Enhanced Methanol Oxidation Activity of PtRu/C$_{100-x}$MWCNTs$_{x}$ ($x = 0–100$ wt.%) by Controlling the Composition of C-MWCNTs Support

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1. Introduction

Currently, green energy research is more urgent than ever due to environmental pollution and the gradual depletion of fossil energy. As a green and clean electric power source, fuel cells are able to directly transform chemical energy into electrical energy, and used as power generation in portable, stationary, and transportation applications [1–3]. Among various types of fuel cells, direct methanol fuel cells (DMFCs) have been considered as a promising energy source owing to their low operation temperature (below 100 °C), operation safety, superior specific energy, and durability [3,4]. The commercialization of DMFCs requires further reducing the cost and increasing the performance of the electrode catalyst. However, precious and expensive metal catalyst (i.e., Pt or Pt alloy) has been generally used as the catalyst for methanol oxidation reaction (MOR) in DMFCs [5–10]. Moreover, carbon monoxide (CO) gas released in MOR poisons Pt catalyst and limits the performance of DMFCs. In order to solve these problems, various Pt-based alloys have been developed to reduce Pt usage and enhance the catalyst activity, including PtRu [11,12], PtCo [13], PtMo [14], PtRuNi [15], PtRuMo [16], etc. Among the catalyst systems, PtRu is well known, owing to its superior performance in preventing the poisoning of the Pt...
surface by CO gas. It is because Ru forms an oxygenated species at lower potentials than that of Pt, and thus Ru promotes the oxidation of CO gas produced during MOR [17].

Membrane electrode assembly (MEA), which is the main component of DMFCs, has a significant effect on fuel cell performance. An effective anode catalyst is one of the prerequisites for an ideal MEA [18]. In DMFCs, supporting materials (or substrates) for catalysts play a certain important role that can significantly affect the catalyst activity. Carbon black (CB) is commonly used for supporting catalyst nanoparticles in DMFCs because of its large specific surface area and high electrical conductivity [19], but it poses several drawbacks—poor corrosion resistance and limitation of mass transfer due to its dense structure [20]. Carbon nanotubes (CNTs) with high chemical stability and high electrical and thermal conductivities are considered as an excellent support material [21]. Indeed, the catalysts/CNTs possess 1.3–1.6 times greater methanol oxidation activity than that of catalysts/Vulcan carbon [22–24]. However, the electrical and thermal conductivities at CNT–CNT inter-tube junctions are at least an order of magnitude lower than those of individual CNTs [25,26]. In recent years, the development of carbon-based nanomaterial supports with different structures–morphologies to enhance DMFCs performance has attracted much attention. Graphene, carbon xerogels, carbon nanofiber, mesoporous carbon, and functionalized or doped carbon supports exhibited the enhancements in methanol oxidation efficiency as compared to the traditional carbon supports [22–24,27–33]. Interestingly, PtRu nanoclusters decorated on three-dimensional porous composite support of graphene sheets (GS) and CNTs presented ~3.2 times higher current intensity than the catalysts on carbon substrate, which was attributed to the decreased aggregation of metallic nanoparticles in the PtRu/GS-CNT [24]. In addition, Yang et al. reported that Pt nanoparticles decorated on a composite support of 10 wt.% MWCNTs and CB resulted in an enhanced power density of 1.5 and 2 times greater than those of the Pt catalyst on MWCNTs- and CB-supports, respectively [34]. Moreover, MWCNTs support showed better durability than CB support [34]. These results suggest that, besides developing catalyst materials, studies on composite carbon-based supporting nanomaterials are a new promising approach toward further enhancement of DMFCs performance.

In this study, PtRu alloy nanoparticles synthesized by a co-reduction method were decorated on C_{100−x}MWCNTs_x composites with various mixing weight percentages (i.e., x = 0–100 wt.%). The structure and morphology of the PtRu/C_{100−x}MWCNTs_x (x = 0–100 wt.%) samples were studied by X-ray diffraction (XRD) and transmission electron microscope (TEM) analyses. The effect of MWCNTs content on the electrocatalytic activity of the nanomaterials was investigated by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) analyses. This study provides the optimal composition of C-MWCNTs support for the enhanced catalytic activity of PtRu/C-MWCNTs, and gains insight into the support role to the overall performance of an electrocatalyst.

2. Materials and Methods

PtRu/C_{100−x}MWCNTs_x (x = 0, 10, 20, 30, 40, 50, and 100 wt.%) were synthesized using the following procedure. First, solutions containing C_{100−x}MWCNTs_x (x = 0, 10, 20, 30, 40, 50, and 100 wt.%) were prepared by mixing accurate amounts of the commercial C (carbon Vulcan XC-72, Fuelcellstore, College Station, TX, USA) and MWCNTs (>95%, OD: 10–20 nm, US Research Nanomaterials, Inc., Houston, TX, USA) with 10 mL deionized (DI) water in an ultrasonic bath for 15 min. Noticeably, since the pristine MWCNTs lacks bonding sites, namely –COOH, =O, and –OH groups, the deposition of metal nanoparticles on the surface of MWCNTs is difficult. Thus, it requires functionalizing MWCNTs to keep metal nanoparticles on its surface by several developed methods [35–37]. The common method is the treatment of MWCNTs with HNO_3 and H_2SO_4 acids under suitable time and temperature to activate MWCNTs. To our knowledge, MWCNTs are activated effectively under refluxing condition in 65% HNO_3 and 98% H_2SO_4 acids (1:1) at 50 °C for 5 h. Next, 30 mL ethylene glycol and 15 mL sulfuric acid (H_2SO_4 98%) solutions were added to
The C$_{100-x}$MWCNTs$_x$ solutions, and the mixture solutions were then stirred at 170 °C for 30 min.

The PtRu precursor solutions were prepared by mixing 3.5 mL H$_2$PtCl$_6$·6H$_2$O 0.02 M and 3.5 mL RuCl$_3$·xH$_2$O 0.02 M (corresponding to 13 mg Pt and 7 mg Ru, the atomic ratio of Pt:Ru = 1:1) in an ultrasonic bath for 15 min. Next, the mixture of PtRu precursor solution was slowly dropped into the C$_{100-x}$MWCNTs$_x$ solutions, following by a sprinkle of 0.2 M NaBH$_4$ solution. The pH solution was adjusted to 10 by using 10 M NaOH. The mixture was stirred at room temperature for 8 h. Finally, the PtRu/C$_{100-x}$MWCNTs$_x$ ($x$ = 0, 10, 20, 30, 40, 50, and 100 wt.%) products were collected by filtration, washed thoroughly with DI water, and dried overnight at 90 °C.

The H$_2$PtCl$_6$·6H$_2$O, RuCl$_3$·xH$_2$O, H$_2$SO$_4$ 98%, HNO$_3$ 65%, NaBH$_4$, CH$_3$OH, and NaOH were purchased from Merck KGaA of Darmstadt, Germany. The mass of each support type, Pt and Ru metals, and their proportions in each sample are listed in Table 1.

### Table 1. Detailed preparation conditions of the catalytic samples investigated.

| Sample           | Carbon Vulcan XC-72 Mass (mg) | MWCNTs Mass (mg) | Mass Ratio of C and C-MWCNTs (wt.%) | Mass Ratio of C-MWCNTs and Sample (wt.%) | Pt Mass (mg) | Ru Mass (mg) | Mass Ratio of Pt + Ru and Sample (wt.%) |
|------------------|-------------------------------|-------------------|-------------------------------------|------------------------------------------|-------------|-------------|----------------------------------------|
| PtRu/C           | 80                            | 0                 | 100                                 | 0                                        | 80          | 13          | 7                                      | 20                      |
| PtRu/MWCNTs      | 0                             | 80                | 0                                   | 100                                      | 80          | 13          | 7                                      | 20                      |
| PtRu/C$_{60}$MWCNTs$_{40}$ | 72                            | 8                 | 90                                  | 10                                       | 80          | 13          | 7                                      | 20                      |
| PtRu/C$_{60}$MWCNTs$_{30}$ | 64                            | 16                | 80                                  | 20                                       | 80          | 13          | 7                                      | 20                      |
| PtRu/C$_{60}$MWCNTs$_{20}$ | 56                            | 24                | 70                                  | 30                                       | 80          | 13          | 7                                      | 20                      |
| PtRu/C$_{60}$MWCNTs$_{10}$ | 48                            | 32                | 60                                  | 40                                       | 80          | 13          | 7                                      | 20                      |

The crystalline orientations of the nanomaterials were studied via XRD analysis using Bruker D8 and Cu Kα (1.5406 Å) radiation. Structural characterization at atomic scale was performed by using a TEM (JEOL JEM1010, Hanoi, Vietnam). A three-electrode test cell configuration using an Ag/AgCl reference electrode was used for electrochemical analyses. The electrolyte was a mixture solution of 0.5 M H$_2$SO$_4$ 98% and 1.0 M CH$_3$OH. The working electrode was made using 4 mg of catalytic powder (Pt and Ru masses were 0.52 mg and 0.28 mg, respectively) mixed with 1 mL of 2-propanol (Merck, Darmstadt, Germany) in an ultrasonic bath. Afterward, the catalytic powder was swept onto 1 cm$^2$ carbon paper using Nafion 117 binder solution (Aldrich, Darmstadt, Germany). The carbon paper was then scanned into catalytic powder, which was assembled in a sealed plastic frame with a blank area of 1 cm$^2$. This active area was completely immersed in the electrolyte during CV measurements. CV curves were recorded using an Autolab 302N system (Ho Chi Minh City, Vietnam) within a potential range of $-0.2$–$1.2$ V vs. Ag/AgCl (3M KCl) at a scan rate of 50 mV·s$^{-1}$. Electrochemical impedance spectroscopy (EIS) measurements were performed using the same system with a potential amplitude of ±10 mV in a frequency range of 0.1–100 kHz.

3. Results and Discussion

3.1. Effect of Catalyst Supports on Structure–Composition and Methanol Oxidation Performance of PtRu/C$_{100-x}$MWCNTs$_x$ ($x$ = 0, 40, 100%)

Figure 1 shows the XRD patterns of PtRu/C, PtRu/MWCNTs, and PtRu/C$_{60}$MWCNTs$_{40}$. Clearly, the XRD patterns of all three types of nanomaterials are similar, whose peaks can be indexed to the (111), (200), (220), and (311) planes of a face-centered cubic (f.c.c) lattice structure of platinum. In addition, the patterns of the hexagonal closest packed (h.c.p) structure of ruthenium should be included inside these diffraction peaks, namely Ru (002) at 42.2°, Ru (101) at 44.1°, Ru (110) at 69.5°, and Ru (112) at 84.8°. In addition, a broad diffraction peak at approximately 26° is attributed to hexagonal graphite structure [C (002)], suggesting that these supports could have good electrical conductivity [38]. The present XRD results confirm for the PtRu alloy on C-based supports, and they are similar to those
results reported in [39–41]. It was found in a PtRu alloy that if Ru content in PtRu alloy is lower than 60 wt.%, the alloys will stay in the f.c.c structure of platinum; inversely, if Ru content in PtRu alloy is higher than 60 wt.%, the PtRu alloy will exhibit h.c.p structure of ruthenium [40,41]. Since the XRD patterns matched better with the f.c.c structure of platinum, the Ru content in the PtRu alloys in this study should be lower than 60 wt.%. Furthermore, no XRD peak shift was observed, thus the composition of PtRu should be stable among the prepared samples.

In addition, a broad diffraction peak at approximately 26° is attributed to hexagonal graphite structure [C (002)], suggesting that these supports could have good electrical conductivity [38]. The present XRD results confirm for the PtRu alloy on C-based support, and they are similar to those results reported in [39–41]. It was found in a PtRu alloy that if Ru content in PtRu alloy is higher than 60 wt.%, the PtRu alloy will exhibit h.c.p structure of ruthenium [40,41].

Figure 2 shows the typical TEM images and the particle size distribution histograms of PtRu/C, PtRu/MWCNTs, and PtRu/C_{60}MWCNTs_{40}. Obviously, PtRu nanoparticles were well distributed and decorated on the C_{100−x}MWCNTs_{x} supports. All the samples had narrow size distributions and small mean values (d_{mean}) of 2.4 ± 0.2, 3.8 ± 0.1, and 2.2 ± 0.1 nm for PtRu/C, PtRu/MWCNTs, and PtRu/C_{60}MWCNTs_{40}, respectively (Figure 2). It is known that particle size of catalysts can affect the methanol oxidation activity of PtRu alloy catalysts. It is plausible that when the present PtRu sizes with d_{mean} between 2.2 ± 0.1 and 3.8 ± 0.1 nm are close to the reported optimal PtRu size of ~3 nm, high methanol oxidation activity is achieved [42]. Importantly, the uniformities in size and distribution of PtRu nanoparticles among the samples investigated were sufficient to allow for studying the compositional effects of C_{100−x}MWCNTs_{x} supports on the electrocatalytic activity of PtRu/C_{100−x}MWCNTs_{x} (x = 0, 40, 100%) as described in a later section. Interestingly, by considering both d_{mean} values and the upper tails of the size distributions, the C_{60}MWCNTs_{40} composite support with high porosity likely hinders the growth of PtRu nanoparticles. This finding agreed well with that in [11], in which the mesoporous carbon support was found to restrict the crystal growth of PtRu nanoparticles.

Cyclic voltammograms (CV) of PtRu/C, PtRu/MWCNTs, and PtRu/C_{60}MWCNTs_{40} are shown in Figure 3a,b. These samples exhibited different current density (J); the peak current density values of forward and reverse scans (J_{f} and J_{r}) and J_{f}/J_{r} ratio were determined and are listed in Table 2. The J_{f} (J_{r}) values are 21.6 (6.0) mA/mg_{PtRu}, 67.0 (36.0) mA/mg_{PtRu}, and 65.4 (19.4) mA/mg_{PtRu} for PtRu/C, PtRu/MWCNTs, and PtRu/C_{60}MWCNTs_{40}, respectively. Obviously, PtRu/C had lowest J_{f} value, while PtRu/MWCNTs and PtRu/C-MWCNTs achieved J_{f} values more than three times higher. In contrast, the PtRu/C obtained the highest J_{f}/J_{r} ratio of 3.6, and PtRu/C_{60}MWCNTs_{40} also reached a high J_{f}/J_{r} value of
3.4, whereas PtRu/MWCNTs exhibited a low $J_f/J_r$ ratio of 1.9. The $J_f/J_r$ ratio is used to describe the catalyst tolerance to carbonaceous species accumulation [43]. The larger $J_f/J_r$ value indicates a better CO resistant catalyst. In MOR, CO is a critical intermediate that reduces both fuel cell potential and energy conversion efficiency. A forward scan is attributable to methanol oxidation, forming Pt-adsorbed carbonaceous intermediates (e.g.,
carbon monoxide). The adsorbed carbon monoxide causes a suppression of the electrocatalyst activity. The reverse oxidation peak is attributed to the additional oxidation of the adsorbed carbonaceous species to carbon dioxide (CO$_2$) [44].

![Figure 2. TEM images and particle size distributions of (a) PtRu/C, (b) PtRu/MWCNTs, and (c) PtRu/C$_{60}$MWCNTs$_{40}$.](image)

### Table 2. Electrochemical parameters of PtRu/C, PtRu/MWCNTs, and PtRu/C$_{60}$MWCNTs$_{40}$.

| Sample                  | $J_f$  | $J_r$  | $J_f/J_r$ | $R_{ct}$ |
|-------------------------|--------|--------|-----------|----------|
| PtRu/C                  | 17.3   | 21.6   | 4.8       | 6.0      | 3.6       | 7.39 |
| PtRu/MWCNTs             | 53.6   | 67.0   | 28.8      | 36.0     | 1.9       | 11.19 |
| PtRu/C$_{60}$MWCNTs$_{40}$ | 52.3   | 65.4   | 15.5      | 19.4     | 3.4       | 6.37 |

Based on these results, the best carbonaceous species tolerance ability ($J_f/J_r = 3.6$) was achieved in the PtRu/C. For the support effect, the $J_f$ value of PtRu/MWCNTs is higher than that of PtRu/C (Figure 3a and Table 2), which could be attributed to the higher porosity and better catalyst dispersion–distribution of MWCNTs support than those of C support [21]. However, the carbonaceous species tolerance ability of PtRu/MWCNTs ($J_f/J_r = 1.9$) is very limited. Nevertheless, PtRu/C$_{60}$MWCNTs$_{40}$ can simultaneously achieve a high $J_f$ of 52.3 mA·cm$^{-2}$ (or 65.4 mA/mgPtRu) and a high $J_f/J_r$ ratio of 3.4. This means that PtRu/C$_{60}$MWCNTs$_{40}$ possesses not only high MOR activity, but also excellent carbonaceous species tolerance ability, suggesting that the composite of C-MWCNTs support
intermediates (e.g., carbon monoxide). The adsorbed carbon monoxide causes a suppression of the electrocatalyst activity. The reverse oxidation peak is attributed to the addition of oxygenated species to the intermediate PtRu/C60MWCNTs40 at a potential of 0.8 V (vs. Ag/AgCl). Although the Nyquist curves of the samples do not show full semicircles, it is still clear that the total complex impedance \( Z \) of the samples has a decreasing order of PtRu/MWCNTs < PtRu/C < PtRu/C60MWCNTs40. For quantitative analysis of the EIS data, we employed the Randles equivalent circuit model to fit the plots with one semicircle [45], whose model was also used to fit the EIS data of Fe2O3 films [46], Pt–MnO2 nanoparticles decorated on reduced graphene oxide sheets [47], and carbon-supported Ru-Pt nanoparticles [48]. The circuit included the electron transfer resistance \( R_{ct} \), solution resistance \( R_s \), and double layer capacity \( C_{dl} \). The circular fits with the Randles circuit yield \( R_{ct} \) values of 7.39, 11.19, and 6.37 \( \Omega \cdot \text{cm}^2 \) for PtRu/C, PtRu/MWCNTs, and PtRu/C60MWCNTs40, respectively. The lowest \( R_{ct} \) was obtained for PtRu/C60MWCNTs40, indicating composite C-MWCNTs support offered excellent electron transfer that was attributed to the highest current density at 0.8 V. The highest electrocatalytic activity and the smallest \( R_{ct} \) of PtRu/C60MWCNTs40 indicates that the composite of C-MWCNTs is a superior support over either C or MWCNTs.

These results can be explained by considering the structure–morphology of the three types of supports. Indeed, MWCNTs are chemically inert, so PtRu nanoparticles will be unable to stick well on the tube walls if MWCNTs are not treated. In this study, after being treated with 98% H2SO4 + 65% HNO3 at 50 °C for 5 h, functional groups =O, –OH, –COOH are formed on the surfaces of MWCNTs, and consequently PtRu nanoparticles reside on these functional groups (Figure 4). Although commercial carbon Vulcan XC-72 has high porosity, it clumps easily and reduces the surface area if this C support is used in a large quantity. The blending of carbon Vulcan XC-72 with the activated MWCNTs allows dispersed C sheets/bulks into the gaps between MWCNTs (Figure 4). Therefore, this composite support can exhibit high porosity and large surface area. Consequently, the deposition of PtRu nanoparticles on C-MWCNTs will be easier and distributed more evenly, which is attributed to the enhanced methanol oxidation catalytic efficiency (Figure 4). Furthermore, C-MWCNTs support can combine the advantages but limit the disadvantages of each component (i.e., C, MWCNTs).
3.2. Effect of MWCNTs Percentage (x = 10–50 wt.%) in PtRu/C\textsubscript{100-MWCNTs\textsubscript{x}} Samples on the Methanol Oxidation Activity

To determine the most suitable C-MWCNTs supports, a series of PtRu/C\textsubscript{100-MWCNTs\textsubscript{x}} (x = 10–50 wt.%) were prepared and characterized. The PtRu/C\textsubscript{100-MWCNTs\textsubscript{x}} samples had the same amount of PtRu nanoparticles with 20 wt.% and Pt/Ru atomic ratio of 1; meanwhile, the C\textsubscript{100-MWCNTs\textsubscript{x}} supports had various weight percentages of MWCNTs (x) from 10 to 50%. Figure 5 shows TEM images and particle size distributions of the PtRu/C\textsubscript{100-MWCNTs\textsubscript{x}} samples. It can be seen clearly that Vulcan XC-72 carbon substrate was dispersed into MWCNTs. In addition, PtRu nanoparticles were deposited and evenly distributed on both carbon Vulcan XC-72 and MWCNTs for all the samples. Moreover, particle size distribution of all the samples was in the range 1–6 nm with the peak of the distribution at 2 nm. Intriguingly, when the MWCNTs content was small (x = 10 wt.%) or large (x = 50 wt.%), the particle sizes were less uniform with wider size distribution as compared to those of the other three samples (x = 20–40 wt.%).

Figure 6a,b present the CV curves of PtRu/C\textsubscript{100-MWCNTs\textsubscript{x}} (x = 10–50 wt.%) in the electrolyte solution. Clearly, the MWCNTs content strongly affected the current density of PtRu/C\textsubscript{100-MWCNTs\textsubscript{x}} samples. The value of \( I_{f} \), \( J_{r} \), and \( I_{f}/J_{r} \) ratio are summarized in Table 3. The \( I_{f} \) and \( J_{r} \) of PtRu/C\textsubscript{100-MWCNTs\textsubscript{x}} increased when x increased from 10% to 30%, and then decreased with further increasing the MWCNTs weight percentage (x = 40–50 wt.%). The PtRu/C\textsubscript{70-MWCNTs\textsubscript{30}} obtained the highest \( I_{f} \) value, 115.8 mA/A mg\textsubscript{PtRu} (92.6 mA cm\textsuperscript{-2}), or achieving the highest MOR activity. Meanwhile, PtRu/C\textsubscript{90-MWCNTs\textsubscript{10}} obtained the highest \( I_{f}/J_{r} \) value of 4.4, and PtRu/C\textsubscript{80-MWCNTs\textsubscript{20}} exhibited a high \( I_{f}/J_{r} \) of 4.0, whose values were higher than that of PtRu/C (\( I_{f}/J_{r} = 3.6 \), Tables 2 and 3), indicating that C\textsubscript{100-MWCNTs\textsubscript{x}} (x = 10–20 wt.%) achieved the enhanced carbonaceous species tolerance. Moreover, Figure 6c shows the Nyquist plot of PtRu/C\textsubscript{100-MWCNTs\textsubscript{x}} (x = 10–50 wt.%) at a potential of 0.8 V (vs. Ag/AgCl). The semicircle of PtRu/C\textsubscript{70-MWCNTs\textsubscript{30}} and PtRu/C\textsubscript{60-MWCNTs\textsubscript{40}} are smaller as compared with that of the other samples. By fitting the semicircles with the Randles equivalent circuit model, PtRu/C\textsubscript{70-MWCNTs\textsubscript{30}} has the smallest \( R_{ct} \), 5.31 Ω cm\textsuperscript{2} (Table 3). Owing to reaching the highest electrocatalytic activity and the smallest \( R_{ct} \), PtRu/C\textsubscript{70-MWCNTs\textsubscript{30}} is proposed as the best sample.

Table 4 summarizes the methanol oxidation activity results of PtRu nanoparticles decorated on various carbon-related supports in the literature and in this study, in which current density (\( I_{f} \)) and current density ratio (\( I_{f}/J_{ic} \)) are used to evaluate the activity. Here, \( I_{f}/J_{ic} \) is the ratio between \( I_{f} \) of the present sample and \( J_{ic} \) of the conventional carbon-supported PtRu nanoparticle sample in each reference and in this study; thus \( I_{f}/J_{ic} \) indicates the current density enhancement of a particular sample relative to the conventional PtRu/C. By observing \( I_{f}/J_{ic} > 1 \) in Table 4, CNTs or MWCNTs, graphene-related, or composite support generally exhibited the enhancements in methanol oxidation activity over the conventional
carbon-supported sample. In other words, PtRu catalytic materials on the modified supports or composite supports present higher catalytic results than samples using traditional carbon support (e.g., 82.7 mA·cm\(^{-2}\) for PtRu/N-CNTs vs. 27.5 mA·cm\(^{-2}\) for PtRu/CB \([23]\), and 136.7 mA·mg\(^{-1}\) for PtRu/CTNs-GS vs. 42.7 mA·mg\(^{-1}\) for PtRu/C \([24]\)). In our study, the current intensity of catalyst with PtRu nanoparticles deposited on C\(_{70}\)MWCNTs\(_{30}\) composite support is 5.35 times higher than that of Vulcan XC-72 carbon support. Therefore, C\(_{70}\)MWCNTs\(_{30}\) composite support is recommended to use in the electrodes of DMFC.

![TEM images and particle size distributions](image.png)

**Figure 5.** TEM images and particle size distributions of (a) PtRu/C\(_{90}\)MWCNTs\(_{10}\), (b) PtRu/C\(_{80}\)MWCNTs\(_{20}\), (c) PtRu/C\(_{70}\)MWCNTs\(_{30}\), (d) PtRu/C\(_{60}\)MWCNTs\(_{40}\), and (e) PtRu/C\(_{50}\)MWCNTs\(_{50}\).
Table 3. Electrochemical parameters of PtRu/C_90MWCNTs_{10}, PtRu/C_80MWCNTs_{20}, PtRu/C_70MWCNTs_{30}, PtRu/C_60MWCNTs_{40}, and PtRu/C_50MWCNTs_{50}.

| Sample          | J_f (mA/cm^2) | J_r (mA/mg_{PtRu}) | J_f/J_r | R_{et} (Ω·cm^2) |
|-----------------|---------------|---------------------|---------|-----------------|
| PtRu/C_90MWCNTs_{10} | 29.8          | 37.3                | 6.7     | 4.4             | 29.2          |
| PtRu/C_80MWCNTs_{20} | 52.8          | 66.0                | 13.5    | 4.0             | 6.16          |
| PtRu/C_70MWCNTs_{30} | 92.6          | 115.8               | 42.9    | 2.2             | 5.31          |
| PtRu/C_60MWCNTs_{40} | 52.3          | 65.4                | 15.5    | 3.4             | 6.37          |
| PtRu/C_50MWCNTs_{50} | 38.6          | 48.3                | 9.7     | 3.9             | 8.87          |

Figure 6a,b present the CV curves of PtRu/C_{100-x}MWCNTs_x (x = 10–50 wt.%) in the electrolyte solution. Clearly, the MWCNTs content strongly affected the current density of PtRu/C_{100-x}MWCNTs_x samples. The value of J_f, J_r, and J_f/J_r ratio are summarized in Table 3. The J_f and J_r of PtRu/C_{100-x}MWCNTs_x increased when x increased from 10% to 30%, and then decreased with further increasing the MWCNTs weight percentage (x = 40–50 wt.%).

The PtRu/C_70MWCNTs_{30} obtained the highest J_f value, 115.8 mA/mgPtRu (92.6 mA·cm^−2), or achieving the highest MOR activity. Meanwhile, PtRu/C_90MWCNTs_{10} obtained the highest J_f/J_r value of 4.4, and PtRu/C_80MWCNTs_{20} exhibited a high J_f/J_r of 4.0, whose values were higher than that of PtRu/C (J_f/J_r = 3.6, Tables 2 and 3), indicating that C_{100-x}MWCNTs_x (x = 10–20 wt.%) achieved the enhanced carbonaceous species tolerance. Moreover, Figure 6c shows the Nyquist plot of PtRu/C_{100-x}MWCNTs_x (x = 10–50 wt.%) at a potential of 0.8 V (vs. Ag/AgCl). The semicircle of PtRu/C_70MWCNTs_{30} and PtRu/C_60MWCNTs_{40} are smaller as compared with that of the other samples. By fitting the semicircles with the Randles equivalent circuit model, PtRu/C_70MWCNTs_{30} has the smallest R_{et}, 5.31 Ω·cm^2 (Table 3). Owing to reaching the highest electrocatalytic activity and the smallest R_{et}, PtRu/C_70MWCNTs_{30} is proposed as the best sample.

Figure 6. (a,b) Cyclic voltammograms of PtRu/C_90MWCNTs_{10}, PtRu/C_80MWCNTs_{20}, PtRu/C_70MWCNTs_{30}, PtRu/C_60MWCNTs_{40}, and PtRu/C_50MWCNTs_{50} with current density units of mA·cm^−2 and mA/mg_{PtRu}. (c) Nyquist plots of the EIS for these samples in a frequency range from 0.1 Hz to 100 kHz. The electrolyte was a mixture solution of 0.5 M H_2SO_4 and 1.0 M CH_3OH.
Table 4. Comparison of CV results of the selected studies of PtRu nanoparticles decorated on novel carbon-related substrates in the literature and in this study. Current density ratio \((J_f/J_{fC})\) is the ratio between \(J_f\) of a PtRu/modified support and the \(J_f\) of a PtRu/conventional carbon support in each reference and in this study.

| Sample          | Support Material          | Measurement Condition                        | Evaluate Performance | Reference |
|-----------------|---------------------------|---------------------------------------------|----------------------|-----------|
|                 |                           |                                             | **Current Density (\(J_f\))** | **Current Density Ratio (\(J_f/J_{fC}\))** |          |
| PtRu/E-Tek      | Vulcan XC-72R             | 2 M CH\(_3\)OH + 0.5 M H\(_2\)SO\(_4\), 0.02 V \(\cdot\) s\(^{-1}\) | 0.29 mA \(\cdot\) cm\(^{-2}\) | –         | [27]     |
| PtRu/CX         | Carbon xerogels           |                                             | 0.36 mA \(\cdot\) cm\(^{-2}\) | 1.44      |          |
| PtRu/C          | Carbon                    | 1 M CH\(_3\)OH + 0.5 M H\(_2\)SO\(_4\), 2 mV \(\cdot\) s\(^{-1}\) | 340 mA \(\cdot\) cm\(^{-2}\) | –         | [28]     |
| PtRu/70%/CNF    | Carbon nanofiber          |                                             | 390 mA \(\cdot\) cm\(^{-2}\) | 1.15      |          |
| PtRu/XC-72      | Vulcan XC-72R Mesoporous Carbon | 1 M CH\(_3\)OH + 0.5 M H\(_2\)SO\(_4\), 50 mV \(\cdot\) s\(^{-1}\) | 27 mA \(\cdot\) cm\(^{-2}\) | –         | [29]     |
| PtRu/CX-72-III  | Vulcan XC-72R             |                                             | 60 mA \(\cdot\) cm\(^{-2}\) | 2.22      |          |
| PtRu/C          | Carbon nanotube           | 1 M CH\(_3\)OH + 0.5 M H\(_2\)SO\(_4\), 20 mV \(\cdot\) s\(^{-1}\) | 22.5 mA \(\cdot\) cm\(^{-2}\) | –         | [22]     |
| PtRu/CNTs       | Carbon nanotube           |                                             | 33.5 mA \(\cdot\) cm\(^{-2}\) | 1.49      |          |
| PtRu/C/CF       | Carbon nanotube doping N  |                                             | 42.7 mA \(\cdot\) mg\(^{-1}\) | –         | [23]     |
| PtRu/CNT        | Carbon nanotubes          | 1 M CH\(_3\)OH + 0.5 M H\(_2\)SO\(_4\), 20 mV \(\cdot\) s\(^{-1}\) | 56.0 mA \(\cdot\) mg\(^{-1}\) | 1.31      | [24]     |
| PtRu/C/CF       | Carbon nanotubes          |                                              | 78.7 mA \(\cdot\) mg\(^{-1}\) | 1.84      |          |
| PtRu/CF/GS      | Graphene sheet            |                                              | 136.7 mA \(\cdot\) mg\(^{-1}\) | 3.20      |          |
| PtRu/CF/GS      | Carbon nanotubes + Graphene sheet | 1 M CH\(_3\)OH + 0.5 M H\(_2\)SO\(_4\), 20 mV \(\cdot\) s\(^{-1}\) | 430 mA \(\cdot\) mg\(^{-1}\) | –         | [31]     |
| PtRu/CG         | Carbon                     | 0.5 M H\(_2\)SO\(_4\) + 1 M CH\(_3\)OH     | 570 mA \(\cdot\) mg\(^{-1}\) | 1.33      |          |
| PtRu/GS/CF      | Carbon nanotubes          | 1 M CH\(_3\)OH + 0.5 M H\(_2\)SO\(_4\), 50 mV \(\cdot\) s\(^{-1}\) | 8.21 mA \(\cdot\) cm\(^{-2}\) | –         | [32]     |
| PtRu/CG/CF      | Carbon nanotubes          |                                              | 14.05 mA \(\cdot\) cm\(^{-2}\) | 1.71      |          |
| PtRu/CG/CF      | Carbon nanotubes + Graphene sheet | 1 M CH\(_3\)OH + 0.5 M H\(_2\)SO\(_4\), 20 mV \(\cdot\) s\(^{-1}\) | 17.3 mA \(\cdot\) cm\(^{-2}\) | –         |          |
| PtRu/MWCNTs     | Multi-walled carbon nanotubes | 1 M CH\(_3\)OH + 0.5 M H\(_2\)SO\(_4\), 50 mV \(\cdot\) s\(^{-1}\) | 53.6 mA \(\cdot\) cm\(^{-2}\) | 3.10      |          |
| PtRu/C\(_{20}\)MWCNTs\(_{50}\) | Multi-walled carbon nanotubes + MWCNTs | 1 M CH\(_3\)OH + 0.5 M H\(_2\)SO\(_4\), 50 mV \(\cdot\) s\(^{-1}\) | 92.6 mA \(\cdot\) cm\(^{-2}\) | 5.35      |          |

Our results
4. Conclusions

PtRu alloy nanoparticles decorated on C, MWCNTs, and C-MWCNTs supports for high-performance methanol oxidation were synthesized by co-reduction method. The synthesized PtRu/C<sub>100-x</sub>MWCNTs<sub>x</sub> (x = 0–100 wt.%) exhibited the crystal structure closed to the f.c.c lattice structure of platinum with (111), (200), (220), and (311) preferred orientations. In addition, PtRu nanoparticles obtained a narrow size distribution and a small mean size (d<sub>mean</sub> = 1.8–3.8 nm). For the support effects, PtRu/C-MWCNTs offered higher J<sub>f</sub> (or higher electrocatalytic activity) and lower R<sub>et</sub> than those of PtRu/C and PtRu/MWCNTs. In addition, PtRu/C-MWCNTs has high J<sub>f</sub>/J<sub>r</sub> values, which means good carbonaceous species tolerance ability. To optimize the C-MWCNTs composition, PtRu/C<sub>100-x</sub>MWCNTs<sub>x</sub> (x = 10–50 wt.%) were synthesized and characterized. The highest J<sub>f</sub>, 115.8 mA/mg PtRu, was obtained for PtRu/C<sub>70</sub>MWCNTs<sub>30</sub>, which was considered an optimal nanomaterial system. Meanwhile, both PtRu/C<sub>70</sub>MWCNTs<sub>30</sub> and PtRu/C<sub>60</sub>MWCNTs<sub>40</sub> exhibited low resistances with R<sub>et</sub> of 5.31–6.37 Ω·cm<sup>2</sup>. The results of this study demonstrate that C-MWCNTs composite support is better than either C or MWCNTs support; significant enhancements in methanol oxidation activity and carbonaceous species tolerance ability can be achieved by controlling the MWCNTs content in C-MWCNTs support.

Author Contributions: D.L.Q. performed the experiments, analyzed the data, and wrote the first draft; P.H.L. revised and edited the paper, and supervised the project. Both authors have read and agreed to the published version of the manuscript.

Funding: This research is funded by Ho Chi Minh City University of Technology (HCMUT), VNU-HCM, under grant number BK-SDH-2021-2080906, and Vietnam National Foundation for Science and Technology Development (NAFOSTED) under Grant No. 103.02-2019.374.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: We acknowledge the support of time and facilities from Ho Chi Minh City University of Technology (HCMUT), VNU-HCM, Can Tho University, and Can Tho University of Medicine and Pharmacy for this study.

Conflicts of Interest: The authors declare no conflict of interest.

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