

## Active Ceramic Anodes for Solid Oxide Fuel Cells: Ce(Mn, Fe)O<sub>2</sub> and La(Sr)Fe(Mn)O<sub>3</sub> Composite Oxide

by Tae Ho Shin

Several oxides have recently attracted great interest as anode material candidates for solid oxide fuel cells (SOFCs) to overcome serious deterioration associated with the traditional Ni-based cermet; particularly, carbon deposition and re-oxidation tolerance<sup>1</sup>. In our previous study, we proposed that a relatively good power generation property as well as excellent redox tolerance could be achieved by using doped CeO<sub>2</sub> and LaFeO<sub>3</sub> composite oxide as an anode for SOFCs.<sup>2</sup> However, in spite of several oxides with positive results reported for oxide anode, the power density of the cells at intermediate temperatures was still smaller than that of the cell using a Ni cermet anode because of insufficient electrical conductivity as well as catalytic activity.

To enhance electrical conductivity and catalytic properties on the anode for SOFCs, metal or oxide catalyst additives have been used. In this work, many type of catalysts were examined to improve anodic performance of the Ce(Mn,Fe)O<sub>3</sub> and La(Sr)Fe(Mn)O<sub>3</sub> composite oxide (CMF-LSMF) as shown in Table I. Among them, it was found that CMF-LSMF modified by small amount of Pd or RuO<sub>2</sub> are highly effective for enhancing anodic performance in not only H<sub>2</sub> but also hydrocarbon fuel. Since one of the attractive things for ceramic anode is possibility for utilization of hydrocarbon as a fuel in SOFC systems, we also examined various possible anodes in CH<sub>4</sub> and C<sub>3</sub>H<sub>8</sub>. Figure 1 shows the impedance plot of oxide

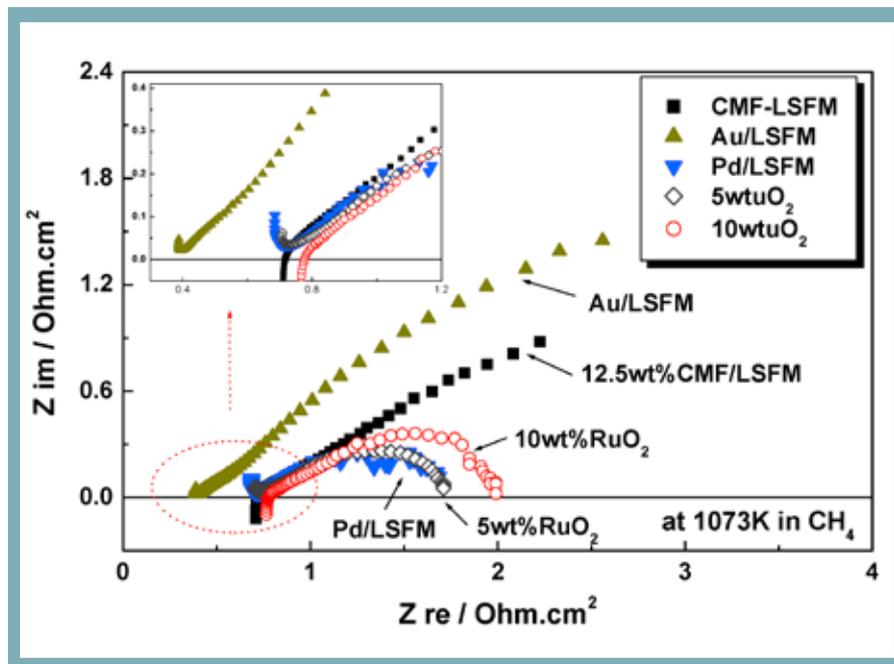


FIG. 1. Impedance plot for various anodes; catalyst metal loaded on oxide anode in the CH<sub>4</sub> at 1073K. A small amount of precious metals (Pt, Au, Pd, and RuO<sub>2</sub>) was modified on oxide anodes (La(Sr)Fe(Mn)O<sub>3</sub>, Ce(Mn, Fe)O<sub>2</sub> and their mixture composite).

anode with various additives in CH<sub>4</sub>. In the case of Au, it seems that a small amount of Au leads to decrease anodic ohmic resistance of oxide anode but much large diffusion resistance was shown in large semicircle at low frequency in Fig. 1. This suggests that simple improvement in conductivity is not

enough for anode performance in SOFC and increased activity on the surface is also strongly requested.

In contrast, when a small amount of Pd and RuO<sub>2</sub> was added to CMF-LSMF composite anode, increased cell performance could

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Table I. Power density and anodic properties of the cell using oxide anode with various catalytic metals.

Oxide anode with additive	At 1073K in H <sub>2</sub>				At 1073K in CH <sub>4</sub>			
	Cell performance		Potential drop (mV) <sup>a</sup>		Cell performance		Potential drop (mV) <sup>b</sup>	
	O.C.V. (V)	M.P.D. (mW/cm <sup>2</sup> )	η <sub>anode</sub>	IR <sub>anode</sub>	O.C.V. (V)	M.P.D. (mW/cm <sup>2</sup> )	η <sub>anode</sub>	IR <sub>anode</sub>
Ce <sub>0.6</sub> Mn <sub>0.3</sub> Fe <sub>0.1</sub> O <sub>2</sub> +La <sub>0.6</sub> Sr <sub>0.4</sub> Fe <sub>0.9</sub> Mn <sub>0.1</sub> O <sub>3</sub> ( Denoted as Composite CMF-LSMF )	1.113	315	34.5	162.5	0.572	24	21.9	56.3
10wt%Fe <sub>2</sub> O <sub>3</sub> + ( Composite CMFLSFM )	1.105	250	37.5	150	0.519	20	-	-
2wt% Pd modified La <sub>0.6</sub> Sr <sub>0.4</sub> Fe <sub>0.9</sub> Mn <sub>0.1</sub> O <sub>3</sub>	1.117	550	25	118.75	0.846	123	15.62	71.87
5wt% Pt loaded on La <sub>0.6</sub> Sr <sub>0.4</sub> Fe <sub>0.9</sub> Mn <sub>0.1</sub> O <sub>3</sub>	1.091	167	93.7	231.3	0.479	-	-	-
5wt% Au loaded on La <sub>0.6</sub> Sr <sub>0.4</sub> Fe <sub>0.9</sub> Mn <sub>0.1</sub> O <sub>3</sub>	1.111	190	75	290.6	0.308	-	-	-
5wt% Au loaded on Ce <sub>0.6</sub> Mn <sub>0.3</sub> Fe <sub>0.1</sub> O <sub>2</sub>	1.109	181	46.9	196.9	0.3	-	-	-
5wt% RuO <sub>2</sub> + ( Composite CMFLSFM )	1.114	330	37.5	187.5	0.927	125	15.62	75.01
10wt% RuO <sub>2</sub> + ( Composite CMFLSFM )	1.109	230	78.13	243.75	0.893	108	21.25	97.5

<sup>a</sup> Potential drop at 0.3A/cm<sup>2</sup>, cathode; Sm<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3</sub>, electrolyte; La<sub>0.8</sub>Sr<sub>0.2</sub>Ga<sub>0.8</sub>Mg<sub>0.15</sub>Co<sub>0.05</sub>O<sub>3</sub> in H<sub>2</sub>

<sup>b</sup> Potential drop at 0.3A/cm<sup>2</sup>, cathode; Sm<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3</sub>, electrolyte; La<sub>0.8</sub>Sr<sub>0.2</sub>Ga<sub>0.8</sub>Mg<sub>0.15</sub>Co<sub>0.05</sub>O<sub>3</sub> in CH<sub>4</sub>

η<sub>anode</sub>: anodic overpotential, IR<sub>anode</sub>: anodic resistance loss

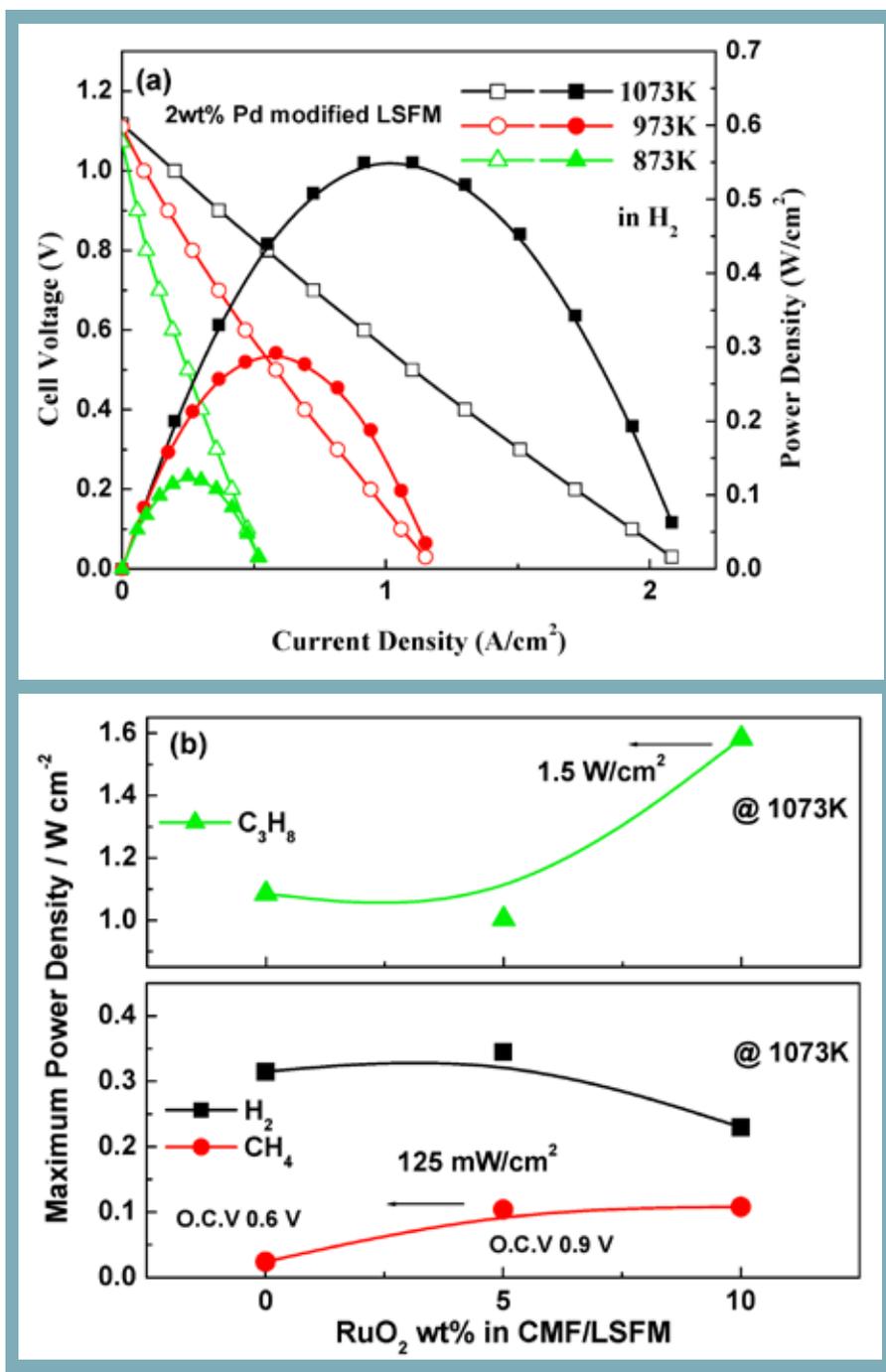


FIG. 2. Improved cell performance by additives: (a) cell voltage and power density versus current density for fuel cell with a La(Sr)Fe(Mn)O<sub>3</sub> perovskite anode modified with 2 wt% Pd in hydrogen at 1173K (■), 1073K (●), and 973K (▲); (b) maximum power density of the cell using CMF-LSFM composite anode as a function of RuO<sub>2</sub> amount in composite anode at 1073K for various fuel conditions. The electrolyte-supporting cell had an electrolyte thickness < 300 μm and Sm<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3</sub> cathode.

be achieved. Figure 2a shows temperature dependent cell voltage and power density versus current density for the cell with a La(Sr)Fe(Mn)O<sub>3</sub> perovskite anode modified with 2 wt% Pd in H<sub>2</sub>. In particular the maximum power density of approximately 0.6 W/cm<sup>2</sup> was achieved at 1073K in H<sub>2</sub>. It is noted that this power density is relatively large compared to the results reported for ceramic anodes. Furthermore, in the case of RuO<sub>2</sub> as an additive, fairly good maximum power density values of 125 and 1500 mW/cm<sup>2</sup> were achieved at 1073K under CH<sub>4</sub> and C<sub>3</sub>H<sub>8</sub> when 5 wt% and 10 wt% of RuO<sub>2</sub> mixed to CMF-LSFM composite oxide anode. Figure 2b shows the optimization of maximum power density as a function of amount of RuO<sub>2</sub> in anode under CH<sub>4</sub> and C<sub>3</sub>H<sub>8</sub> at 1073K. Further study is now underway and it could be concluded that CMF-LSFM composite oxide modified with Pd or RuO<sub>2</sub> is highly attractive as an active ceramic anode for SOFC.

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