# Alternative Oxide-Supported Electrocatalysts for PEFCs

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## Introduction

Longer-term durability of electrocatalysts is essential for cells (PEFCs), where polymer electrolyte fuel electrocatalyst support materials act as a very important role. During the fuel cell start-stop cycles, however, the potential of the cathode can reach up to 1.5 V (versus reversible hydrogen electrode, RHE). Fluctuation of cell voltage up to such higher potentials can cause oxidationinduced carbon support corrosion especially for cathode electrocatalysts [1-3]. In this study, as alternatives to the conventional carbon black electrocatalyst support, conductive oxides are mainly considered as carbon-free catalyst support materials [4-6]. Thermochemical calculations have revealed, as shown in Fig. 1 [4], that several oxides could be stable under the PEFC cathode conditions.

Li Li <sup>+</sup> Na	Be Be <sup>2+</sup> Mg Mg <sup>2+</sup>	Metal-H <sub>2</sub> O system at 80℃ Molality m (m=10 <sup>6</sup> mol/kgH <sub>2</sub> O) PH=0 Cathode Eh(vs.SHE)=1.0V										B H <sub>3</sub> BO <sub>3</sub> (a) Al Al <sup>3+</sup>	C CO <sub>2</sub> (a) CO <sub>2</sub> (g) Si H <sub>2</sub> SiO <sub>3</sub> (a) (H <sub>4</sub> SiO <sub>4</sub> )	N P H <sub>4</sub> P <sub>2</sub> O <sub>3</sub> (a)	O S HSO4	F CI
Κ	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
$\mathbf{K}^{*}$	Ca <sup>2+</sup>	Sc3+	TiO <sub>2</sub>	VO4	Cr <sup>3+</sup>	Mn <sup>2+</sup>	Fe <sup>37</sup> (Fe <sub>2</sub> O <sub>3</sub> )	Co <sup>2+</sup>	Ni <sup>2+</sup>	Cu <sup>2+</sup>	Zn <sup>2+</sup>	Ga <sup>3+</sup>	GeO2	HAsO4(a)	H2SeO3(a)	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
$\mathbf{Rb}^+$	Sr <sup>2+</sup>	<b>Y</b> <sup>3+</sup>	ZrO <sup>2+</sup>	Nb <sub>2</sub> O <sub>5</sub>	MoO <sub>3</sub>		RuO <sub>2</sub>	RhO <sub>2</sub> (g)	PdO <sub>2</sub>	$Ag^+$	Cd <sup>2+</sup>	In <sup>3+</sup>	SnO <sub>2</sub>	Sb <sub>2</sub> O <sub>5</sub>	Te(OH)3 <sup>+</sup> (H2TeO4)	
Cs	Ba		Hf	Та	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At
$\mathbf{Cs}^+$	Ba <sup>2+</sup>		HfO <sub>2</sub>	Ta <sub>2</sub> O <sub>5</sub>	O2W(OH)2	ReO4	OsO <sub>4</sub> (a) (OsO <sub>2</sub> )	IrO2	Pt	Au		$\Pi^+$	Pb <sup>2+</sup>	Bi <sub>2</sub> O <sub>3</sub>		

Fig.1: Most stable substances under the typical PEFC cathode condition at 80°C, derived from pH-potential diagrams thermochemically calculated [4].

## Experimental

In this study, electrocatalysts with different oxide supports were wet-chemically prepared and their nanostructure, electrochemical surface area (ECSA), and durability under high potential conditions were evaluated and compared. Voltage cycling up to 60,000 cycles was applied for the electrocatalysts. MEAs using Pt/doped-SnO<sub>2</sub> cathodes have been prepared and their I-V characteristics and their durability have been studied, before and after voltage cycling up to  $1.5 V_{RHE}$ .

### **Results and Discussion**

Figure 2 shows the CV diagrams of the Pt electocatalysts supported on various oxides. Some electrocatalysts exhibited small CV signals probably due to poor electrical conductivity of the support materials. While  $WO_3$  and MoO<sub>3</sub> could be used as catalyst support materials, SnO<sub>2</sub> exhibited clear CV signals.

Figure 3 shows the I-V curves before and after such startstop cycle tests for an MEA with the cathode electrocatalyst layer consisting of the Pt/Sn<sub>0.98</sub>Nb<sub>0.02</sub>O<sub>2</sub> mixed with 5wt % vapor grown carbon fibers (VGCF-H) as the electron-conductive filler. In the case with commericial Pt/C (TEC10EA20E, Tanaka Kikinzoku,

Japan), carbon black was oxidized by the cycles up to the high potential, so that no power was then generated after 15,000 cycles. However, in the case with the Pt electrocatalyst using Nb-doped SnO<sub>2</sub> support, only a slight degradation was distinguished up to 60,000 cycles. This result confirms that Nb-doped SnO<sub>2</sub> can be an alternative electrocatalyst support material for e.g. fuel cell vehicles (FCVs) which are suffered from the voltage cycling up to a high potential. Especially, the MEA with Pt/Sn<sub>0.98</sub>Nb<sub>0.02</sub>O<sub>2</sub> mixed with 5wt % VGCF-H conductive filler exhibited high durability while maintaining relatively high I-V performance.

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Fig. 3: I-V characteristics for an MEA with Pt/ Sn<sub>0.98</sub>Nb<sub>0.02</sub>O<sub>2</sub> mixed with 5 wt% VGCF-H conductive filler, used as the cathode measured after the start-stop cycle (1.0 - 1.5  $V_{RHE}$ ) durability test, measured at 80°C.