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Article

Polyol-synthesized $\text{Pt}_{2.6}\text{Sn}_1\text{Ru}_{0.4}/\text{C}$ as a high-performance anode catalyst for direct ethanol fuel cells

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ABSTRACT

PtSnRu/C catalysts with different atomic ratios and metal loadings were prepared using a polyol process to improve the performance of direct ethanol fuel cells (DEFCs). The catalysts were characterized using transmission electron microscopy and X-ray photoelectron spectroscopy. The DEFC performance was evaluated using a single-cell test. The ethanol electro-oxidation process and anode products were analyzed using in situ Fourier-transform infrared spectroscopy (FTIRS), gas chromatography, and neutralization titration. The performance of the $\text{Pt}_{2.6}\text{Sn}_1\text{Ru}_{0.4}/\text{C}$ catalyst was better than those of the $\text{Pt}_3\text{Sn}_1/\text{C}$ and $\text{Pt}_2\text{Sn}_1\text{Ru}_1/\text{C}$ catalysts. The carbon-supported $\text{Pt}_{2.6}\text{Sn}_1\text{Ru}_{0.4}$ catalyst with a 60 wt% metal loading gave a maximum power density of 121 mW/cm² at 90 °C. In situ FTIRS and anode product analysis indicated that ethanol was electro-oxidized to acetaldehyde, acetic acid, ethyl acetate, and CO₂. The ethanol oxidation efficiency on the $\text{Pt}_{2.6}\text{Sn}_1\text{Ru}_{0.4}/\text{C}$ catalyst was higher than that on the $\text{Pt}_3\text{Sn}_1/\text{C}$ catalyst. The activation energy of ethanol electro-oxidation at the anode and surface composition analysis indicated that interactions among the surface elements resulted in a lower apparent activation energy and greater ethanol electro-oxidation efficiency on the $\text{Pt}_{2.6}\text{Sn}_1\text{Ru}_{0.4}/\text{C}$ catalyst.

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1. Introduction

The use of ethanol, which is a green fuel, in low-temperature fuel cells is attractive because of its low toxicity and high theoretical energy density (8.0 kW h kg⁻¹) [1–6]. However, the performance of direct ethanol fuel cells (DEFCs) is poor and need to be greatly improved. Table 1 lists the performances of state-of-the-art DEFCs with proton-exchange membranes using different anode catalysts [7–19]. The cell temperature cannot be greater than 110 °C because it is limited by the critical temperatures of perfluorinated proton-exchange membranes (mostly Nafion®-based membranes). It is well known that the slow kinetics of ethanol electro-oxidation in acidic media at low

temperatures is a major challenge for the development of DEFCs. Much effort has been devoted to screening effective catalysts for ethanol electro-oxidation [7–24]. Pt is the most effective catalyst for ethanol adsorption and dissociation, but the current density on Pt is low as a result of poisoning by adsorbed CO (denoted by CO_{ads}) derived from ethanol dissociation [22,25,26]. The use of Pt-based binary or ternary catalysts to increase the activities of ethanol electro-oxidation catalysts has been investigated.

The results listed in Table 1, which are for DEFC anode catalysts, show that PtRu- and PtSn-based catalysts achieve much greater peak power densities than Pt (12 mW/cm²) [27]. It has been reported that second elements such as Ru or Sn perform

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Table 1

Performance of DEFCs using proton-exchange membranes at low temperatures.

Anode catalyst	Preparation method	Cell temperature (°C)	Peak power density (mW/cm ²)	Refs.
Pt ₈₀ Sn ₂₀ /C	Pechini method	90	37	[7]
Pt ₁ Ru ₁ /C	Johnson Matthey (commercial)	90	29	[8]
Pt ₈₀ Sn ₁₀ Ni ₁₀ /C	Bönnemann's method	80	46	[9]
PtSnCo/C	Bönnemann's method	80	35	[10]
Pt ₂₀ In ₅ Sn ₁₅ /C	impregnation reduction method	90	29	[11]
Pt ₃ Sn ₁ /C+PtRu black	modified polyol method	90	96	[12]
Pt ₁ Sn ₁ Ru _{0.3} /C	formic acid reduction method	110	32	[13]
Pt ₈₆ Sn ₁₀ Ru ₄ /C	Bönnemann's method	80	50	[14]
Pt ₃ Sn ₁ /C	modified polyol method	90	80	[15]
PtRu black	Johnson Matthey (commercial)	90	32	[16]
Pt ₁ Sn ₁ Ru ₁ /C	modified polyol method	90	38	[17]
Pt ₉ Sn ₁ /C-Sb ₂ O ₅ ·SnO ₂	alcohol reduction process	100	60	[18]
Pt ₂₀ Re ₅ Sn ₁₅ /C	co-impregnation reduction method	100	30.5	[19]

different roles during ethanol adsorption, dissociation, and oxidation. The role of Ru is to promote water dissociation at low potentials during ethanol electro-oxidation, producing oxygenated species (e.g., adsorbed OH, denoted by OH_{ads}) and giving a higher yield of CO₂ than that obtained with Pt catalysts [28,29]. When Pt is modified with Sn, the effect of CO_{ads} poisoning is weakened, and the ethanol electro-oxidation pathway yields acetaldehyde, which is then oxidized to acetic acid [29–31].

We fabricated a double-layered anode catalyst using PtRu black and Pt₃Sn₁/C catalysts to combine the promotional roles of Ru and Sn on Pt for ethanol electro-oxidation. The performance of the DEFC with a double-layered anode catalyst was better than those of DEFCs with single-layered PtRu black and Pt₃Sn₁/C anode catalyst layers, and a maximum power density of 96 mW/cm² was obtained. Another method is to use PtSnRu catalysts. Several methods have been developed for preparing PtRuSn/C catalysts, e.g., the Pechini, formic acid reduction, and liquid-crystalline templating methods. However, the DEFC performance is not high, usually less than 50 mW/cm² [13,14,17,30–32]. The preparation method has a strong influence on the particle-size and composition distribution of the catalyst and therefore affects the electrocatalytic activity. Among different approaches, the polyol process using ethylene glycol has been widely used to prepare carbon-supported Pt-based catalysts with accurate size control and a uniform distribution of metal nanoparticles on the carbon support. Polyol-synthesized Pt-based catalysts also have superior electrocatalytic activities for methanol/ethanol electro-oxidation and oxygen reduction reactions [33–35].

In this work, we prepared PtSnRu/C catalysts with different atomic ratios and metal loadings using the polyol process. The morphologies and compositions of the catalysts were determined using transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). Single-cell tests and anode polarization measurements were conducted to evaluate the catalyst activities for ethanol electro-oxidation. Apparent activation energy analysis, in situ Fourier-transform infrared spectroscopy (FTIRS), and anode product analysis were performed to investigate the ethanol electro-oxidation mechanism on the PtSnRu/C catalyst.

2. Experimental

2.1. Catalyst preparation

H₂PtCl₆·6H₂O, SnCl₂·2H₂O, and RuCl₃·xH₂O were used as the PtSnRu/C catalyst precursors. Three catalysts with metal loadings of 45 wt% and Vulcan XC-72R as the support material were prepared; the atomic ratios of Pt, Sn, and Ru were 3:1:0, 2.6:1:0.4, and 2:1:1. The atomic ratios of the different elements were varied by controlling the amounts of different precursors during catalyst preparation. The prepared catalysts were denoted by Pt₃Sn₁/C, Pt_{2.6}Sn₁Ru_{0.4}/C, and Pt₂Sn₁Ru₁/C, according to the atomic ratios of the elements. A catalyst with a metal loading of 60 wt% and Ketjen Black EC 300J as the support material was prepared with Pt, Sn, and Ru atomic ratios of 2.6:1:0.4. This catalyst was denoted by Pt_{2.6}Sn₁Ru_{0.4}/C-H. The typical preparation procedure was as follows. Calculated amounts of H₂PtCl₆·6H₂O, SnCl₂·2H₂O, RuCl₃·xH₂O, and Vulcan XC-72R or Ketjen Black EC 300J carbon black were dissolved in ethylene glycol in a three-necked flask. The pH of the solution was increased to about 13 with 1 mol/L NaOH solution. The solution was heated to 165 °C at a rate of 10 K/min and kept at that temperature for 4 h, and then the solution was cooled to 90 °C. An HCl solution of concentration 1.5 mol/L was then added to adjust the pH to about 2, and the solution was kept at 90 °C for 24 h. Finally, the obtained catalyst was filtered, washed, and dried at 80 °C for 10 h in a vacuum oven.

2.2. Physicochemical characterization

The catalyst morphologies were investigated by TEM using a TECNAI F30 or G2 microscope (FEI Corp.), and more than 200 particles were measured to obtain the average particle size and particle-size distribution of the catalysts. XPS measurements were carried out using a JEOL JPS-9010MC spectrometer with an Mg K α radiation source. The Pt 4f, Ru 3p, and Sn 3d signals were collected. The position of the C 1s peak, i.e., 284.2 eV, was used to correct the catalyst binding energies.

2.3. Membrane electrode assembly (MEA) fabrication and single-cell tests

Anode and cathode diffusion layers were prepared by brushing a slurry consisting of carbon black, polytetrafluoroethylene (PTFE), and ethanol on hydrophobic carbon paper (0.19 mm thick, SGL Carbon Group, Short Hills, NJ, USA) and subsequent drying as previously described [36]. Anode catalyst layers containing $\text{Pt}_3\text{Sn}_1/\text{C}$, $\text{Pt}_{2.6}\text{Sn}_1\text{Ru}_{0.4}/\text{C}$, or $\text{Pt}_2\text{Sn}_1\text{Ru}_1/\text{C}$ were prepared as follows. A water/alcohol solution of the catalyst was mixed with a Nafion® solution (Dupont), and the resulting mixture was ultrasonically agitated with vigorous mechanical stirring to form a homogeneous ink. The ink was then brushed onto the anode diffusion layer held on a heating table at 60 °C. The resulting catalyst loading was 4.5 mg/cm² and the Nafion® content of the anode catalyst layer was 10 wt%. The anode catalyst layer with $\text{Pt}_{2.6}\text{Sn}_1\text{Ru}_{0.4}/\text{C}$ -H had a catalyst loading of 5.8 mg/cm², and a Nafion® content of 10 wt%. In all cases, identical cathode catalyst layers were prepared by brushing the cathode ink onto the cathode diffusion layer held on a heating table at 60 °C. The resulting Pt loading was 3.7 mg/cm², and the Nafion content was 12 wt%. The obtained anode and cathode were placed on both sides of a Nafion® 1135 membrane and hot pressed at 135 °C and 2000 pounds for 2 min to form an MEA.

Single-cell tests were carried out using an Arbin® instrument at 90 °C. The anode was fed with 1.5 mol/L ethanol solution at a flow rate of 1 mL/min. The cathode was fed with oxygen at a flow rate of 200 mL/min and gas pressure of 0.2 MPa. Linear sweeping voltammetry of the anode catalyst layers was performed at 90 °C using an EG&G PAR 273 potentiostat at a scan rate of 1 mV/s. For these measurements, the anode was fed with 1.5 mol/L ethanol solution at a flow rate of 1 mL/min as the working electrode, and the cathode was fed with hydro-

gen gas as the counter and pseudo-reference electrodes. The hydrogen pressure and flow rate were 0.1 MPa and 50 mL/min, respectively.

2.4. In situ FTIRS and anode product analysis

In situ FTIRS was performed in a PTFE cell with a CaF_2 optical window using a JASCO FT/IR-6100 spectrometer equipped with a triglycine sulfate detector. A gold disk (10 mm in diameter) was used as the electrode substrate. The catalyst layers were deposited on a gold electrode surface using a previously described method [37]. The electrode was pressed against the CaF_2 window to create a thin ethanol layer in 0.1 mol/L HClO_4 solution. IR spectra were recorded at a scan rate of 0.25 mV/s, and 25 interferograms were co-added to each spectrum. All potentials were referenced to the reversible hydrogen electrode. The measurements were performed at room temperature. The trap for the outlet products has been described previously [12]. The DEFC was operated at a certain cell voltage for 3 h under the same operating conditions as in the single-cell tests. The concentrations of ethanol, acetaldehyde, and ethyl acetate were determined using a VARIAN CP-3800 gas chromatograph, and the concentration of acetic acid was determined by titration with standardized NaOH solution. The content was calculated from the weight of BaCO_3 .

3. Results and discussion

3.1. Physicochemical characterization

Figure 1 shows TEM images and corresponding size distributions

Fig. 1. TEM images (a–c) and corresponding particle size distributions (d–f) of $\text{Pt}_3\text{Sn}_1/\text{C}$ (a,d), $\text{Pt}_{2.6}\text{Sn}_1\text{Ru}_{0.4}/\text{C}$ (b,e) and $\text{Pt}_2\text{Sn}_1\text{Ru}_1/\text{C}$ (c,f) catalysts.

bution diagrams of the catalysts. It can be seen that the particles are uniformly distributed on the carbon support with mean diameters of 2.6, 2.1, and 1.8 nm for the $\text{Pt}_3\text{Sn}_1/\text{C}$, $\text{Pt}_{2.6}\text{Sn}_1\text{Ru}_{0.4}/\text{C}$, and $\text{Pt}_2\text{Sn}_1\text{Ru}_1/\text{C}$ catalysts, respectively. The particles in the $\text{Pt}_{2.6}\text{Sn}_1\text{Ru}_{0.4}/\text{C}$ and $\text{Pt}_2\text{Sn}_1\text{Ru}_1/\text{C}$ catalysts are distributed more evenly with a narrower range on the support than those in the $\text{Pt}_3\text{Sn}_1/\text{C}$ catalyst, which might be because the addition of Ru inhibits nanoparticle aggregation.

XPS measurements were carried out to elucidate the surface compositions and oxidation states of Pt, Sn, and Ru in the $\text{Pt}_3\text{Sn}_1/\text{C}$, $\text{Pt}_{2.6}\text{Sn}_1\text{Ru}_{0.4}/\text{C}$, and $\text{Pt}_2\text{Sn}_1\text{Ru}_1/\text{C}$ catalysts. The spectra of Pt 4f, Ru 3p, and Sn 3d in these catalysts are shown in Fig. 2. The Pt 4f spectra contain two peaks corresponding to the Pt 4f_{7/2} and Pt 4f_{5/2} states from spin orbital splitting. The Pt 4f_{7/2} spectra were deconvoluted with three different Pt oxidation states, i.e., Pt(0), Pt(II), and Pt(IV), corresponding to the three peaks at 71.0, 72.1, and 73.9 eV, respectively, for the $\text{Pt}_3\text{Sn}_1/\text{C}$ catalyst. The standard XPS Pt(0) peak is at 70.9 eV according to previous reports [38]. The small deviation from the standard value could be attributed to interactions between the metals and the carbon support and/or a small-particle effect [39]. The data in Table 2 show that the atomic ratio of Pt(0) in the $\text{Pt}_{2.6}\text{Sn}_1\text{Ru}_{0.4}/\text{C}$ catalyst is 35.3%, which is lower than that in $\text{Pt}_3\text{Sn}_1/\text{C}$ (49.4%), indicating that the content of alloyed Pt decreases on addition of a small amount of Ru to the $\text{Pt}_{2.6}\text{Sn}_1\text{Ru}_{0.4}/\text{C}$ catalyst. However, the content of alloyed Pt increases to 42.5% with increasing Ru content in the $\text{Pt}_2\text{Sn}_1\text{Ru}_1/\text{C}$ catalyst, indicating that a considerable amount of PtRu alloy was formed in the catalyst.

The Ru 3p_{3/2} signals can be deconvoluted into two peaks with binding energies corresponding to Ru(0) and Ru(IV) oxide as shown in Fig. 2(b). The Ru(IV) contents are 41.8% and 41.7% for the $\text{Pt}_{2.6}\text{Sn}_1\text{Ru}_{0.4}/\text{C}$ and $\text{Pt}_2\text{Sn}_1\text{Ru}_1/\text{C}$ catalysts, respectively. This indicates that there are considerable amounts of ruthenium oxide in the catalysts. During catalyst preparation using the polyol method, some Ru³⁺ is reduced to Ru(0) by ethylene glycol to form a PtRu alloy, and the rest of the Ru is oxidized to amorphous RuO₂ in the air [40]. As the data in Table 2 shows, the atomic oxidation states of Ru in the $\text{Pt}_{2.6}\text{Sn}_1\text{Ru}_{0.4}/\text{C}$ and $\text{Pt}_2\text{Sn}_1\text{Ru}_1/\text{C}$ catalysts are similar because the same prepa-

Table 2

Surface atomic oxidation states of Pt and Ru in $\text{Pt}_3\text{Sn}_1/\text{C}$, $\text{Pt}_{2.6}\text{Sn}_1\text{Ru}_{0.4}/\text{C}$, and $\text{Pt}_2\text{Sn}_1\text{Ru}_1/\text{C}$ catalysts obtained from XPS spectra in Fig. 2.

Catalyst	Species	Binding energy (eV)	Peak half-width (eV)	Assignment	Atomic ratio (%)
$\text{Pt}_3\text{Sn}_1/\text{C}$	Pt 4f _{7/2}	71.0	1.5	Pt	49.4
		72.1	2.1	PtO	28.7
		73.9	3.6	PtO ₂	21.9
$\text{Pt}_{2.6}\text{Sn}_1\text{Ru}_{0.4}/\text{C}$	Pt 4f _{7/2}	71.3	1.6	Pt	35.3
		72.3	2.1	PtO	33.9
		74.0	3.1	PtO ₂	30.8
	Ru 3p _{3/2}	462.6	3.6	Ru	58.2
		465.1	5.6	RuO ₂	41.8
$\text{Pt}_2\text{Sn}_1\text{Ru}_1/\text{C}$	Pt 4f _{7/2}	71.3	1.6	Pt	42.5
		72.3	2.1	PtO	34.0
		74.1	3.2	PtO ₂	23.5
	Ru 3p _{3/2}	462.6	3.6	Ru	58.3
		465.2	5.3	RuO ₂	41.7

ration method was used. From the spectra in Fig. 2(c), it can be seen that the main Sn 3d_{5/2} peak is at 486.5 eV with a half-peak width of about 1.8 eV. This is assigned to one surface state of SnO_x (e.g., SnO, SnO₂, or Sn hydroxides); SnO and SnO₂ cannot be distinguished because the difference between Sn(II) and Sn(IV) binding energies is only 0.2 eV. Sn atoms on the catalyst surfaces could have been oxidized when the catalysts were exposed to air before the XPS measurements because of the low redox potentials for Sn/Sn²⁺ and Sn²⁺/Sn⁴⁺ [41,42].

3.2. Single-cell performance

Figure 3 shows the single-cell performance of DEFCs with $\text{Pt}_3\text{Sn}_1/\text{C}$, $\text{Pt}_{2.6}\text{Sn}_1\text{Ru}_{0.4}/\text{C}$, $\text{Pt}_2\text{Sn}_1\text{Ru}_1/\text{C}$, and $\text{Pt}_{2.6}\text{Sn}_1\text{Ru}_{0.4}/\text{C-H}$ as the anode catalysts. The open-circuit voltage (OCV) for $\text{Pt}_{2.6}\text{Sn}_1\text{Ru}_{0.4}/\text{C}$ catalyst is 0.86 V, which is slightly higher than those of the other catalysts (0.84 and 0.81 V for $\text{Pt}_3\text{Sn}_1/\text{C}$ and $\text{Pt}_2\text{Sn}_1\text{Ru}_1/\text{C}$, respectively). The OCV of a DEFC is mainly determined by the catalytic activity for ethanol electro-oxidation on the anode catalyst and ethanol crossover from the anode to the cathode. It is known that ethanol crossover is affected by the

Fig. 2. XPS spectra of Pt 4f (a), Ru 3p (b), and Sn 3d (c) of $\text{Pt}_3\text{Sn}_1/\text{C}$, $\text{Pt}_{2.6}\text{Sn}_1\text{Ru}_{0.4}/\text{C}$, and $\text{Pt}_2\text{Sn}_1\text{Ru}_1/\text{C}$ catalysts.

Fig. 3. Single-cell performance of DEFCs with Pt₃Sn₁/C, Pt_{2.6}Sn₁Ru_{0.4}/C, Pt₂Sn₁Ru₁/C, and Pt_{2.6}Sn₁Ru_{0.4}/C-H as anode catalysts under the following conditions: 90 °C (cell temperature), 1 mL/min of 1.5 mol/L ethanol solution at the anode, and 0.2 MPa oxygen at the cathode.

cell temperature, ethanol concentration, and cathode gas back-pressure. The single-cell-test operating conditions were the same for all the catalysts, and therefore the higher OCV reflects a greater catalytic activity for ethanol electro-oxidation on the Pt_{2.6}Sn₁Ru_{0.4}/C catalyst. The cell voltage decreases in the order Pt_{2.6}Sn₁Ru_{0.4}/C > Pt₃Sn₁/C > Pt₂Sn₁Ru₁/C with increasing current density. As the current density continues to increase (>100 mA/cm²), the anode is strongly polarized, and the cell voltage declines more rapidly for the Pt₃Sn₁/C catalyst than for the Pt₂Sn₁Ru₁/C catalyst, leading to a crossover point of 0.33 V at 200 mA/cm². This can be explained by the presence of some PtRu alloy in the Pt₂Sn₁Ru₁/C catalyst because the PtRu catalyst is more active than the Pt₃Sn₁/C catalyst at high current densities [12]. There is little difference between the maximum power densities of the Pt₃Sn₁/C and Pt₂Sn₁Ru₁/C catalysts: 70 mW/cm² for Pt₃Sn₁/C and 66 mW/cm² for Pt₂Sn₁Ru₁/C. The Pt_{2.6}Sn₁Ru_{0.4}/C catalyst gives higher DEFC performance across the entire current density region than Pt₃Sn₁/C and Pt₂Sn₁Ru₁/C catalysts, with a maximum power density of 91 mW/cm² at 175 mA/cm². Figure 3 shows that when the metal loading on the Pt_{2.6}Sn₁Ru_{0.4}/C-H catalyst is further increased to 60 wt%, the maximum power density reaches 121 mW/cm² at 213 mA/cm²; this is a better performance than those previously reported for similar operating conditions [7,8,11,12,15–17].

3.3. Anode polarization results

Figure 4 shows the anode polarization curves of the DEFCs with Pt₃Sn₁/C, Pt_{2.6}Sn₁Ru_{0.4}/C, and Pt₂Sn₁Ru₁/C as the anode catalysts. The concentration and flow rate of ethanol were set at 1.5 mol/L and 1.0 mL/min, respectively, to ensure a fuel supply. The maximum polarization potential was set at 0.6 V to prevent Sn dissolution; the maximum current was set at 1.0 A and was limited by the potentiostat. The faradic current was normalized based on the geometric electrode area. It can be seen from the profiles that the current density in the studied potential region is greatest for Pt_{2.6}Sn₁Ru_{0.4}/C. Ethanol oxidation takes place at 0.05 V on the Pt_{2.6}Sn₁Ru_{0.4}/C, which is a negative shift of about 20 and 90 mV compared with the Pt₃Sn₁/C

Fig. 4. Anode polarization curves for Pt₃Sn₁/C, Pt_{2.6}Sn₁Ru_{0.4}/C, and Pt₂Sn₁Ru₁/C catalysts at a scan rate of 1 mV/s under conditions 1 mL/min of 1.5 mol/L ethanol solution.

and Pt₂Sn₁Ru₁/C, respectively, suggesting a positive effect on the catalytic activity for ethanol electro-oxidation. The decisive factor is the activation energy, which is related to the reaction barrier of ethanol electro-oxidation, and will be discussed in Section 3.4. In the potential region 0.0–0.49 V, the ethanol electro-oxidation current density is greatest for the Pt_{2.6}Sn₁Ru_{0.4}/C catalyst, corresponding to the highest cell voltage in the single-cell tests. The order of the catalyst activity for ethanol oxidation is Pt_{2.6}Sn₁Ru_{0.4}/C > Pt₃Sn₁/C > Pt₂Sn₁Ru₁/C.

3.4. Activation energy analysis

The apparent activation energy (E_a) values are calculated by plotting the current density at a specific potential as a function of temperature according to the Arrhenius equation. The slope of a linear fit is used to calculate E_a :

$$\ln j = (\ln j_0 - E_a)/RT \quad (1)$$

where j is the current density at a specific potential, j_0 is the exchange current density, R is the gas constant, T is the temperature, and E_a is the apparent activation energy at the potential. Previous work [3,21,28,43–45] shows that ethanol electro-oxidation in an acidic solution can be described by two parallel reaction pathways. One pathway is C–C bond cleavage to form CO₂, and the other is a direct oxidation pathway to form acetaldehyde and then acetic acid. Ethanol is first dissociated on the active catalytic sites by either pathway. The dissociated species (CO_{ads} and CH₃CO_{ads}) are adsorbed on these active sites and then oxidized by OH_{ads} species generated from water. Figure 5 shows the apparent activation energies at different potentials on the Pt₃Sn₁/C, Pt_{2.6}Sn₁Ru_{0.4}/C, and Pt₂Sn₁Ru₁/C catalysts. It can be seen that the E_a value on the Pt₂Sn₁Ru₁/C catalyst is minimal (21.43 kJ/mol) when the electrode potential is 0.1 V; this means that ethanol adsorption and dissociation are easiest on Pt₂Sn₁Ru₁/C. However, the C1 or C2 species produced by ethanol dissociation cannot be oxidized at these potentials because no current density generated from ethanol electro-oxidation on the Pt₂Sn₁Ru₁/C catalyst is observed in the linear sweep voltammetry curves in Fig. 4. The E_a value on Pt₂Sn₁Ru₁/C increases with increasing electrode potential and becomes greater than those on Pt_{2.6}Sn₁Ru_{0.4}/C and Pt₃Sn₁/C.

Fig. 5. Activation energies for ethanol electro-oxidation on $\text{Pt}_3\text{Sn}_1/\text{C}$, $\text{Pt}_{2.6}\text{Sn}_1\text{Ru}_{0.4}/\text{C}$, and $\text{Pt}_{2.6}\text{Sn}_1\text{Ru}_1/\text{C}$ catalysts as a function of electrode potential.

The atomic states and compositions of Pt and Sn in the $\text{Pt}_{2.6}\text{Sn}_1\text{Ru}_1/\text{C}$ catalyst are very different from those in the $\text{Pt}_3\text{Sn}_1/\text{C}$ catalyst as a result of the formation of PtRu alloy, resulting in increasing E_a with increasing electrode potential.

The E_a value on the $\text{Pt}_{2.6}\text{Sn}_1\text{Ru}_{0.4}/\text{C}$ catalyst is 37.12 kJ/mol at 0.1 V, which is greater than that on $\text{Pt}_3\text{Sn}_1/\text{C}$ (34.61 kJ/mol). This indicates that adsorption and dissociation of ethanol on the active catalytic sites become more difficult. However, the E_a value decreases sharply with increasing electrode potential, resulting in the lowest value among the catalysts when the electrode potential is greater than 0.2 V. It is therefore proposed that the adsorbed species can be oxidized more quickly on $\text{Pt}_{2.6}\text{Sn}_1\text{Ru}_{0.4}/\text{C}$ than on $\text{Pt}_3\text{Sn}_1/\text{C}$ and $\text{Pt}_{2.6}\text{Sn}_1\text{Ru}_1/\text{C}$. The small amount of Ru in the $\text{Pt}_{2.6}\text{Sn}_1\text{Ru}_{0.4}/\text{C}$ catalyst compared with the $\text{Pt}_3\text{Sn}_1/\text{C}$ catalyst offers more oxygenated species, facilitating electro-oxidation of adsorbed species derived from ethanol dissociation. The synergetic effects of Pt, Sn, and Ru in the $\text{Pt}_{2.6}\text{Sn}_1\text{Ru}_{0.4}/\text{C}$ catalyst therefore improve the ethanol electro-oxidation efficiency, and thus the maximum power density of the DEFC.

3.5. In situ FTIRS and anode product analysis

Figure 6 shows in situ spectra recorded during ethanol electro-oxidation on the $\text{Pt}_{2.6}\text{Sn}_1\text{Ru}_{0.4}/\text{C}$ catalyst from potentials of 0.05 to 0.70 V. A positive peak is located at 2343 cm^{-1} , which is attributed to the asymmetric stretching vibrations of CO_2 in water. This appears at 0.25 V and the intensity increases with increasing potential, indicating that CO_2 is one of the products,

Fig. 6. In situ FTIR spectra of the $\text{Pt}_{2.6}\text{Sn}_1\text{Ru}_{0.4}/\text{C}$ catalyst deposited on gold substrate surface in 0.1 mol/L HClO_4 + 0.1 mol/L ethanol at different potentials. The reference spectrum was recorded at 0 V.

and its yield increases with DEFC discharging. Another dominant feature of the spectra is the peak at 2042 cm^{-1} . The bipolar shape is the result of subtraction of two Stark-shifted single-beam spectra at the sample and reference potentials [46]. The stretching vibrations of the carbonyl groups ($\text{C}=\text{O}$) in acetic acid, acetaldehyde, or ethyl acetate cause the peak at 1717 cm^{-1} . However, this peak is affected by the strong negative peak located at 1650 cm^{-1} , which indicates consumption of interfacial water during the reaction. The positive absorption band at 1395 cm^{-1} is associated with $\text{C}-\text{O}$ stretching in acetic acid and/or ethyl acetate. The peak at 1368 cm^{-1} is attributed to CH_3 symmetric deformation in acetaldehyde. The positive peak at 1274 cm^{-1} is attributed to $\text{O}-\text{H}$ deformation in acetic acid. The peak at about 1100 cm^{-1} is assigned to adsorption of ClO_4^- on the electrode surface from the electrolyte solution. The broad peak located at 2620 cm^{-1} is probably the characteristic vibration of aldehydic ($\text{O}=\text{C}-\text{H}$). The results show that CO_2 , acetic acid, acetaldehyde, and ethyl acetate are produced during ethanol electro-oxidation.

Table 3 lists the anode product distributions and current efficiencies of DEFCs with $\text{Pt}_3\text{Sn}_1/\text{C}$ and $\text{Pt}_{2.6}\text{Sn}_1\text{Ru}_{0.4}/\text{C}$ as the anode catalysts. It can be seen that acetaldehyde, acetic acid, ethyl acetate, and CO_2 are detected in the DEFC anode effluent, in agreement with the in situ FTIRS results. Acetic acid is the major anode product, with over 90% current efficiency. The

Table 3

Product concentrations, product yields, and current efficiencies of acetaldehyde (AAL), ethyl acetate (EA), acetic acid (AA), and CO_2 formed in DEFCs with $\text{Pt}_3\text{Sn}_1/\text{C}$ or $\text{Pt}_{2.6}\text{Sn}_1\text{Ru}_{0.4}/\text{C}$ anode catalyst.

Catalyst	Cell voltage (V)	Product concentration (mmol/L)				Product distribution (%)				Current efficiency (%)			
		AAL	EA	AA	CO_2	AAL	EA	AA	CO_2	AAL	EA	AA	CO_2
$\text{Pt}_3\text{Sn}_1/\text{C}$	0.6	9.32	3.52	204	0.19	4.29	1.62	94.00	0.09	2.19	1.65	95.88	0.27
	0.5	12.95	2.84	233	0.44	5.20	1.14	93.48	0.18	2.66	1.17	95.62	0.55
	0.4	21.14	2.95	262	0.81	7.37	1.03	91.32	0.28	3.80	1.06	94.27	0.87
$\text{Pt}_{2.6}\text{Sn}_1\text{Ru}_{0.4}/\text{C}$	0.6	9.55	3.75	200	0.089	4.47	1.76	93.73	0.04	2.28	1.80	95.79	0.13
	0.5	11.14	3.07	237	0.245	4.43	1.22	94.25	0.10	2.26	1.24	96.20	0.30
	0.4	25.45	3.30	251	0.55	9.08	1.17	89.55	0.20	4.74	1.23	93.42	0.61

Fig. 7. Ethanol oxidation efficiencies of DEFCs with Pt_{2.6}Sn₁Ru_{0.4}/C and Pt₃Sn₁/C as anode catalysts.

current density contributions of acetaldehyde and ethyl acetate are less than 5% and 2%, respectively. The yield is lowest, lower than 1%. Ethanol therefore cannot be completely oxidized to CO₂ under the present operating conditions. The C₂ products are the key factors in the DEFC performance, and the product distributions and current efficiencies on the Pt_{2.6}Sn₁Ru_{0.4}/C and Pt₃Sn₁/C catalysts are similar, indicating that the addition of Ru to PtSn enhances the electrochemical performance [14].

The ethanol electro-oxidation efficiencies were calculated using Eq. (2):

$$\eta = (0.5M_{\text{CO}_2} + 2M_{\text{EA}} + M_{\text{AAL}} + M_{\text{AA}})V_{\text{out}} / (M_{\text{ethanol}}V_{\text{in}}) \times 100\% \quad (2)$$

where η is the ethanol electro-oxidation efficiency, M_{CO_2} , M_{EA} , M_{AAL} , and M_{AA} are the concentrations of CO₂, ethyl acetate, acetaldehyde, and acetic acid, respectively, M_{ethanol} is the initial concentration of ethanol, and V_{in} and V_{out} are the inlet and outlet solution volumes, respectively, for the DEFC anode. The results are shown in Fig. 7. It can be observed that the ethanol electro-oxidation efficiency increases as the cell voltage decreases because more ethanol can be oxidized on further discharging. The electro-oxidation efficiencies at the studied cell voltages were higher for Pt_{2.6}Sn₁Ru_{0.4}/C than for Pt₃Sn₁/C, which resulted in a higher current density and therefore a better DEFC performance.

4. Conclusions

PtSnRu/C catalysts with uniform and narrow particle-size distributions were prepared using the polyol process. Optimization of Pt, Sn, and Ru ratios and increasing the catalyst metal loading resulted in a maximum power density of 121 mW/cm² for the DEFC with Pt_{2.6}Sn₁Ru_{0.4}/C-H as the anode catalyst under the operating conditions 90 °C, 1.5 mol/L ethanol solution, and 0.2 MPa oxygen. The product distribution with the Pt_{2.6}Sn₁Ru_{0.4}/C catalyst was similar to that with Pt₃Sn₁/C catalyst: acetic acid was the major anode product with over 90% current efficiency, and the yield of CO₂ was lowest with less than 1%. The ethanol oxidation efficiency on the Pt_{2.6}Sn₁Ru_{0.4}/C catalyst was greater than that on the Pt₃Sn₁/C catalyst. These results suggest that the synergetic effects of Pt, Sn, and Ru in the Pt_{2.6}Sn₁Ru_{0.4}/C catalyst decreased the activation energy for

ethanol electro-oxidation, thus improving the ethanol electro-oxidation efficiency and maximum power density of the DEFC.

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Graphical Abstract

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Polyol-synthesized $\text{Pt}_{2.6}\text{Sn}_1\text{Ru}_{0.4}/\text{C}$ as a high-performance anode catalyst for direct ethanol fuel cells

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A polyol-synthesized 60 wt% $\text{Pt}_{2.6}\text{Sn}_1\text{Ru}_{0.4}/\text{C}$ catalyst achieved a maximum power density of 121 mW/cm^2 at 90 °C, and ethanol was mainly electro-oxidized to acetic acid with a negligible amount of CO_2 .

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多元醇法合成的 $\text{Pt}_{2.6}\text{Sn}_1\text{Ru}_{0.4}/\text{C}$ 用作直接乙醇燃料电池高性能阳极催化剂王琪^{a,*}, 陆兴^a, 辛勤^b, 孙公权^{b,#}^a大连交通大学材料科学与工程学院中心实验室, 辽宁大连116028^b中国科学院大连化学物理研究所洁净能源国家实验室, 辽宁大连116023

摘要: 采用多元醇法制备了不同原子比例和载量的 PtSnRu/C 催化剂, 利用透射电镜和X射线光电子能谱表征了所制备催化剂的催化性能, 采用直接乙醇燃料电池(DEFC)单池性能测试了其电化学性能, 并利用电化学原位光谱、气相色谱和中和滴定分析了乙醇电氧化过程和产物。DEFC单池测试表明 $\text{Pt}_{2.6}\text{Sn}_1\text{Ru}_{0.4}/\text{C}$ 催化剂具有较高的电池性能, 其中, 以60 wt% $\text{Pt}_{2.6}\text{Sn}_1\text{Ru}_{0.4}/\text{C}$ 催化剂为阳极的DEFC性能最高, 90 °C下最高功率密度为121 mW/cm^2 。电化学原位红外光谱和阳极产物分析表明乙酸、乙醛、乙酸乙酯和 CO_2 是乙醇电化学氧化产物, $\text{Pt}_{2.6}\text{Sn}_1\text{Ru}_{0.4}/\text{C}$ 催化剂上乙醇的氧化效率较高。阳极乙醇氧化活化能和催化剂表面组成分析结果表明, 表面组成的相互作用使 $\text{Pt}_{2.6}\text{Sn}_1\text{Ru}_{0.4}/\text{C}$ 催化剂具有较低的乙醇氧化活化能和较高的乙醇氧化活性。

关键词: 直接乙醇燃料电池; 阳极催化剂; 多元醇法; 阳极产物; 乙醇氧化效率

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