Preparation of Carbon-Supported Ternary Nanocatalysts Palladium-Vanadium-Cobalt for Alcohol Electrooxidation

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1.Introduction

The blooming interest in using Direct Alcohol Fuel Cells (DAFCs) as portable and mobile power sources is rooted in their desirable features of relatively small environmental footprint, compact system design, and higher volumetric energy densities compared with existing technologies. [1, 2] DAFC relies on the oxidation of alcohol, such as methanol, ethanol, or glycerol, on a catalyst layer to form carbon dioxide (CO2). Water (H2O) is consumed at the anode and produced at the cathode. Hydrogen ions formed during the oxidation of alcohol are transported across the proton exchange membrane to the cathode, where they react with oxygen (O2) to produce water. Electrons are transported through an external circuit from the anode to the cathode, providing power to external devices.

Pd-based electrocatalysts are known to achieve better alcohol electrocatalytic oxidation activity than Pt-based ones. [3–6] Moreover, the incorporation between one or multiple transition metals and Pd to design carbon-supported Pd-based bimetallic-alloy [7–14] and trimetallic-alloy [15–19] catalysts or surface modification of Pd-based catalyst, such as PdCu@C [12, 20, 21], PdCo@C [7, 22, 23], PdAg@C [10], and PdNi@C [8, 24], not only promotes the electrochemical activity and stability but also proposes an efficient way to reduce cost at the same time due to their adjusted d-band electronic structure and surface atom rearrangement. [19, 25, 26] Rostami and coworkers [27] reported the enhancement of ethanol electrooxidation of ternary PdCuNi catalyst when Ni was incorporated; the addition of Ni accelerated the removal of adsorbed carbonaceous intermediate species during ethanol oxidation. Huang and colleagues [28] prepared a core-shell ternary PdCuBi/C catalyst that exhibited an excellent performance toward ethylene glycol oxidation.

Ethylene glycol reduction is common process for the preparation of metal nanoparticles, but this process needs to be assisted by high temperature or microwave irradiation to improve the reduced performance. [6, 15, 28] However, NaBH4 is considered as a force reducing agent which can
reduce metallic ions at room temperature, and the disadvantage of NaBH₄ process is the formation of irregular particle size. [29–33] As a consequence, the combination process of ethylene glycol (EG) and NaBH₄ can get better reduction to prepare the nanoparticles.

In this work, we prepared the carbon-supported ternary nanocatalysts palladium-vanadium-cobalt (PdVCo) by ethylene glycol reduction process and, the NaBH₄-assisted reduction was also considered. The nanocatalysts PdVCo showed a comparable alcohol electrocatalytic oxidation activity and stability as compared to the original Pd catalyst.

2. Experimental

2.1. Materials. Analytical grade PdCl₂ (ReagentPlus®, 99%, Sigma Aldrich), Co(NO₃)₂·6H₂O (Sigma Aldrich, >99.9%), Vulcan XC-72R (Cabot, USA), polytetrafluoroethylene solution (PTFE, Sigma Aldrich, 65% in water), V₂O₅ (Merck, 99.5%), NaBH₄ (Merck, 99.5%), and ethylene glycol (EG, Merck, 99.5%) were used without further purification. All references' solutions H₂PdCl₄, Na₂VO₃, and Co(NO₃)₂ with the stoichiometry Pd:V:Co ratio of 1:1:1 were stirred in an ultrasonic condition; then, 100 mg pretreated Vulcan XC-72R carbon powder was added, and the mixture was ultrasonicated for 30 minutes. The reduction agents were EG and 0.01M NaBH₄.

The carbon-supported nanocatalysts PdVCo at 20 wt% were prepared by the polyl reduction process. The precursor’s solutions H₂PdCl₄, Na₂VO₃, and Co(NO₃)₂ with the stoichiometry Pd:V:Co ratio of 1:1:1 were stirred in an ultrasonic condition; then, 100 mg pretreated Vulcan XC-72R carbon powder was added, and the mixture was ultrasonicated for 30 minutes. The reduction agents were dropped into the mixture, following four samples: (i) 15 mL EG, (ii) 20 mL EG, (iii) 15 mL EG + 20 mL NaBH₄, and (iv) 20 mL EG + 20 mL NaBH₄. The products were filtered, washed with DI water several times, and dried in an oven at 120°C for 2 hours. We then denoted the respective nanocatalyst samples: (i) PdVCo-15EG; (ii) PdVCo-20EG; (iii) PdVCo-15EG-20NaBH₄; and (iv) PdVCo-20EG-20NaBH₄.

The structure was characterized by X-ray diffraction by using a D8-Advance Diffractometer (Bruker) with Cu Kα radiation (λ = 1.5406 Å). The size and morphological features were analyzed by SEM with energy-dispersive X-ray (EDX) detector using a Hitachi S-4800 instrument, and transmission electron microscopy (TEM) was performed using a JEOL JEM 1400 microscope at 120 kV. Brunauer–Emmett–Teller specific surface area (S₆₅₃₋₇₅) was determined by nitrogen adsorption measurement (Quanachrome Autosorb 1C) with an out-gas process at 200°C for 2 hours.

2.3. Electrochemical Measurements. All the electrochemical measurements were carried out at room temperature under nitrogen atmosphere on potentiostat/galvanostat PGSTAT320N (Metrohm, AG) apparatus with a three-electrode cell, including a glassy carbon electrode (GCE, 3 mm in diameter) as working electrode, a platinum wire as counter electrode, and a Ag/AgCl in 3.5 M KCl electrode as reference electrode. To prepare the working electrode, 2.5 mg nanocatalysts PdVCo were put into 1.0 mL ethanol and 25 μL PTFE solution; the mixture was then ultrasonicated for 1 hour to obtain a homogeneous suspension. 75 μL of suspension was dropped on GCE and dried at 40°C in 1 hour. The electrocatalytic behavior of synthesized nanocatalysts was studied by cyclic voltammetry (CV) and chronoamperometry (CA). In order to determine the electrochemical surface areas (ECSAs) of the nanocatalysts, the CV measurements were carried out in a solution of 1 M KOH at a scan rate of 50 mV/s from −1 V to 0.5 V. For the alcohol oxidation electroactivity, the CV measurements in a solution of 1 M CH₃OH + 1 M KOH and 1 M C₂H₅OH + 1 M KOH were conducted from −0.8 V to 0.3 V with a scan rate of 50 mV/s. CA measurements were performed in the same alcohol-contained KOH solution at an applied voltage of −0.130 V or −0.150 V for an hour.

3. Results and Discussion

3.1. Physiochemical Characterization. Figure 1 shows the typically XRD pattern of carbon-supported nanocatalysts PdVCo with the metal loading of 20 wt% (sample PdVCo-20EG-NaBH₄). The characteristic peaks of face-center cubic crystalline Pd (JCPDS Card 00-005-0681) are observed with phase structure for all nanocatalysts. Compared to the original phase Pd (a = 3.8971 Å), the characteristic peaks of PdVCo-20EG-NaBH₄ quietly shift toward higher 2θ and 3.8618 Å (detailed in Table S1) due to the decreased to a = 3.8618 Å (detailed in Table S1) due to the smaller atom radius of Co and V. The broadening of the diffraction peaks is considered as the nanocrystalline characteristic of nanocatalysts PdVCo. The average crystallite size is calculated from the full width of the half maximum (FWHM) of highest intensity peak (111) through Debye–Scherrer equation (1) [13, 20]:

$$d_{hkl} = \frac{\lambda}{\beta \cos \theta}$$  \hspace{1cm} (1)

where $d_{hkl}$ is the average crystallite size; $k$ is the constant depending on the crystallite shape (0.9); $\lambda$ is the wavelength
of copper Kα X-ray radiation (1.5406 Å); β is the FWHM (in radian) of the most intense peak (in radian) and is determined by X’Pert HighScore Plus software; and θ is the diffraction angle. The average crystallite sizes of nanocatalysts PdVCo are gathered in Table S1. We observed that the crystallite sizes are around 5-6 nm. Although no Co and V peaks can be seen in XRD patterns, the EDX spectrum (Figure 2) of nanocatalysts indicates clearly the presence of the elements V and Co in ternary alloy; the mass ratios of Pd:V:Co are shown in Table 1. The Co-content and especially V-content in two NaBH4-assisted reduction samples are higher than those in the other samples; the atomic ratios of Pd:V:Co in PdVCo-15EG-NaBH4 and PdVCo-20EG-NaBH4 are 1 : 0.35 : 0.59 and 1 : 0.55 : 0.86, respectively. The results revealed the beneficial support of NaBH4 for trimetallic-alloy reduction.

Figure 3 shows the TEM images and particle size distribution of the nanocatalysts. The synthesized nanoparticles PdVCo have a small and uniform size and are well dispersed on the carbon surface with a narrow particle size distribution of 3 nm to 9 nm. In case of EG reduction agent, the nanoparticles are found with an average particle diameter of 6.8 nm, and the particle size larger 6 nm occupied more than 50%. Rather, in case of NaBH4-assisted reduction agents, the nanoparticles look smaller; the major particle size lies in range 5 nm to 7 nm. The NaBH4 assisted in the polyol reduction process that leads to little smaller and more uniformly sized nanoparticles. [29] Moreover, the incorporation of V and Co also supports a decrease of catalyst particle size and the modified-surface structure of Pd that leads to the surface-adsorbed species, and the electronic effect contributes to the alcohol electrooxidation on the Pd nanoparticles. [31, 34, 35].

The BET surface area (S_{BET}) of nanocatalysts was evaluated by N2 absorption and is detailed in Table 2. The increase of S_{BET}, which was caused by the increase of EG, decreased the nanoparticle size. The smaller nanoparticle size can be favorable for the higher ECSA and catalytic activity for alcohol electrochemical reaction.

3.2. Electrochemical Behaviors. In order to estimate the electrochemical surface area (ECSA), the CV measurement was performed in 1 M KOH at a scan rate of 50 mV/s (Figure 4). Commonly, the CV curve of Pd-based nanocatalysts in KOH media presents three regions: (i) a potential region lower than −0.7 V assigned to the oxidation of the absorbed and the absorption of hydrogen from the catalyst surface; (ii) a potential region from −0.7 to −0.2 V corresponding to the formation of palladium hydroxides; and (iii) a potential region from −0.2 to 0.4 V relating to the palladium oxidation. For the reverse scan, the reduction of palladium oxide (Pd–O layers) to Pd0 appeared around −0.35 V. [10, 27, 33] The ECSA can be estimated by PdO reduction peak in CVs according to the following equation [27]:

\[
\text{ECSA} = \frac{Q_{c} \times 10^{-4}}{(Q_{c} \times m)},
\]

where Q_c is the total charge (mC) determined by integrating current peak of palladium oxide reduction, Q_c is the charge needed for the reduction of PdO monolayer, and m is the Pd loading in mg. The ECSA was also determined by the Coulombic charge corresponding to the oxide reduction peak at a negative potential of −0.36 V (vs. Ag/AgCl) in Figure 4. The calculated ECSAs are detailed in Table 3. The PdVCo-15EG-20NaBH4 (282 cm²/mg with Q_c = 0.581 mC/cm²) and PdVCo-20EG-20NaBH4 (375 cm²/mg with Q_c = 0.741 mC/cm²) catalysts exhibit higher ECSAs than the EG-reduced catalyst.

The alcohol electrooxidation was performed by cyclic voltammetry on the nanocatalysts PdVCo in alkaline medium. The cyclic voltammograms are shown in Figures 5 and 6. Although mechanisms of electrooxidation of methanol and ethanol are different, their cyclic voltammograms exhibit the same motif with two well-defined peaks in each curve. [2] In the forward scan, the oxidation peak can be assigned to the oxidation of freshly chemisorbed species coming from methanol or ethanol adsorption. The oxidation peak in the reverse scan associated with the removal of
carbonaceous species (mostly in the form of linearly bonded Pd–C–O) is not completely oxidized in the forward scan compared to the oxidation of freshly chemisorbed species. [36–40] The magnitude of the peak current in the forward scan indicates the electrocatalytic activity of the electrocatalysts for alcohol oxidation. Furthermore, the ratio of the forward anodic peak current density ($I_f$) to the reverse anodic peak current density ($I_b$), $I_f/I_b$, is used to determine the catalyst’s tolerance to the intermediate carbonaceous species accumulated on the electrode surface. [41, 42] A higher ratio of $I_f/I_b$ promotes a better electrocatalytic activity and resistance to CO poisoning on the electrode surface. The potential and current density of the alcohol oxidation peak in the forward scan and $I_f/I_b$ ratio are detailed in Table 3.

Figure 5 displays the cyclic voltammetry on nanocatalysts PdVCo at a scan rate of 50 mV/s in the solution of 1 M CH$_3$OH + 1 M KOH. We observed that the current density became higher with the increase of reduction agent. Particularly, the highest current density (86.7 mA/cm$^2$) can be found in the mixture of reduction agent (sample PdVCo-20EG-20NaBH$_4$), which can be attributed to the fact that the NaBH$_4$ assisted in the EG reduction process with highly dispersed nanoparticles with a uniform size (4-5 nm) and the highest electrochemical surface area. [29] Moreover, the $I_f/I_b$ ratio varies among the PdVCo nanocatalysts. For EG reduction agent, the ratios are almost 2.5; for NaBH$_4$-assisted reduction, they increased significantly. The ratios for PdVCo-15EG-20NaBH$_4$ and PdVCo-20EG-20NaBH$_4$ are 2.82 and 2.98, respectively. On the other hand, the onset potential of PdVCo nanocatalysts looked more negative than those of sample Pd-20EG-20NaBH$_4$ (Figure S3 and Table S2). The more negative onset potential can suggest the enhancement of Co tolerance and increase of electrocatalytic performance as well as stability. [31, 33, 43] In sum, the data from CV measurements indicated that the nanocatalyst PdVCo-20EG-20NaBH$_4$ exhibited superior catalytic activity for methanol oxidation.

The CVs of the nanocatalysts in a solution of 1 M KOH + 1 M C$_2$H$_5$OH are shown in Figure 6. Two well-defined oxidation peaks can be observed in the five CV curves. The PdVCo-20EG-20NaBH$_4$ catalyst shows the best catalytic activity and poisoning tolerance among the five catalysts, as evidenced by its largest peak current and $i_1/i_2$ ratio. It is apparent that the size effect promotes the higher catalytic activity of nanocatalysts PdVCo for the alcohol electrooxidation.

In order to evaluate the long-term activity of the alcohol oxidation reaction on nanocatalysts PdVCo, we performed the CA measurements for 3600 s at −0.130 V (vs. Ag/AgCl) in solution of 1 M KOH + 1 M CH$_3$OH (shown in Figure 7)}
Figure 3: Continued.
Figure 3: TEM images and particle size distribution nanocatalysts: (a) PdVCo-15EG; (b) PdVCo-20EG; (c) PdVCo-15EG-20NaBH₄; and (d) PdVCo-20EG-20NaBH₄.

Table 2: Specific area and particle size distribution of nano-PdVCo catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>S_{BET} (m²/g)</th>
<th>Particle size average (nm)</th>
<th>% of particle size larger than 6 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>PdVCo-15EG</td>
<td>69.6</td>
<td>6.76</td>
<td>56.8</td>
</tr>
<tr>
<td>PdVCo-20EG</td>
<td>73.6</td>
<td>6.72</td>
<td>54.1</td>
</tr>
<tr>
<td>PdVCo-15EG-20NaBH₄</td>
<td>73.4</td>
<td>6.10</td>
<td>31.7</td>
</tr>
<tr>
<td>PdVCo-20EG-20NaBH₄</td>
<td>75.2</td>
<td>6.14</td>
<td>33.2</td>
</tr>
</tbody>
</table>

Figure 4: CVs of nanocatalysts PdVCo in 1 M KOH at a scan rate of 50 mV/s.

Table 3: Electrochemical parameters from alcohol oxidation of nanocatalysts PdVCo.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ECSA (cm²/mg)</th>
<th>CH₃OH</th>
<th>CH₂OH</th>
<th>CH₃OH</th>
<th>CH₂OH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E (V.)</td>
<td>Iₜ (mA/cm²)</td>
<td>Iₒ (mA/cm²)</td>
<td>Iₜ/Iₒ</td>
<td>E (V.)</td>
</tr>
<tr>
<td>PdVCo-15EG</td>
<td>128</td>
<td>−0.130</td>
<td>60.0</td>
<td>25.5</td>
<td>2.35</td>
</tr>
<tr>
<td>PdVCo-20EG</td>
<td>137</td>
<td>−0.124</td>
<td>70.6</td>
<td>28.4</td>
<td>2.49</td>
</tr>
<tr>
<td>PdVCo-15EG-20NaBH₄</td>
<td>282</td>
<td>−0.125</td>
<td>81.8</td>
<td>29.0</td>
<td>2.82</td>
</tr>
<tr>
<td>PdVCo-20EG-20NaBH₄</td>
<td>375</td>
<td>−0.100</td>
<td>86.7</td>
<td>29.0</td>
<td>2.98</td>
</tr>
</tbody>
</table>
and at $-0.150\text{V (vs. Ag/AgCl)}$ in solution of $1\text{M KOH} + 1\text{M } \text{C}_2\text{H}_5\text{OH}$ (shown in Figure 8), respectively. In general, all CA curves present a gradual decline in current density that results from the poisoning of the electrocatalysts, such as the formation of oxides or hydroxides of Pd and other poisoning intermediates adsorbed on the electrocatalysts during alcohol electrooxidation. [44] It is clear that the current densities on the PdVCo-15EG-20NaBH$_4$ and PdVCo-20EG-20NaBH$_4$ catalysts are higher than those of all CA measurements.

In methanol solution, the current densities remain about 49 and 52 mA/cm$^2$ on PdVCo-15EG-20NaBH$_4$ and PdVCo-20EG-20NaBH$_4$, respectively, compared with the other catalysts. Likewise, in an ethanol solution, the PdVCo-20EG-20NaBH$_4$ catalyst exhibits excellent stability. The steady current densities are 8.9 and 11.5 mA/cm$^2$ on PdVCo-15EG and PdVCo-20EG catalysts, respectively, while the steady current on PdVCo-20EG-20NaBH$_4$ is about 21.9 mA/cm$^2$. PdVCo-20EG-20NaBH$_4$ possesses the highest activity in the steady-state region for the oxidation of methanol or ethanol.

4. Conclusion

The ternary-alloy nanocatalysts PdVCo were successfully prepared by EG reduction, and the atoms V and Co were incorporated into Pd lattice to form a single phase. Moreover, the NaBH$_4$ assisted not only in enhancing V-content and Co-content but also in slightly decreasing nanoparticle size, which led to a better electrocatalysis performance for alcohol oxidation. The PdVCo-20EG-20NaBH$_4$ exhibited superior catalytic activity and stability as compared to the
other synthesized samples with the steady current of 52 mA/cm² in methanol and 21.9 mA/cm² in ethanol.

Data Availability
The data used to support the findings of this study are included within the supplementary information files.

Conflicts of Interest
The authors declare that they have no conflicts of interest regarding the publication of this paper.

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Supplementary Materials
Figure S1: XRD patterns of nanocatalysts (a) PdVCo-15EG, (b) PdVCo-20EG, and (c) PdVCo-15EG-20NaBH4. Figure S2: TEM images and particle size distribution of sample PdVCo-20NaBH4. Figure S3. CVs of nanocatalysts Pd-20EG-S2: TEM images and particle size distribution of sample Pd-20EG-S2 (a) 1M KOH+1M CH3OH (b) PdVCo-20EG, and (c) PdVCo-15EG-20NaBH4. Figure S3. CVs of nanocatalysts Pd-20EG-20NaBH4 in a solution of (a) 1 M KOH + 1 M CH3OH (I/IP = 2.60) and (b) 1 M KOH + 1 M CH2OH (I/IP = 0.63). Table S1: Average crystallite size of nanocatalysts. Table S2. Onset potential (V vs. Ag/AgCl) of nanocatalysts in a solution of 1 M KOH + 1 M CH2OH and 1 M KOH + 1 M CH3OH. (Supplementary Materials)

References


