Influence of Solvents on the Electroactivity of PtAl/rGO Catalyst Inks and Anode in Direct Ethanol Fuel Cell

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This paper presents research on the effects of common solvents such as n-butyl acetate, isopropanol, and ethanol on the properties and electroactivity of catalyst ink based on PtAl/rGO. The inks prepared by mixing PtAl/rGO catalyst, Nafion solution (5 wt%), and solvent were coated on carbon cloth by the spin coating method. The results obtained showed that ethanol was the most suitable solvent for the preparation of catalyst ink with a volume ratio between catalyst slurry and solvent of 1:1 (CI-EtOH (1/1) ink). The surface of the CI-EtOH (1/1) coated electrode was smooth, flat, and even and had no cracks due to the increase of Nafion mobility, resulting in significant improvement in the interaction between Pt particles and ionomer. Moreover, the electrochemical activity of the CI-EtOH (1/1) ink in ethanol electrooxidation reaction, in both acidic and alkaline media, has the highest value, with the forward current density, \( I_{F} \), reaching 1793 mA mgPt\(^{-1}\) and 4751 mA mgPt\(^{-1}\), respectively. In the application in direct ethanol fuel cell (DEFC), the CI-EtOH ink-coated anode also exhibited the highest power density in both PEM-DEFC (with a proton exchange membrane) and AEM-DEFC (with an anion exchange membrane) at 19.10 mW cm\(^{-2}\) and 27.07 mW cm\(^{-2}\), respectively.

1. Introduction

Nowadays, the replacement of traditional fossil fuels and reducing greenhouse gas emissions have attracted much attention. Direct ethanol fuel cells (DEFCs) that show remarkable advantages such as safety and a high energy density [1], 6.28 kWh L\(^{-1}\), could become a good solution. Moreover, as a renewable energy source, ethanol can be produced from biomass.

Being one of the most important components among several parts in the fuel cell, membrane electrode assembly (MEA) determines both fuel cell performance and durability. An MEA like a “sandwich” that has a proton exchange membrane (PEM) or an anion exchange membrane (AEM) between anode and cathode coated respective catalyst layer. The catalyst layers called the heart of the fuel cell are prepared from catalyst inks that are a mixture of a catalyst, an ionomer (mostly Nafion) and/or a hydrophobic agent, and a certain solvent. There are two main MEA preparation processes [2], including catalyst coated on the membrane (CCM) and catalyst coated on the substance (CCS). CCM typically uses colloidal inks from moderate to high viscosity, and CCS typically uses liquid inks of low viscosity. Some solvents are studied in catalyst ink preparation such as water [3], n-propanol, ethylene glycol [4–7], 1-hexanol [8], tetrahydrofuran, isopropanol [9–12], n-butyl acetate [11], ethanol [9, 12–14], dimethyl sulfoxide, and N-methyl-2-pyrrolidone [14].

Good ink is a combination that has homogeneous dispersion of catalyst particles and Nafion in a suitable solvent, which are as well-dispersed as a catalyst on the electrode. The performance of catalyst layers with an advanced ink has been significantly improved by employing different fabrication methods [3, 7, 15–17], researching on the dielectric constant of dispersing solvent [18] and the catalyst ink composition [9, 19–21], changing the concentration of Nafion, and studying an agglomeration in the catalyst ink layers [3, 22–24].

Some authors [12, 14, 18, 20, 25] have observed that the structure and mobility of the main chain and side-chain of
Nafion greatly affect the structures, particularly the morphology of the catalyst layer. Accordingly, increased mobility leads to a better connection at the 3-phase boundary (catalyst phase, Nafion phase, and reactant). As a result, the electrochemically active surface area increases, while the resistance of the catalytic layer decreases, and the current density and capacity of the battery are increased. On the other hand, the size of the catalyst-Nafion agglomerates is more affected by the solvent-Nafion bond than the solvent-ionic liquid interaction. Consequently, the nature of the solvent in catalyst ink preparation has a great influence on the efficiency of the electrode working in the fuel cells.

To date, the PtRu black catalyst and Pt dispersed on the C rGO catalyst were reported as the traditional catalysts for the application of proton exchange membrane fuel cell [26–29]. Therefore, the studies on catalyst ink mostly focused on these two catalysts and applied in manufacturing electrodes for hydrogen fuel cells [7, 9, 14–16, 20, 30] or direct methanol fuel cells [8, 11, 18, 30]. To our knowledge, there have been no published studies on catalyst ink for direct ethanol fuel cells.

Recently, Pt catalysts dispersed on the rGO support have been the object of substantial interest for the electro-oxidation of methanol and ethanol [31–37]. It has been demonstrated that the dispersion of the active Pt particles on rGO is more enhanced than that on carbon black [38–41] due to many extraordinary properties of the graphene support, such as its high surface area, high electrical conductivity, and good thermal properties.

Besides this advantage, restacking of individual graphene sheets causes an agglomeration of the active phases and a decrease in catalytic efficiency [42, 43]. In addition, previous studies have shown that the properties of the solvent, the dilution rate of the catalyst ink, and the evaporation condition have a significant impact on the microstructure of the catalyst layer on the anode electrode [18, 30]. The study of the preparation method of the catalyst ink is essential to preserve the advantages of the Pt/rGO catalyst.

However, up to now, there has been no research on the preparation of catalyst ink based on Pt/rGO catalyst for the application of fuel cell in general and DEFC in particular.

In our previous articles [34–37], PtAl/rGO catalyst’s activity and stability were high in ethanol electrooxidation. In order to follow our research development, the preparation of the catalyst ink coating anode electrode in a direct ethanol fuel cell in both acidic and alkaline media was carried out. This paper presents research on the effects of common, less toxic, volatile with well Nafion-dispersed solvents such as n-butyl acetate, isopropanol, and ethanol on the morphology and microstructure of catalyst layer and the electroactivity of the ink based on PtAl/rGO catalyst.

2. Materials and Methods

2.1. Chemicals and Materials. All chemicals were of analytical grade and used as received. Expanded graphite powder (ExG) (carbon content in 99.0%, expansion ratio in 300–600) was provided by SGL Carbon GmbH. Aluminum tri-isopropoxide (99.99%), sodium hydroxide (98.8%), sulfuric acid (95–98%), sodium nitrate (98%), n-Butyl acetoacetate (NBA) (≥99.5%), isopropyl alcohol (IPA) (99.95%), ethanol (EtOH), and ethylene glycol were purchased from Merck. Hydrogen peroxide (30%), chloroplatinic acid hexahydrate (99%), potassium permanganate, hydrochloric acid (37%), and a Nafion solution (5 wt% in a mixture of lower aliphatic alcohol and water) were bought from Sigma Aldrich. Pure nitrogen gas (99.999%) was obtained from Air Liquide. Deionized (DI) water owning a resistivity of 18 MΩ was used in all experiments.

A Nafion 117 membrane and an FAA-3-PK-130 membrane were used as the proton/anion exchange electrolyte. A commercial electrode 20%Pt/C coated on carbon cloth (2 mg cm⁻²) was used as the cathode of DEFC modeling. All components were purchased from Fuelcell-Store (USA). A carbon foam sheet (Porous C) from MTI Cooperation (USA) was used as a substance to coat the catalyst inks.

2.2. Preparation of Catalyst Inks and Anode for DEFCs. Graphene oxide (GO) was synthesized from expanded graphite powder (ExG) by a modified Hummers’ method [44], with a small improvement in the GO washing process. Specifically, the centrifuged solid after the reaction was dispersed in an HCl 5% aqueous solution instead of water to completely remove impurities such as KMnO₄, NaNO₃, and MnO₂ [45].

The synthesis of the PtAl/rGO catalyst was similar to the preparation in [37].

The inks are prepared by mixing the catalyst, Nafion solution, and a solvent with the help of a 750 W ultrasonic device. Solvents consisted of n-butyl acetate, isopropanol, and ethanol. For example, 15 mL of a PtAl/rGO slurry in water (5 mg mL⁻¹), 15 mL NBA solvent, and 550 µL Nafion solution (5 wt%) were mixed by the ultrasonic wave, in a fixed mixture time of 5 minutes [46]. The period is long enough for the ink to become completely homogeneous but the ionomer chains cannot be sheared or broken during mixing, which can inhibit the conduction of protons to active catalyst sites and reduce the efficiency of the fuel cell [47].

The volume ratios between catalyst slurry and the solvent were 1 : 1, 1 : 0.5, and 1 : 2. The catalyst inks are, respectively, designated as CI-NBA (1/1), CI-NBA (1/0.5), CI-NBA (1/2), CI-IPA (1/1), CI-IPA (1/0.5), CI-IPA (1/2), CI-EtOH (1/1), CI-EtOH (1/0.5), and CI-EtOH (1/2). Deionized (DI) water was used as a reference solvent, and the ink with the ratio 1 : 1 was denoted as CI-WATER.

Some physical properties of the used solvents are presented in Table 1 [48].

A carbon foam sheet (porous C) provided by MTI Corporation was used as a gas diffusion layer. Catalyst inks were coated on carbon cloth by a spin coating method. Firstly, a carbon cloth with a 3 cm x 3 cm dimension was put on the substrate (diameter of 600 mm) in a KW-4E Spin Coater. Secondly, the speed was set up at 150 rpm and the vacuum was turned on. Thirdly, catalyst inks were dropped on a carbon cloth with a density of 2, 5 mg cm⁻². Finally, the
electrode as an anode was dried at ambient temperature for 2 hours and then used. The MEA was prepared by hot pressing method (130°C, 5 Mpa cm⁻²) from the anode, the cathode, and the membrane, in order.

2.3. Catalysts Characterization. A JEOL JEM 2100 transmission electron microscope (TEM) and an S-4800 scanning electron microscope (SEM) (Hitachi, Japan) were used to investigate the morphology and microstructure of materials. The X-ray diffraction (XRD) patterns were performed on a D8 Advance diffractometer (Bruker) using filtered CuKα (λ = 1.5405 A) as a radiation source. The energy-dispersive X-ray spectroscopy was addressed on a JEOL JED-2300 Analysis Station to determine the elemental composition of materials. A LabRam HR (Horiba Jobin Yvon) spectrometer was operated to record Raman spectra.

2.4. Electrochemical Measurement. Electrochemical measurements were performed with a PGS-ic-HH12 Potentiostat/Galvanostat electrochemical workstation. All experiments were conducted in a three-electrode system at room temperature: a platinum counter electrode, an Ag/AgCl reference electrode, and a glassy carbon working electrode (whose diameter is 5mm) coated by a small AgCl reference electrode, and a glassy carbon working electrode as an anode and the cathode O2 pressure of 2.0 atm.

The XRD pattern of the PtAl/rGO catalyst (see Figure 1(c)) exhibited representative diffraction peaks at 39°, 46°, and 69°, which correspond to the (111), (200), and (220) planes of the FCC structure of Pt (JCPDS No. 04–0802) [34], respectively. This shows the successful Pt dispersion on rGO support. However, no characteristic peaks of Al compounds were observed, possibly because of an amorphous form or nanocrystalline form, which were not large enough to be observed by the XRD diffraction diagram.

In the Raman spectra of ExG (see Figure 2(a)) and GO (see Figure 2(b)), there are two peaks observed. They are the D-band (I_D) at 1350 cm⁻¹ that characterizes the oscillation of sp³ hybridized carbon in the 2-dimensional structure of the graphene sheets and the G-band (I_G) at 1575 cm⁻¹ that corresponds to the sp² hybrid state of adjacent carbon atoms in the hexagonal rings in graphitic structure [50]. The D-band corresponds to defects in the curved graphene sheets. It was observed that for expanded graphite, the intensity of the D-band (I_D) was much lower than that of G-band G (I_G), corresponding to the ratio of I_D/I_G = 0.20. Meanwhile, in GO, the ratio I_D/I_G = 0.73, compatible with a Raman spectroscopic characteristic mentioned in [49]. The increased intensity of the D-band of GO indicates a decrease in the size of the in-plane sp² domains, which is due to the oxidation and ultrasonic delamination of the exfoliated graphite to form GO. This result is compatible with the results shown by the XRD diffraction patterns.

PtAl/rGO catalyst (see Figure 2(d)) and rGO (see Figure 2(c)) exhibit the G and D bands at similar positions, ~1600 and 1350 cm⁻¹, respectively. The I_D/I_G value increased from 0.73 (GO) to 1.07 (PtAl/rGO) and 1.42 (rGO), indicating a reduction in the average domain size of the sp²-hybridized carbon atoms upon reduction of exfoliated GO.

Figure 3(a) shows the EDX spectra of GO with peaks that correspond to C, O, S, and Cl elements. The mass ratio of C:O in GO was estimated to 2.49, which was within the typical C:O ratio range of graphene oxide materials [44, 49, 51]. This is a confirmation that graphene oxide was actually formed. The presence of sulfur can be explained by the fact that H₂SO₄ was used as an oxidizing agent leading to the formation of –SO₃H groups on the GO surface [52]. Cl was present in trace amount, because of HCl solution used as a washing agent.

| Solvents          | Boiling point (°C) at 760 mmHg | Dielectric constant | Solubility in water (g) in 100 mL (20°C) | Viscosity/cP (25°C) |
|-------------------|-------------------------------|---------------------|----------------------------------------|-------------------|
| n-Butyl acetate   | 126.1                         | 5.07                | 0.68                                   | 0.685             |
| Isopropanol       | 82.6                          | 20.18               | Miscible                               | 1.96              |
| Ethanol           | 78.2                          | 25.30               | Miscible                               | 1.07              |
| Water             | 100.2                         | 80.10               | —                                      | 0.890             |

3. Results and Discussion

3.1. Characterization of GO, PtAl/rGO Catalyst, and Catalyst Inks. Figure 1 gives the X-ray diffraction (XRD) patterns of the ExG (a), GO (b), and PtAl/rGO (c). Expanded graphite (see Figure 1(a)) showed a very strong peak at 2θ = 26°, corresponding to an average interlayer spacing of 0.4 nm. Meanwhile, in the XRD pattern of GO (see Figure 1(b)), there is an appearance of a broad diffraction peak with high intensity at 2θ = 11°, corresponding to an average interlayer spacing of 0.8 nm; the characteristics of the average interlayer spacing of GO range from 0.70 to 0.95 nm [49]. This is due to the intercalating oxygen-containing functional groups on the surface of the exfoliated graphite layers. On the other hand, no characteristic peak of ExG was observed on the XRD pattern of GO. Thus, ExG was delaminated by oxidation to graphene oxide.

The XRD pattern of the PtAl/rGO catalyst (see Figure 1(c)) exhibited representative diffraction peaks at 39°, 46°, and 69°, which correspond to the (111), (200), and (220) planes of the FCC structure of Pt (JCPDS No. 04–0802) [34], respectively. This shows the successful Pt dispersion on rGO support. However, no characteristic peaks of Al compounds were observed, possibly because of an amorphous form or nanocrystalline form, which were not large enough to be observed by the XRD diffraction diagram.

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The EDX spectrum of PtAl/rGO catalyst shown in Figure 3(b) not only confirmed the presence of carbon and oxygen but also saw the appearance of Pt and Al. The masses of Pt and Al were estimated to be 13.98 wt% and 14.26 wt%, respectively. Thus, the mass ratio of Pt:Al was evaluated to be approximately 1:1, which corresponds to the ratio used in the preparation of the PtAl/rGO catalyst.
3.2. Characterization of Anode Electrode. According to previous studies [7, 12, 18], cracks in catalyst layers may have a few impacts on the performance and durability of a fuel cell. The cracks are formed due to some conditions, in which the direct effects are the interaction between the ionomer and the catalyst, and the dispersion of the catalyst in a solvent. The presence of cracks is represented by a rough surface, on which the catalyst layer is split into small clusters and easily flakes off after drying.

Figure 5(a) shows the smooth surface of the substance. Meanwhile, the surface of the CI-WATER catalyst layer has a few cracks as observed in Figure 5(b). The reason may be that water is not a suitable solvent to disperse the Nafion and the catalyst, so the interaction of the catalyst with the Nafion in the ink may be insufficient to prevent the separation of the ionomers from the substance during the agglomeration. A carbon foam layer would be seen in Figure 6(a). Figure 6(b) shows an SEM image of the CI-WATER catalyst layer with the I-shape cracks and pinholes due to the low interaction between ionomers and the PAI/rGO catalyst.

Figure 7 introduces the CN-NBA catalyst layers including many cracks with different shapes. For instance, in CN-NBA (1/1), the primary cracks such as I-shape and V-shape cracks were presented in the surface of the layer because of the isotropic and anisotropic stress in an inhomogeneous microstructure [12]. Meanwhile, in CN-NBA (1/0.5) and CN-NBA (1/2), a large number of secondary cracks like T-shape and Y-shape cracks appeared. Moreover, there were large voids between the separated clumps of different sizes and shapes. SEM images of the electrode-coated CN-NBA inks showed that the surface is not smooth; the catalyst layer had an uneven density (see Figure 8). The results exhibited that n-butyl acetate may be not a suitable solvent to combine with the catalyst slurry in water. Moreover, its solubility in water is low, 0.68 g per 100 g water. The ink exists as an emulsion, which may be the cause for the separation of the ionomer from the catalyst. As a result, isolated clumps were formed and the surface of the layers had a high fracture toughness [25].

The photographs of the surface of CI-IPA ink-coated electrodes in Figure 9 showed that their surface was smoother than CI-NBA and CI-WATER catalyst layers. There are no cracks observed on the surface of CI-IPA (1/1) and CI-IPA (1/0.5) catalyst layers (see Figures 9(a) and 9(b)), but there are a few I-shape and U-shape cracks presented in CI-IPA (1/2) catalyst layer (see Figure 9(c)). SEM images showed that the surface of the CI-IPA (1/1) layer was the smoothest surface and there was no crack present (see Figure 10(a)). While the CI-IPA (1/0.5) surface was uneven, including a number of clusters and pinholes (see Figure 10(b)), the surface of the CI-IPA (1/2) electrode was smoother than that of CI-IPA (1/0.5) but there are a few cracks on it. According to previous studies [12, 25], the dilution ratio of the catalyst inks and evaporation conditions have a significant impact on the catalyst layer microstructure. In the case of the CI-IPA (1/2) electrode, as the IPA solvent content increases in the catalyst ink droplets, the droplet becomes more spread out on the surface of the carbon cloth substrate and the catalyst particles are more nonuniformly distributed, with significantly more surface roughness. The inhomogeneous microstructure of catalyst layers is also related to the risk of cracking in terms of stress concentration to create cracks [12].

A more concentrated solution of the CI-IPA (1/0.5) ink makes the catalyst ink less spread out on the surface of the substrate, with a larger droplet height. In other words, CI-IPA (1/0.5) ink has a poorer leveling flow. This promotes the creation of voids and the surface unevenness of the catalyst layer after drying [12].

Thus, for CI-IPA inks, the volumic ratio between the catalyst slurry and the solvent of 1:1 (CI-IPA (1/1) ink) is the most appropriate ratio to obtain a coated electrode with a uniform surface without cracks.

The photographs of the electrode-coated CI-EtOH inks in Figure 11 showed that their surface was smoother than that of CI-NBA, CI-WATER, and CI-IPA catalyst layers. SEM images (see Figure 12) showed that the EtOH (1/1) layer was the smoothest and flattest surface (see Figure 12(a)). While the CI-EtOH (1/0.5) surface was uneven and on it there were several holes and indentations in a human foot-like shape (see Figure 12(b)), the surface of the CI-EtOH (1/2) electrode was as smooth as that of CI-EtOH (1/1) electrode but less flat. Compared with the CI-IPA (1/1) electrode, the surface of the CI-EtOH (1/1) electrode was much flatter, smoother, and more uniform. This may be explained by the fact that ethanol solvents have a lower viscosity than IPA solvents (1.07 versus 1.96), resulting in CI-EtOH (1/1) ink having better leveling flow than CI-IPA (1/1) ink. This helps to create a thin surface and spread evenly, minimizing shrinkage and the appearance of surface roughness during drying.

The above discussions were confirmed in SEM images with a larger magnification (1 : 50.000). Figure 13(a) shows that the CI-WATER (1/1) catalyst layer was split into a number of clumps by large cracks. The surface of the CI-NBA (1/1) catalyst layer (see Figure 13(b)) is not uniform, containing pinholes. Meanwhile, there are no cracks that appeared in both CI-IPA (1/1) and CI-EtOH (1/1) catalyst layers (see Figures 13(c) and 13(d)). The surface of the CI-EtOH (1/1) ink layer is smoother and more homogeneous than that of the CI-IPA (1/1) ink layer.

Based on a comparison of the microstructure of catalyst ink layers prepared by using different solvents, the CI-EtOH
(1/1) ink was found to be the most suitable for fabrication coated electrodes with homogeneous microstructure.

3.3. Electrochemical Measurement. The activity of catalyst inks with different solvents was through the CV curve of ethanol electrooxidation in acidic and alkaline medium, which was presented in Figure 13 and Table 2.

In the first place, the electroactivity of all catalyst inks in alkaline media seems to be higher than in acidic media, which is quite similar to some published articles about DEFCs [53, 54] because of faster kinetics of ethanol
Figure 5: Photographs of the surface of the carbon cloth substance (a) and the CI-WATER ink-coated electrode (b).

Figure 6: SEM images of the carbon cloth substance (a) and the CI-WATER ink-coated electrode (b).

Figure 7: Photographs of the surface of the electrode-coated CI-NBA (1/1) (a), CI-NBA (1/0.5) (b), and CI-NBA (1/2) ink.
electrooxidation in alkaline media than in acidic media. Moreover, the mechanism of the reaction was different in each media.

In an acidic environment, according to Flórez-Montaño et al. [55], the reaction could happen in a mechanism, as follows:

(i) Firstly, water and ethanol were adsorbed on Pt following reactions (1) and (2):

\[ \text{Pt} + \text{H}_2\text{O} \rightleftharpoons \text{Pt-OH} + \text{H}^+ + e^- \]  

(ii) Next, acetaldehyde and acetic acid were formed in reaction from (3) to (5):

\[ \text{Pt-CH}_3\text{CHOH} \rightleftharpoons \text{Pt-CHOCH}_3 + 2\text{H}^+ + 2e^- \]  

\[ \text{Pt-CHOCH}_3 \rightleftharpoons \text{Pt} + \text{CH}_3\text{CHO} \]  

\[ \text{Pt-CHOCH}_3 + \text{Pt-OH} \rightleftharpoons 2\text{Pt} + \text{CH}_3\text{COOH} + \text{H}^+ + e^- \]  

(iii) Finally, CO₂ was formed in reaction from (6) to (8):

\[ \text{CH}_3\text{CH}_2\text{OH} + \text{Pt} \rightleftharpoons \text{Pt-CH}_3\text{CH}_2\text{OH} \]  

\[ \text{Pt-CH}_3\text{CH}_2\text{OH} \rightleftharpoons \text{Pt-CHOCH}_3 + 2\text{H}^+ + 2e^- \]

Figure 8: SEM images of the electrode-coated CI-NBA (1/1) (a), CI-NBA (1/0.5) (b), and CI-NBA (1/2) ink.

Figure 9: Photographs of the surface of the electrode-coated CI-IPA (1/1) (a), CI-IPA (1/0.5) (b), and CI-IPA (1/2) ink (c).

Figure 10: SEM images of the electrode-coated CI-IPA (1/1) (a), CI-IPA (1/0.5) (b), and CI-IPA (1/2) ink (c).
Pt-CHOCH₃ + Pt ⇌ Pt₂-CHOCH₃ (6)
Pt₂-CHOCH₃ ⇌ Pt-CO + Pt-CH₃ + H⁺ + e⁻ (7)
Pt-CH₃ + 2Pt-OH ⇌ CO₂ + 3Pt + 5H⁺ + 5e⁻ (8)

In alkaline media, the mechanism reported by Lianqin Wang et al. [56] with Pt catalyst would be

Pt + OH⁻ ⇌ Pt-OH + e⁻ (9)
Pt + CH₃CH₂OH ⇌ Pt-CH₃CH₂OH (10)
Pt-CH₃CH₂OH + 2Pt-OH ⇌ Pt-CHOCH₃ + 2H₂O + 2Pt (11)
Pt-CHOCH₃ ⇌ Pt + CH₃CHO (12)
Pt-CHOCH₃ + 2Pt-OH ⇌ Pt-CHOCH₃ + 2H₂O + 2Pt (13)
Pt-CH₃COOH + OH⁻ ⇌ Pt + CH₃COO⁻ + H₂O (14)
Pt-CH₃COOH + Pt-OH + 4OH⁻ ⇌ Pt + 2CO₃²⁻ + H₂O (15)

Consequently, reaction products analyzed include acetic acid (or acetate ion in alkaline), acetaldehyde, and CO₂ (or carbonate ion in alkaline) with different composition ratios depending on the reaction medium. In an acidic medium, acetaldehyde was mainly obtained with more than 81.0%. The rest are acetic acid (≈12.0%) and a small amount of CO₂ (less than 2.0%). In alkaline media, the chemical yield of acetaldehyde decreases while that of acetic acid and CO₂ increases, about 53.0, 27.2, and 18.1%, respectively. These results resembled the observation in our previous study [37], which indicated that the formation of acetic acid or CO₂ seemed favored and more facile in an alkaline medium.

In the second place, the electroactivity of CI-NBA inks was lower than CI-WATER (see Figures 14(a) and 14(b)) in both media. For example, in acidic media, the forward current densities (Iₚ) were in the following order: CI-WATER (1486 mA mg⁻¹ Pt) > CI-NBA (1/1) (1257 mA mg⁻¹ Pt) > CI-NBA (1/0.5) (857 mA mg⁻¹ Pt) > CI-NBA (1/2) (742 mA mg⁻¹ Pt). Respectively, the backward current density (Iᵦ) was the following: CI-WATER (1784 mA mg⁻¹ Pt) > CI-NBA (1/1) (1478 mA mg⁻¹ Pt) > CI-NBA (1/0.5) (1310 mA mg⁻¹ Pt) > CI-NBA (1/2) (661 mA mg⁻¹ Pt). In this case of an alkaline medium, Iₚ was in an arrangement: CI-WATER (3951 mA mg⁻¹ Pt) > CI-NBA (1/1) (3114 mA mg⁻¹ Pt) > CI-NBA (1/0.5) (721 mA mg⁻¹ Pt) > CI-NBA (1/2) (476 mA mg⁻¹ Pt), Iᵦ was in the following order: CI-WATER (1894 mA mg⁻¹ Pt) > CI-NBA (1/1) (1182 mA mg⁻¹ Pt) > CI-NBA (1/0.5) (1182 mA mg⁻¹ Pt) > CI-NBA (1/2) (220 mA mg⁻¹ Pt), and the Iₚ/Iᵦ ratio would be as follows: CI-NBA (1/1) (2.63) > CI-IPA (1/2) (2.17) > CI-WATER (2.09) = CI-NBA (1/0.5) (1.98) (see Table 2). The reason may be that a low interaction of catalyst with the Nafion in the ink, which has been explained by the above results of the characteristic properties, brings out the poor connection at the 3-phase [14]. As a result, the ethanol electrooxidation with CI-NBA ink occurred harder than with CI-WATER ink.

In the third place, the electroactivity of CI-IPA inks would be improved (see Figures 14(c) and 14(d)). In acidic
media, \( I_c \) presented in the following order: CI-WATER (1486 mA mg\(_{Pt}^{-1}\)) > CI-IPA (1/1) (1187 mA mg\(_{Pt}^{-1}\)) > CI-IPA (1/2) (1133 mA mg\(_{Pt}^{-1}\)) > CI-IPA (1/0.5) (723 mA mg\(_{Pt}^{-1}\)). However, there is a little difference from \( I_b \) that was arranged as follows: CI-IPA (1/1) (2046 mA mg\(_{Pt}^{-1}\)) > CI-WATER (1784 mA mg\(_{Pt}^{-1}\)) > CI-IPA (1/2) (1693 mA mg\(_{Pt}^{-1}\)) > CI-IPA (1/0.5) (1261 mA mg\(_{Pt}^{-1}\)). It means that the ratio \( I_c/I_b \) of CI-IPA inks is lower than that of CI-WATER ink. The ratio should be in the following order: CI-WATER (0.83) > CI-IPA (1/2) (0.70) > CI-IPA (1/1) (0.58) > CI-IPA (1/0.5) (0.57). According to previous research [57, 58], in acid media, CI-IPA may have electroactivity higher and lower stability than CI-WATER ink do. In alkaline media, the arrangement of the \( I_c \) was as follows: CI-WATER (3951 mA mg\(_{Pt}^{-1}\)) > CI-IPA (1/0.5) (3431 mA mg\(_{Pt}^{-1}\)) > CI-IPA (1/1) (3234 mA mg\(_{Pt}^{-1}\)) > CI-IPA (1/2) (2877 mA mg\(_{Pt}^{-1}\)).

**Table 2: CV data of the catalyst inks in ethanol electrooxidation**

| Catalyst ink          | \( I_c \) mA mg\(_{Pt}^{-1}\) | \( I_b \) mA mg\(_{Pt}^{-1}\) | \( I_c/I_b \) | \( I_c \) mA mg\(_{Pt}^{-1}\) | \( I_b \) mA mg\(_{Pt}^{-1}\) | \( I_c/I_b \) |
|-----------------------|-------------------------------|-------------------------------|--------------|-------------------------------|-------------------------------|--------------|
| CI-WATER              | 1486                          | 1784                          | 0.83         | 3951                          | 1894                          | 2.09         |
| CI-NBA (1/1)          | 1257                          | 1478                          | 0.85         | 3114                          | 1182                          | 2.63         |
| CI-NBA (1/0.5)        | 857                           | 1310                          | 0.65         | 721                           | 364                           | 1.98         |
| CI-NBA (1/2)          | 742                           | 661                           | 1.12         | 476                           | 220                           | 2.17         |
| CI-IPA (1/1)          | 1187                          | 2046                          | 0.58         | 3435                          | 1724                          | 1.99         |
| CI-IPA (1/0.5)        | 723                           | 1261                          | 0.57         | 3080                          | 1496                          | 2.06         |
| CI-IPA (1/2)          | 1133                          | 1693                          | 0.67         | 2911                          | 1298                          | 2.24         |
| CI-EtOH (1/1)         | 1793                          | 2553                          | 0.70         | 4751                          | 2438                          | 1.95         |
| CI-EtOH (1/0.5)       | 719                           | 1095                          | 0.66         | 3980                          | 1726                          | 2.31         |
| CI-EtOH (1/2)         | 987                           | 1532                          | 0.64         | 2364                          | 1103                          | 2.14         |

**Figure 13:** SEM images of electrode-coated CI-WATER (a), CI-NBA (1/1) (b), CI-IPA (1/1) (c), and CI-EtOH (1/1) (d) inks at a magnification of 1:50,000.
mgPt\(^{-1}\)), \(I_B\) was as follows: CI-WATER (1894 mA mgPt\(^{-1}\)) > CI-IPA (1/0.5) (1694 mA mgPt\(^{-1}\)) > CI-IPA (1/1) (1557 mA mgPt\(^{-1}\)) > CI-IPA (1/2) (1267 mA mg Pt\(^{-1}\)), and the \(I_F/I_B\) would be as follows: CI-IPA (1/2) (2.24) > CI-WATER (2.09) = CI-IPA (1/0.5) (2.06) = CI-IPA (1/1) (1.99) (see Table 2). The results were explained by the elimination of Nafion in an inhomogeneous microstructure of CI-IPA layers, which were introduced above, because of the
reducing proton conductivity in the catalyst layer during the reaction. Consequently, the activity decreased.

A better electroactivity in the case of CI-EtOH inks was presented in Figures 14(e) and 14(f); especially, in the case of the CI-EtOH (1/1) sample, the activity was higher than that of CI-WATER. For example, in acidic media, \( I_F \) should be in the following order: CI-EtOH (1/1) (1793 mA mg\(_{Pt}^{-1}\) > CI-WATER (1486 mA mg\(_{Pt}^{-1}\) > CI-EtOH (1/2) (987 mA

**Figure 15:** Polarization and power density curve of PEM-DEFCs (a), (c), (e) and AEM-DEFCs (b), (d), (f) using the anode-coated different catalyst inks. Cathode: O\(_2\) flow with a pressure of 2 atm. Anode: C\(_2\)H\(_5\)OH 2 M, 10 mL min\(^{-1}\) (with PEM-DEFCs). C\(_2\)H\(_5\)OH 2 M + NaOH 1 M, 10 mL min\(^{-1}\) (with AEM-DEFCs). Temperature: 50°C.
was higher than the reference, which was presented in the reference. In PEM-DEFC, the power density of CI-IPA anodes follows: CI-WATER (0.83) > CI-EtOH (1/1) (2438 mA mg Pt\(^{-1}\)) > CI-EtOH (1/0.5) (2364 mA mg Pt\(^{-1}\)) > CI-EtOH (1/2) (1103 mA mg Pt\(^{-1}\)), and the IF/IB ratio was as follows: CI-WATER (0.83) > CI-EtOH (1/1) (0.70) > CI-EtOH (1/0.5) (0.66) > CI-EtOH (1/2) (0.64). Meanwhile, in alkaline media, the arrangement of IF was the following: CI-EtOH (1/1) (4751 mA mg Pt\(^{-1}\)) > CI-WATER (3959 mA mg Pt\(^{-1}\)) > CI-EtOH (1/0.5) (3980 mA mg Pt\(^{-1}\)) > CI-EtOH (1/2) (2364 mA mg Pt\(^{-1}\)).

In PEM-DEFC and AEM-DEFC using CI-EtOH ink-coated anodes, the highest value of the tested electrodes was from 19.10 mW cm\(^{-2}\) with CI-EtOH electrode (1/0.5) anode to 27.07 mW cm\(^{-2}\) with CI-EtOH electrode (1/1) anode compared to 4.42 with CI-EtOH electrode (1/2) anode. In the same way, in AEM-DEFCs, the power was from 1.3 to 1.8 times higher than the reference, which was from 19.61 mW cm\(^{-2}\) with CI-EtOH electrode (1/0.5) anode to 27.07 mW cm\(^{-2}\) with CI-EtOH electrode (1/1) anode compared to 15.17 with CI-WATER electrode (see Table 3).

These results were quite corresponding to the electroactivity of all catalyst inks mentioned above.

To sum up, ethanol with the solvent ratio of 1/1 not only brings out the highest electroactivity of the PtAl/rGO catalyst inks in both acidic and alkaline media but also contributes to the best power density of CI-EtOH anode in PEM-DEFCs and AEM-DEFCs.

### Table 3: Power density of DEFC with anode-coated different catalyst inks.

| Catalyst inks | Maximum power density, mW cm\(^{-2}\) |
|---------------|---------------------------------------|
|               | PEM-DEFC | AEM-DEFC |
| CI-WATER      | 4.42     | 15.17    |
| CI-NBA (1/1)  | 3.29     | 12.23    |
| CI-NBA (1/0.5)| 2.57     | 10.19    |
| CI-NBA (1/2)  | 2.17     | 6.48     |
| CI-IPA (1/1)  | 13.86    | 14.21    |
| CI-IPA (1/0.5)| 6.60     | 11.35    |
| CI-IPA (1/2)  | 11.09    | 12.72    |
| CI-EtOH (1/1) | 19.10    | 27.07    |
| CI-EtOH (1/0.5)| 15.29   | 19.61    |
| CI-EtOH (1/2) | 17.38    | 21.99    |

4. Conclusion

In this work, we investigated the effect of common solvents such as ethanol, isopropanol, and n-butyl acetate on the electrochemical activity of catalyst inks and on the properties of catalyst inks coated on anode electrodes. According to the experiment results, ethanol that allows increased Nafion mobility, resulting in a significant improvement in the interaction between Pt particles and ionomer, is the most suitable solvent for the preparation of PtAl/rGO catalyst inks in both acidic and alkaline media. Moreover, the electrochemical activity of CI-EtOH ink-coated anodes, 19.10 mW cm\(^{-2}\) and 27.07 mW cm\(^{-2}\), respectively, are the highest value of the tested electrodes. These results would promote the application of Pt/rGO ink-coated electrodes in fuel cell in life especially in transportation, military, electronics, and telecommunication.
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