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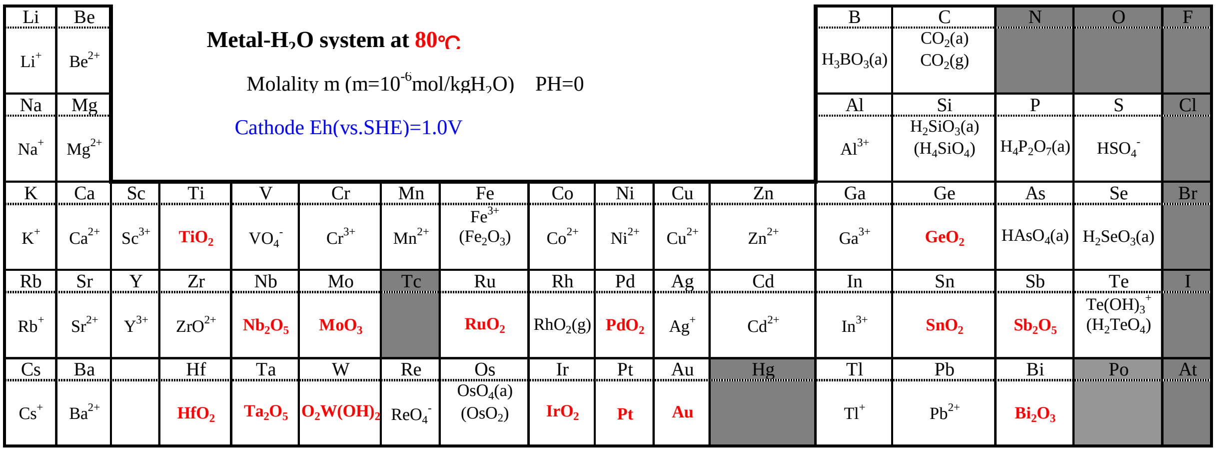
1 Introduction

Higher performance and long-term durability of electrocatalysts are essential for polymer electrolyte fuel cells (PEFCs), where electrocatalyst support materials act as a very important role. In this study, as alternatives to the conventional carbon black catalyst support, semiconducting oxides and carbon nanofibers have been applied. Colloidal impregnation procedure was applied to prepare highly-dispersed Pt catalysts on such support materials.

2 Thermochemical Stability of Electrode Materials

Thermochemical calculations were applied to derive pH-potential (Pourbaix) diagrams for almost all elements. Stable substances at 80 °C under the PEFC cathode condition are shown in Fig. 1. Among stable materials in strongly acidic environment at 1.0 V vs. standard hydrogen electrode, we can select elements including Sn, Ti, Nb, Ta, W, and Sb stable under PEFC cathode conditions.



Metal-H_2O system at 80°C

Molality m (m=10^{-6}mol/kgH_2O) PH=0

Cathode Eh(vs.SHE)=1.0V

Li Li^+	Be Be^{2+}											B H_3BO_3(a)	C CO_2(a) CO_2(g)	N	O	F
Na Na^+	Mg Mg^{2+}											Al Al^{3+}	Si H_2SiO_3(a) (H_4SiO_4)	P $H_4P_2O_7$(a)	S HSO_4^-	Cl
K K^+	Ca Ca^{2+}	Sc Sc^{3+}	Ti **TiO_2**	V VO_4^-	Cr Cr^{3+}	Mn Mn^{2+}	Fe Fe^{3+} (Fe_2O_3)	Co Co^{2+}	Ni Ni^{2+}	Cu Cu^{2+}	Zn Zn^{2+}	Ga Ga^{3+}	Ge **GeO_2**	As $HAsO_4$(a)	Se H_2SeO_3(a)	Br
Rb Rb^+	Sr Sr^{2+}	Y Y^{3+}	Zr ZrO^{2+}	Nb **Nb_2O_5**	Mo **MoO_3**	Tc	Ru **RuO_2**	Rh RhO_2(g)	Pd **PdO_2**	Ag Ag^+	Cd Cd^{2+}	In In^{3+}	Sn **SnO_2**	Sb **Sb_2O_5**	Te $Te(OH)_3^+$ (H_2TeO_4)	I
Cs Cs^+	Ba Ba^{2+}		Hf **HfO_2**	Ta **Ta_2O_5**	W **$O_2W(OH)_2$**	Re ReO_4^-	Os OsO_4(a) (OsO_2)	Ir **IrO_2**	Pt **Pt**	Au **Au**	Hg	Tl Tl^+	Pb Pb^{2+}	Bi **Bi_2O_3**	Po	At

Figure 1: Most stable substances under the typical PEFC cathode condition at 80 °C, derived from pH-potential diagrams thermochemically calculated.

3 Carbon-free Pt Electrocatalysts Supported on SnO_2 for PEFCs

For PEFCs, the electrocatalysts in which Pt nano-particle are homogeneously distributed on carbon black (Pt/C) are widely used. However, fluctuation of cell voltage up to higher potentials can cause oxidation-induced carbon support corrosion especially for cathode electrocatalysts. Our group has studied the electrocatalysts using oxide supports to solve these issues. Fig. 2 shows FESEM micrograph of the Pt electrocatalyst supported on SnO_2. Pt nano-particles (with ca. 3 nm in diameter) were homogeneously distributed on the support material. Pt/SnO_2 electrocatalyst is relatively stable in the PEFC cathode environment, and has the electrochemical property comparable to Pt/C [1]. Further modification in the electronic conductivity of SnO_2 may be expected by doping with hypervalent (e.g. Nb^{5+}) or hypovalent (e.g. Al^{3+}) ions. In this study, electrocatalysts with different oxide supports including Pt/SnO_2, Pt/$Sn_{0.95}Nb_{0.05}O_2$, Pt/$Sn_{0.98}Nb_{0.02}O_2$ and Pt/$Sn_{0.95}Al_{0.05}O_2$, were prepared and their nanostructure, electrochemical surface area (ECSA) and durability under high potential conditions were evaluated and compared. Voltage cycling up to 10,000 cycles between 0.6 and 1.3 V_{RHE} was applied for the electrocatalysts. Fig. 3 indicates the ECSA of the electrocatalysts as a function of the number of cycles. In comparison with Pt/SnO_2, Pt/$Sn_{0.95}Nb_{0.05}O_2$ and Pt/$Sn_{0.98}Nb_{0.02}O_2$ exhibited larger ECSA in the initial stage. The ECSA of Pt/C rapidly decreased down to nearly zero within 3000 times of voltage cycles. Carbon corrosion and agglomeration of Pt particles would be the main reasons of these phenomena. In contrast, Pt/SnO_2-based electrocatalysts exhibited considerably longer durability compared to Pt/C [2]. Even after 10,000 times of voltage cycles, the carbon-free Pt/$Sn_{0.98}Nb_{0.02}O_2$ electrocatalyst still has sufficient ECSA above 30 m^2g^{-1}.

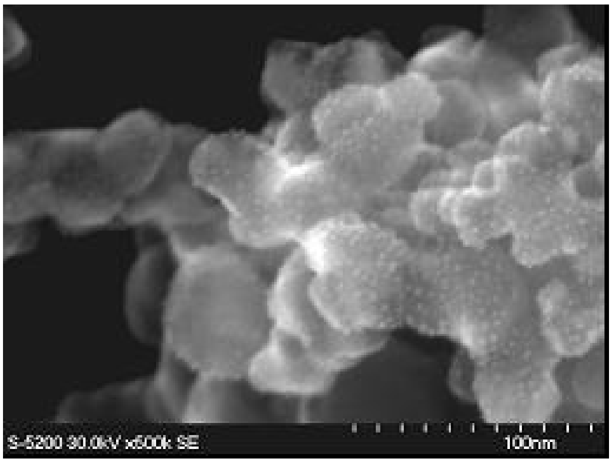


Figure 2: **FESEM micrograph of Pt/SnO_2.**

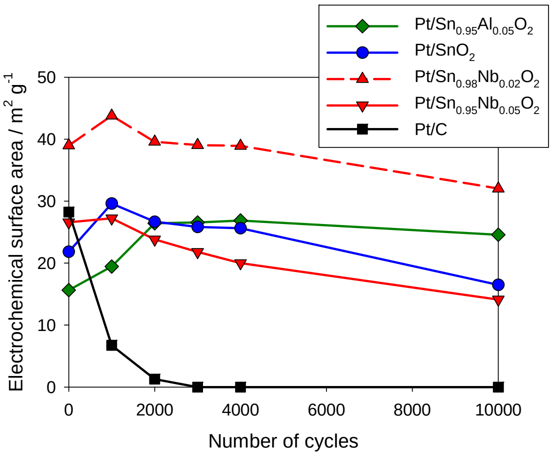


Figure 3: **ECSA vs. number of cycles in the potential range between 0.6 and 1.3 V_{RHE}.**

These results indicate that SnO_2-based carbon-free electrocatalysts may improve long-term durability of PEFCs against voltage cycling [1-2].

I-V characteristics of single cells with Pt/C or Pt/SnO_2 as the cathode catalyst are shown in Fig. 4, for which the identical preparation procedures and a simple MEA structure (e.g. without MPL) were applied just for comparison. Sufficient performance comparable to that of the conventional cell with Pt/C was achieved using Pt/SnO_2 as a cathode catalyst.

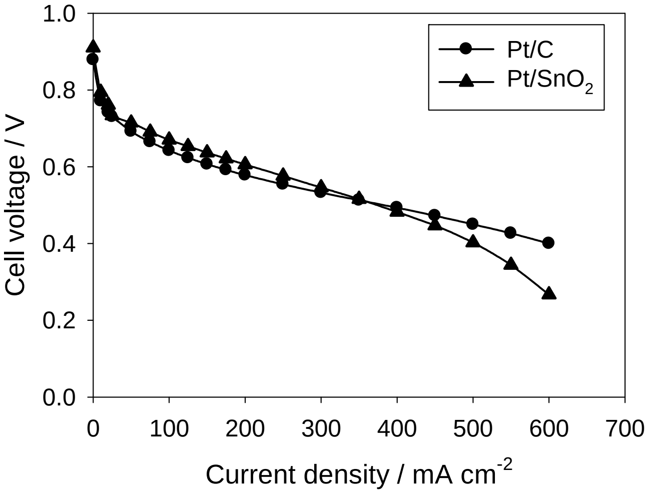


Figure 4: **I-V characteristics of a single cell using Pt/SnO_2 as a cathode electrocatalyst, measured at 80 °C. For comparison, I-V characteristics of a cell using Pt/C as a cathode are also shown [1].**

4 Pt electrocatalysts Supported on Various Carbon Nanofibers

As the colloidal impregnation was useful to prepare highly-dispersed Pt electrocatalysts on carbon black and other support materials, this procedure was also applied for carbon nanofibers with various crystallographic structures illustrated in Fig. 5. Table 1 shows Pt crystallite size on various carbon nanofibers, determined by XRD. We have found that the colloidal impregnation was suitable for preparing nanocrystalline electrocatalyst particles on various carbon supports.

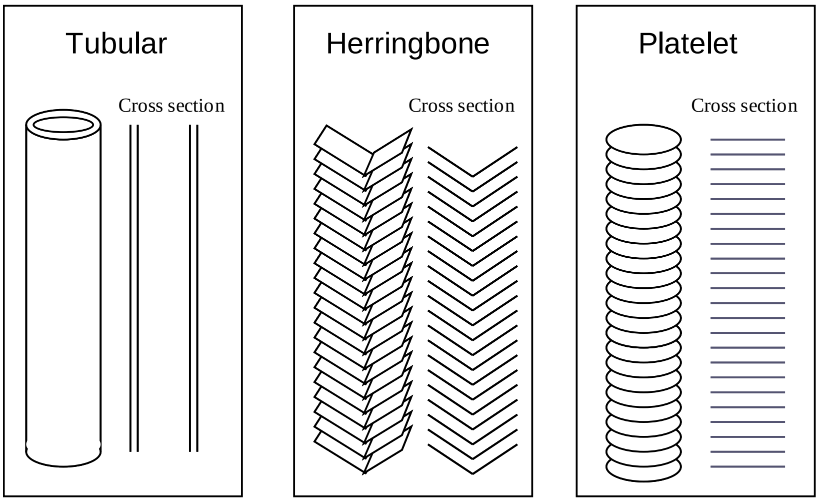


Figure 5: **Structures of tubular, herringbone and platelet carbon nanofibers.**

FESEM micrograph of Pt electrocatalysts supported on tubular carbon fibers (nanotubes) is shown in Fig. 6. Pt particles were a few nm in diameter, but their distribution was rather inhomogeneous. It can be considered that high dispersion of Pt catalysts on carbon nanotubes was still difficult even using this colloidal process. Fig. 7 shows FESEM micrograph of Pt electrocatalysts supported on herringbone-type carbon nanofibers, in which their graphene plain is tilted ca. 45° from the fiber direction. It has been found that homogeneity of Pt distribution was improved, whereas no Pt particles existed on some parts of fiber surfaces. Fig. 8 shows FESEM micrograph of Pt electrocatalysts supported on platelet-type carbon fibers. We can clearly find that Pt particles are distributed homogeneously on the surface of this carbon fiber. This impregnation process was also applied to vapour-grown carbon nanofibers (VGCF). We have succeeded to prepare nanocrystalline Pt catalysts on the fibers of this type, as shown in Fig. 9 [3].

Table 1: Pt crystallite size measured by XRD peak broadening.

Carbon support	Crystallite size (nm)
Carbon black (Vulcan)	3.4
CNF-Platelet	3.3
CNF-Herringbone	3.9
CNF-Tubular	3.6
VGCF	5.6

Table 2 shows effective surface area of the Pt electrocatalysts, determined by CV. These well-dispersed Pt electrocatalysts possess comparable effective surface area to the catalyst on the state-of-the-art carbon support (Vulcan). Pt catalysts especially on VGCFs and on herringbone-type fibers exhibit higher effective surface areas. In addition, kinetically-controlled current density of Pt catalysts on VGCFs and on herringbone-type fibers was also higher, compared to that on the other types of carbon fibers. In order to demonstrate the feasibility of Pt electrocatalysts supported on carbon nanofibers, PEFCs were prepared using such electrocatalysts. Fig. 10 shows the cross section of the electrocatalyst layers with VGCF support, exhibiting a typical microstructure with conductive fiber network and open porosity. We have obtained I-V characteristics of such PEFCs at 80 °C, exhibiting a high electrochemical performance, while long-term durability should be controlled and optimized because Pt nanoparticles on such carbon nanofibers tend to agglomerate.

Table 2: Pt effective surface area measured by cyclic voltammetry.

Carbon support	Pt effective surface area / m^2g^{-1}
Carbon black (Vulcan)	52.4
CNF-Platelet	42.7
CNF-Herringbone	56.7
CNF-Tubular	49.7
VGCF	68.3

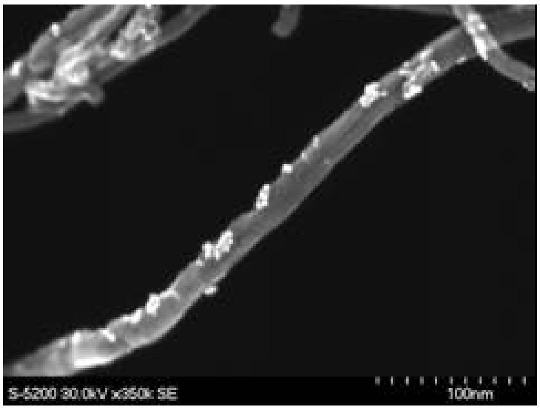


Figure 6: FESEM micrograph of Pt electrocatalysts supported on tubular carbon nanofibers (nanotubes).

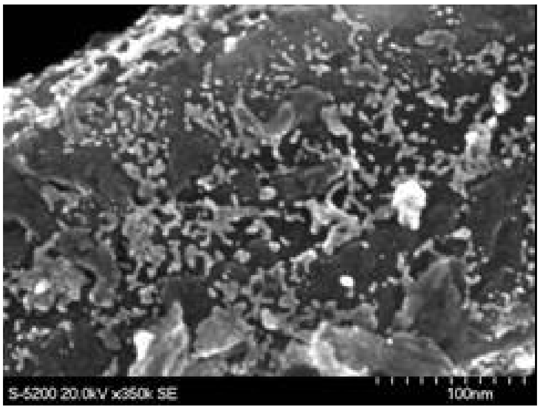


Figure 7: FESEM micrograph of Pt electrocatalysts supported on herringbone-type carbon nanofibers.

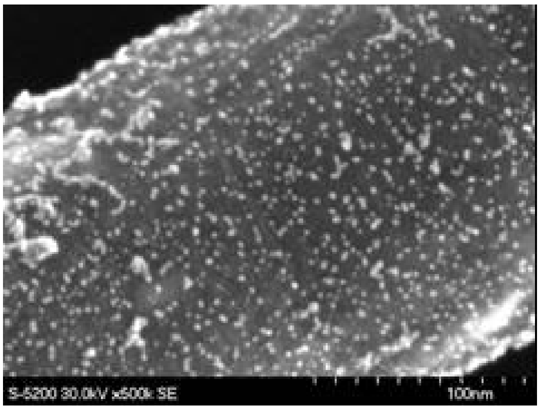


Figure 8: FESEM micrograph of Pt electrocatalysts supported on platelet-type carbon nanofibers.

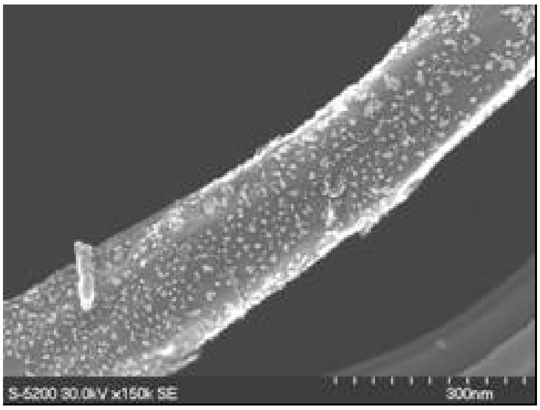


Figure 9: FESEM micrograph of Pt/C (VGCF) electrocatalysts prepared via colloidal impregnation.

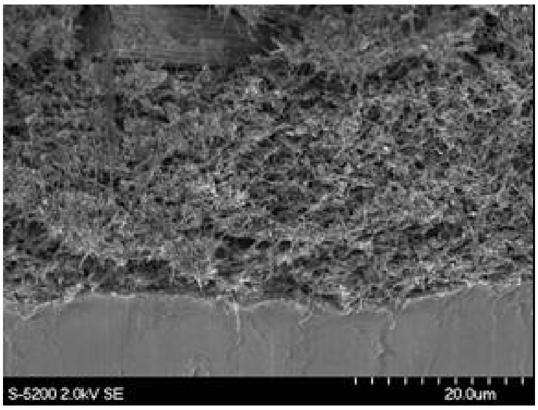


Figure 10: FESEM micrograph of Pt/C (VGCF) porous electrocatalyst layer, with highly-conductive network structure and open porosity.

5 Summary: Electrocatalyst Design from Catalyst Support Materials

Among (semi)conducting oxides, (relatively inexpensive) SnO_2-based oxides exhibit a satisfactory durability against voltage cycling, so that such materials may be applied as alternative catalyst support materials, in order to improve the durability of PEFC systems. Other oxides may be interesting to be tested in a future. Carbon nanofibers are also interesting materials as catalyst supports to prepare electrocatalyst layers with highly-conductive network structure and open porosity, for which the catalyst support stability and the homogeneous dispersion of Pt nanoparticles should be simultaneously optimized.

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