Electrochemical and surface characteristics of carbon-supported PtSn electrocatalysts for ethanol electro-oxidation: possible application for inkjet ink formulations

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Received 29 September 2012
Accepted for publication 14 January 2013
Published 7 February 2013
Online at stacks.iop.org/ANSN/4/015012

Abstract

Pt and Pt\textsubscript{80}Sn\textsubscript{20} catalysts with different atomic ratios (90:10, 80:20, 70:30, 60:40 and 50:50) supported on carbon support (Vulcan XC-72) were prepared using the modified polyol method. The composition, particle size and structure of these catalysts were characterized by energy dispersive x-ray spectroscopy (EDX) and x-ray diffraction (XRD). XRD data revealed that the estimated particle sizes of all synthesized catalysts were approximately 2.0–3.0 nm. Cyclic voltammetric data showed that Pt\textsubscript{80}Sn\textsubscript{20} exhibited the highest catalytic activity toward ethanol oxidation compared to other ratios in terms of area-normalized current densities. Chronoamperometry (CA) data confirmed that Pt\textsubscript{70}Sn\textsubscript{30} was the most stable among the prepared catalysts with long-term poisoning rate of 4.25 × 10^{-3} \% s^{-1}, which was four times lower than Pt (1.70 × 10^{-2}). The catalyst with the optimum performance was used as the ink pigment of the inkjet ink formulations.

Keywords: Ethanol oxidation, Pd-NiO, Carbon functionalization, Palladium catalyst

Classification numbers: 5.00, 5.06

1. Introduction

The development of polymer electrolyte membrane fuel cell (PEMFC) has been regarded as a promising alternative power source for future energy needs [1, 2]. PEMFCs have been investigated extensively due to its low operating temperature, easy start-up and high conversion efficiency [3, 4]. Pt nanoparticles usually constitute as the catalyst layer on the anode part of the fuel cell. Numerous studies have reported that Pt is the best known catalyst for the oxidation of small organic molecules such as ethanol [5, 6] and methanol [7, 8]. However, the high price and the significant loss of its catalytic activity during operations constitute a major issue for the commercialization of PEMFCs [9]. These reasons serve as a driving force in developing anodes with low Pt content and with increasing efficiency toward oxidations of small organic molecules.

In order to overcome these critical obstacles, one strategy is to explore possible fabrication methods that would efficiently utilize the Pt catalysts in the anode system. Many fabrication methods have been adopted to resolve issues concerning efficient anode preparations, and one possible approach is that with the inkjet printing technique. Recently, there has been a growing interest in
inkjet printers as a popular option for preparing functional materials due to its compatibility with various substrates, low-temperature processing, simplicity and low cost [10]. However, most studies reported in the literature focus on the fabrication of the anode using inkjet printing technique without giving consideration to the importance of ink formulation. Thus, for the envisioned wide use of this method in industry, it is essential to understand that the crucial part of using inkjet printing is the ink and its physical properties [11,12]. These reasons have prompted investigation of the physical characteristics of ink formulation for future commercialization.

The motivation of this research is to develop anode materials relevant to fuel cells with low Pt content by incorporating Sn, and to explore the possibility of ink-jet printing technique for the mass fabrication of the bimetallic electrocatalyst. Pt and Pt-based electrocatalysts were synthesized using the modified-polyol method. Electrochemical investigations were carried out using cyclic voltammetry (CV) and chronoamperometry (CA). X-ray diffraction (XRD) and energy dispersive x-ray (EDX) analyses were used to characterize the synthesized catalysts.

2. Experimental

2.1. Preparation of catalysts

PtSn catalysts (subscripts denote the atomic percentage) were prepared in different atomic percentages of Pt: Sn of 80: 20, 70: 30, 60: 40 and 50: 50. A typical catalyst preparation [13,14] procedure of a Pt80Sn20 consisted of the following steps: 1.25 ml of 0.01 M SnCl2·2H2O was added to 50.0 ml of ethylene glycol and was refluxed at 190 °C for 30 min under constant stirring. The resulting solution was then cooled down to room temperature and 5.0 ml of 0.01 M H2PtCl6·6H2O was then introduced. Subsequently, the pH of the solution was adjusted to pH 11.7 ± 0.1 using 1.0 M NaOH and the temperature was increased to 130 °C and kept constant for 2 h. The required amount of carbon black (44.92 mg) was mixed to the solution and stirred continuously for another 1 h. Afterwards, the black solution was filtered, washed and dried at 75 °C for 12 h.

2.2. Physical characterizations

The crystalline structure of the carbon-supported catalysts was evaluated using the XRD technique. XRD analyses were done with Siemens Kristalloflex 760 (DOST-PNRI, Applied Physics Laboratory) using Cu Kα (λ = 0.15405 nm) source. The source was operated with a tube current of 100 mA and tube voltage of 32 kV. The 2θ Bragg angles were scanned over the range of 15°—85° and were explored at a scan rate of 5 min^{-1}. Energy dispersive x-ray (EDX) analysis was done using JEOL JSM 5310 SEM (Surface Physics Laboratory, DLSU, Manila) with an accelerating voltage of 15000 V. Pt/C and PtSn/C catalyst powders were mounted on a carbon tape and placed in the SEM chamber for EDX analysis.

2.3. Electrochemical characterizations

Electrochemical studies were performed in a conventional three-electrode electrochemical cell at room temperature. All solutions were prepared with milli-Q water and were purged by bubbling with high-purity N2 gas for 15 min. Pt rod and Ag/AgCl (saturation KCl) were used as the counter and reference electrode, respectively. All electrochemical measurements were carried out using EDAQ potentiostat (Australia) under control of dedicated software (EChem, EDAQ).

A glassy carbon electrode (GCE) was used as a substrate for the catalysts. Before the catalyst ink was drop-cast onto the substrate, the glassy carbon electrode was polished mechanically using emery paper (grade 1200–1500) and was cleaned by potential cycling between E = −0.2 and 1.2 V at 50 mV s^{-1} in 0.5 M H2SO4. Typically, the ink catalyst was prepared as follows: a mass of 5.0 ± 0.2 mg of the carbon-supported catalysts was dispersed in 100.0 µl of isopropanol. The resulting solution was then sonicated to achieve homogeneity. After ultrasonic homogenization, 20 µl of the dispersed catalyst was drop-cast on a glassy carbon substrate (area: 0.0697 cm2), and dried in the oven for 15 min at 70 °C. Afterwards, 10.0 µl of Nafion® solution was drop-cast on top of the dried catalyst and dried again in the oven for 15 min at 70 °C.

2.4. Preparation of catalytic ink for inkjet printing

Ink solutions were prepared by combining the carbon supported catalysts and the dispersant (Afcona-4570) into the aqueous solution (water, isopropanol and ethylene glycol). The resulting solution was sonicated for 30 min and stirred for another 30 min to achieve homogeneity. Afterwards, the dispersion was transferred to a homemade ball mill with 3/8” stainless steel balls and milled for 1 h at 350 rpm [15,16].

The homogenized ink was then filtered using Whatman® grade 5 (2.5 µm pore size). Adjustment of the pH to 10 with NH4OH buffer was done to prevent undesirable agglomeration of the carbon-supported catalysts in the solution [16].

3. Results and discussion

3.1. Physico-chemical characterization of the carbon-supported catalysts

XRD patterns for the prepared Pt and PtSn catalysts are shown in figure 1. The peaks observed for all the composites are characteristics of the face-centered cubic (fcc) crystalline Pt. The diffraction peak at around 25° is associated with the (002) plane of the hexagonal structure of the carbon support (Vulcan XC-72). Meanwhile, peaks at 40°, 46°, 68° and 81° correspond to the (111), (200), (220) and (311) planes of the Pt phase, respectively.

The mean particle sizes of the synthesized catalysts were estimated from the (220) peak width according to the Scherrer equation

\[ D = \frac{0.9λ_kα}{2sinθ_{max}} \]
assuming that the particles are spherical. In equation (1) \( D \) is the mean particle diameter, \( \lambda \) is the x-ray wavelength (1.54056 nm), \( \theta_{\text{max}} \) is the angular position at the (220) peak maximum, and \( 2B \) is the full-width at half-maximum (FWHM) of the (220) peak broadening in radians. The (220) reflection of the fcc structure of the Pt and PtSn catalysts was selected to calculate the particle size and lattice parameters in order to avoid possible disturbance from carbon and tin, which has no nearby signal around this angle [17–19].

The results indicated that the addition of tin onto the catalyst system led to smaller particle size (table 1), this would be explained by the fact that the SnO\(_2\) in the solution can act as a separator, thus inhibiting agglomeration of the particles during synthesis [20]. The change in the lattice parameter of the Sn-containing catalysts is indicative of the formation of a certain degree of alloying. The increase in the lattice parameters of the PtSn catalysts is due to the partial substitution of platinum by tin which has larger atomic radius than Pt (1.61 Å against 1.39 Å), thus inducing the stretching or expansion of the Pt fcc lattice [21, 22].

EDX analyses were used to determine the actual content of platinum and tin on the different prepared catalysts in comparison with their nominal content. EDX results obtained for the nanocatalysts (table 2) show that the actual contents of different catalysts are close to the nominal content. This could indicate that the polyol method is effective in reducing the metal salts present in the precursor solutions.

Table 1. Calculated particle size and lattice parameter from XRD data.

| Catalysts | Particle size (nm) | Lattice parameter (Å) |
|-----------|--------------------|-----------------------|
| Pt        | 3.27               | 0.3922                |
| Pt\(_{50}\)Sn\(_{10}\) | 2.39               | 0.3939                |
| Pt\(_{60}\)Sn\(_{20}\) | 2.13               | 0.3929                |
| Pt\(_{70}\)Sn\(_{30}\) | 2.33               | 0.3935                |
| Pt\(_{80}\)Sn\(_{40}\) | 2.18               | 0.3944                |
| Pt\(_{95}\)Sn\(_{5}\) | 2.67               | 0.3915                |

Table 2. EDX results for the various bulk compositions of carbon-supported PtSn electrocatalysts prepared by the polyol method (20% metal loading).

| Catalysts     | Pt percentage (%) | Sn percentage (%) |
|---------------|-------------------|-------------------|
| Pt            | 100               | 0.00              |
| Pt\(_{50}\)Sn\(_{10}\) | 92.80              | 7.20              |
| Pt\(_{60}\)Sn\(_{20}\) | 79.94              | 20.06             |
| Pt\(_{70}\)Sn\(_{30}\) | 65.99              | 34.01             |
| Pt\(_{80}\)Sn\(_{40}\) | 60.07              | 39.93             |
| Pt\(_{95}\)Sn\(_{5}\) | 48.50              | 51.50             |

3.2. Electrochemical characterizations

The electrocatalytic properties of the carbon-supported catalysts were evaluated using cyclic voltammetric technique. Background characterizations were done with 0.1 M H\(_2\)SO\(_4\) supporting electrolyte at a scan rate of 10 mV s\(^{-1}\) at the potential range from −0.2 to 1.2 V (versus Ag/AgCl) prior to ethanol electro-oxidation. It is evident from the voltammogram (figure 2) that the well-defined peaks of the carbon-supported Pt catalyst could be observed, which corresponds to different electrochemical processes (hydrogen adsorption–desorption peak, adsorption of oxygenated species and surface oxides reduction) taking place on the surface of the catalysts.

The background characterizations of both Pt/C and PtSn/C catalysts exhibited almost similar features. However, it is noteworthy that the PtSn/C catalyst did not manifest well-defined hydrogen desorption peaks, characteristics of Pt with different crystalline facets. It could be inferred that the Sn adsorbed on the Pt surface may have caused structural modification on the Pt lattice due to the Pt–Sn interaction [17, 23, 24].

The cyclic voltammograms of ethanol electro-oxidation on the Pt/C and Pt\(_{x}\)Sn\(_{y}\)/C catalysts are depicted in figure 3. It can be clearly seen that there are two oxidation peaks observed in the system. The oxidation peak for the forward scan, which is denoted by A′ can be attributed to the oxidation of ethanol to carbon dioxide. While the peak observed for the reverse scan (A′′) corresponds to the re-oxidation of the carbonaceous intermediates adsorbed on the Pt surface [16].
As shown in figure 3, the oxidation peak at the reverse sweep for the Pt$_x$Sn$_y$/C catalyst is higher compared to the Pt/C. This indicates that the addition of Sn in the system promotes the oxidative removal of the adsorbed species on the Pt surface.

A comparison of the current densities of the synthesized catalysts shows a considerable improvement in ethanol electro-oxidation for the Pt$_x$Sn$_y$/C compared with the Pt/C (figure 3). Various studies have stated that the increase in the activity of the bimetallic catalyst could be due to the electronic effect of the Sn in the Pt-based catalysts or by the bifunctional mechanism [17, 25]. According to the bifunctional mechanism, the water on the surface of the catalysts is then activated by the oxophilic SnO$_2$, which constitutes the oxidation of the carbonaceous species to carbon dioxide (CO$_2$). Another possible reaction pathway (electronic effect or ligand effect) is the modification of the electronic structure of the Pt catalysts induced by the addition of Sn in the system.

As the addition of Sn in the system facilitates the removal of carbonaceous species, thus freeing up additional Pt active site and increasing turnover rate of reactions as seen in table 3. Further addition of Sn onto the system, however, renders it ineffective as a promoter and could block the Pt sites instead that could lead to the substantial reduction of activity toward ethanol oxidation.

Chronoamperometry measurements were conducted in 1.0 M ethanol in 0.1 M H$_2$SO$_4$ at a fixed potential of 0.300 V (versus Ag/AgCl). At this potential, the bifunctional effect of the bimetallic catalysts could be observed, due to the activation of interfacial water [26]. In all chronoamperometry measurements, an initial high current density could be observed and is associated mainly with the double-layer charging. This was followed by a sudden drop of the current, then an exponential decay of the current with time and finally the current becoming relatively stable. It could be rationalized that at the beginning of the analysis, the active sites of the catalysts were free of adsorbed ethanol molecules, thus explaining the high current density. However, the adsorption of new ethanol molecules is dependent on the liberation of the active sites from the intermediate species. Thus, the exponential decay of the current density could presumably be due to the slow poisoning of the catalysts by the CO adsorbed intermediates.

From the obtained chronoamperograms, the rate of poisoning [27–29] of the catalysts, expressed as the percentage of poisoned catalyst per second (% s$^{-1}$), can be calculated using the following equation:

$$\delta = \frac{100}{I_0} \left( \frac{dI}{dt} \right)_{t>500\,s}, \quad (2)$$

where $(dI/dt)_{t>500\,s}$ is the slope of the linear portion of the current decay, while $I_0$ is the current at the start of polarization back extrapolated from the linear current decay.

The evaluated $\delta$ values are listed in table 4. It was observed that the current densities obtained from Pt$_{80}$Sn$_{20}$ catalysts shows the highest activity toward ethanol oxidation which is consistent with the CV results. However, chronoamperometry is used to evaluate the stability of the catalysts at a certain potential over an extent of time. Although Pt$_{80}$Sn$_{20}$ exhibited the highest activity, Pt$_{70}$Sn$_{30}$ gave the highest resistance against poisoning due to the adsorbed Sn.

![Figure 3](image-url)

**Figure 3.** Cyclic voltammograms for the oxidation of 1.0 M ethanol in 0.1 M H$_2$SO$_4$ on Pt/C and Pt$_x$Sn$_y$/C electrocatalysts with different atomic ratios. Scan rate: 20 mV s$^{-1}$.

![Figure 4](image-url)

**Figure 4.** Current-time curves at 0.3 V on Pt/C and Pt$_x$Sn$_y$/C electrocatalysts with different atomic ratios in 1.0 M ethanol in 0.1 M H$_2$SO$_4$ for 3600 s.

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### Table 3. Summary of the performance of the synthesized catalyst in the absence and presence of 1.0 M ethanol in 0.1 M H$_2$SO$_4$.

| Catalysts | Pt loading (mg cm$^{-2}$) | Electrochemical surface area (m$^2$ g$^{-1}$ Pt) | Forward peak current density (mA cm$^{-2}$) |
|-----------|---------------------------|-----------------------------------------------|-------------------------------------------|
| Pt        | 0.884                     | 3.076                                         | 34.642                                    |
| Pt$_{60}$Sn$_{40}$ | 0.796                     | 8.696                                         | 71.944                                    |
| Pt$_{50}$Sn$_{50}$ | 0.707                     | 26.789                                        | 107.485                                   |
| Pt$_{30}$Sn$_{70}$ | 0.619                     | 24.416                                        | 84.365                                    |
| Pt$_{40}$Sn$_{60}$ | 0.531                     | 10.024                                        | 61.745                                    |
| Pt$_{50}$Sn$_{50}$ | 0.442                     | 7.198                                         | 47.885                                    |

### Table 4. The long-term poisoning rate for the carbon-supported Pt and Pt$_x$Sn$_y$ electrocatalysts.

| Catalysts | Poisoning rate (% s$^{-1}$) |
|-----------|-----------------------------|
| Pt        | 1.97 × 10$^{-2}$            |
| Pt$_{60}$Sn$_{40}$ | 5.77 × 10$^{-3}$            |
| Pt$_{50}$Sn$_{50}$ | 5.97 × 10$^{-3}$            |
| Pt$_{30}$Sn$_{70}$ | 4.25 × 10$^{-3}$            |
| Pt$_{40}$Sn$_{60}$ | 4.71 × 10$^{-3}$            |
| Pt$_{50}$Sn$_{50}$ | 1.04 × 10$^{-2}$            |
species based from the calculations. The long-term poisoning rate of the Pt catalysts is found to be four times the value of the Pt$_{70}$Sn$_{30}$. Likewise, the rate of poisoning of the tin-containing catalysts was much lower by one magnitude as compared to the Pt catalysts. This can be explained that in the Sn enriched catalysts, the tin oxides can supply oxygenated species to oxidize the CO adsorbates [28–30].

3.3. Catalytic ink formulations for inkjet printing technique

Metal catalyst powder usually dispersed in aqueous or organic solvents is commonly used to produce ink for electrode fabrication. However, one critical issue must be addressed when this catalyst ink is used for inkjet printing application. It must be ensured that the ink has a long shelf-life and does not require frequent redispersion of the metal particles in the liquid vehicle [16]. This is because the extent of dispersion of the pigment in the solvent system affects the inkjet printing characteristics such as ejectability, print quality and optical density.

The catalyst ink was subjected to ball milling to make sure that the particle size is reduced to the desired value [31]. With ball milling, the carbon-supported catalysts are reduced to individual aggregates, after which the dispersant in the solvent system coats the particles producing individual micelles. It should be taken into consideration that the solution is basic, making the polymeric dispersant negatively charged. Thus, the negatively charged dispersant would surround the particle and produce electrostatic repulsive forces between individual particles that makes the particles less prone to settling during storage (figures 5(A) and (B)). Figures 5(C) and (D) illustrate the successful printing of the catalytic ink onto an 8.5″ × 11″ sheet of paper. The following figures could also illustrate the versatility of the inkjet printing method to deposit materials to specific shapes and areas. However, the presence of banding is noticeable when printing a single layer. This is because by using commercially available thermal inkjet printer, the printing parameters (number of nozzles, droplet size and jetting frequency) cannot be manually controlled.

4. Conclusions

In this paper, carbon-supported PtSn/C catalysts for ethanol electro-oxidation were obtained using the successive reduction polyl method. Performance evaluation using cyclic voltammetry showed that the Pt$_{80}$Sn$_{20}$ catalyst showed the highest catalytic activity toward ethanol electro-oxidation. Electrocatalysis of ethanol at 0.3 V revealed that Pt$_{70}$Sn$_{30}$ was the most stable among the prepared electrocatalysts. It was clearly observed that the addition of the dispersant in the system increase the overall stability of the metal catalysts in the ink solution. Moreover, it was successfully demonstrated that inkjet printing technique can be used as a mode of depositing precise amounts of the catalysts onto a substrate. Future work will include the fabrication and characterizations of the printed anodes.

Acknowledgments

HH gratefully acknowledges the financial support of the Department of Science and Technology–Accelerated Science and Technology Human Resource Development Program (DOST-ASTHRDP), Philippines.

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