5, Advances in electrocatalysis, materi-als, diagnostics and durability, Chichester, UK: Wiley, 2009, Vol. 5, pp250-263.
23 Ignaszak, A.; Song, C.; Zhu, W.;Wang, Y. –J.; Zhang, J.; Bauer, A.; Baker, R.; Neburchilov, V.; Ye, S.; Campbell, S. Electrochimica Acta 2012, 75, 220-228.