Bioethanol as a new sustainable fuel for anion exchange membrane fuel cells with carbon nanotube supported surface dealloyed PtCo nanocomposite anodes

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Abstract

In this account, we report a facile and environmentally friendly method for preparing surface dealloyed nanocomposite (SD-PtCo/CNT) as an active electrocatalyst towards the ethanol oxidation, and as a low-cost technique for the fabrication of direct bioethanol fuel cell using biomass-derived ethanol. The scanning transmission electron microscopy (STEM) images confirmed the dealloyed nanostructure surface of the as-prepared catalysts. The electrochemical tests indicated that the SD-PtCo/CNT nanocomposites had higher electrocatalytic activities and excellent durabilities toward the ethanol electrooxidation. The enhanced performance resulted from the superior distribution of the bimetallic PtCo catalyst nanoparticles and the dealloyed surface structure. Moreover, the anion membrane-based direct bioethanol fuel cells assembled from this nanocomposites as anodes demonstrated a superior output performance of 88.6 mW cm⁻². This value was enhanced to 3.2-folds of that acquired on the commercial Pt/C. These findings suggested that the fabricated direct bioethanol fuel cells had substantial performance and low cost, and thus could be potential for future applications.

Keywords:
Fuel cell
Bioethanol
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Nanocomposite

1. Introduction

As a prospective application to electric vehicles and portable devices, direct alcohol fuel cells (DAFCs) have advantages in many aspects such as cheap, renewable, extensive sources and other features. [1–3] The direct methanol fuel cells have made a significant contribution to the energy field, but methanol is known for its corrosive aspects and its high toxicity. In addition, because methanol is more volatile than heavier alcohols, when mixed with air it can easily form explosive mixtures. As a result, other fuel alternatives were investigated. [4] and ethanol is the most interesting substitute as it has a similar electrochemical activity as methanol under certain conditions. Furthermore, ethanol has a number of advantages over methanol, such as low toxicity and high hydrogen content [5]. Ethanol can also be produced using a larger range of sources, including agricultural by-products based-biomass through fermentation processes [5]. More importantly, ethanol can be derived from plants, which also can exhaust carbon dioxide through photosynthesis during the process of energy conversion.
yielding zero total carbon dioxide emission [5]. Therefore, ethanol is a promising carbon neutral fuel resource.

Tremendous efforts have been devoted to direct ethanol fuel cells (DEFCs) due to their great significance in contributing to solving the energy shortage and long-term environment protection. Meanwhile, utilization of biomass for biofuel production has created exceptional opportunities dealing with the increasing demand and escalating prices of fossil fuel. Biofuel is effective and sustainable renewable resources, mainly because of its contribution to reducing the emission of CO₂ and other harmful gases. Direct bioethanol fuel cells are eco-friendly with prospective clean energy conversion.

The major obstruction in developing DEFCs deals with the slow anodic reaction kinetics either in alkaline or acidic environments. This mainly is caused by the entire oxidation to CO₂, involving the split of carbon-carbon bonds and releasing 12 electron per ethanol molecule. This process is difficult to achieve at room temperature [6]. The introduction of anion exchange membranes (AEMs) can accelerate the anodic reaction kinetics with many other significant advantages over the traditional proton exchange membrane fuel cells (PEMFCs), including: i) enhanced catalyst stability with negligible electro-kinetic performance losses, ii) reduced corrosion problems associated with the acid electrolyte, iii) use of low-cost metal current collectors, iv) prevention of formed precipitates based on carbonate mobile cations, v) reduced alcohol fuel crossover, and vi) improvement in eliminating electrolyte leakages.

Platinum (Pt) is the most suitable metal electrocatalyst capable of shearing the carbon-carbon bond of ethanol with considerably low temperatures [7]. However, Pt monometallic catalyst usually lacks from long-term stability as it is easily poisoned with formed intermediates like CO produced in the process of incomplete oxidation of alcoholic. CO species is easy to be absorbed onto the surface of the Pt and occupies active sites on the surface, and thus leads to platinum catalyst poisoning and slow reaction kinetics [8]. A second metal (such as Co, Ni, Sn, Ag) was added to platinum to be alloyed is to alleviate poisoning which is mainly ascribed to the bifunctional mechanism and ligand effect [9–12]. Pt-Ru alloy is by far the most efficient bimetallic catalyst, but Ru dissolution has been unable to solve [13–15]. Hence, in order to put the direct ethanol fuel cells into practical applications, one of the effective means is to develop new Pt-based bimetallic catalysts to solve above issues as well as improving the utilization of platinum.

A number of previously published studies employed in situ voltammetry methods for the preparation of surface dealloyed metal catalysts tested for oxygen reduction reaction (ORR) in PEMFC [16–19]. However, this method was found tedious to some extent and not suitable for large-scale production [20].

In this study, we presented a simpler ex-situ method to prepare surface dealloyed nanocomposite materials. These dealloyed composites have been known for their potential in accelerating the electro-oxidation of glyceral and enhancing alkaline direct crude glycerol fuel cell performance [21]. Here, we used low-cost biomass-derived ethanol as an alternative fuel for the fabrication of alkaline direct bioethanol fuel cells, expecting that the surface dealloyed composite would exhibit superior catalytic properties.

2. Experimental

2.1. Chemicals

Sodium borohydride (NaBH₄, 99%) was purchased from Thermo Fisher Scientific. Ethanol (extra pure, 99%) and potassium hydroxide (pellets, 85%) were bought from Acros. Multiwalled carbon nanotube (MWCNT, 10–20 nm outer diameter, 0.5–2 µm length), chloroplatinic (IV) acid hydrate (H₂PtCl₆·6H₂O, ≥ 37.5% Pt) and cobalt (II) chloride hexahydrate (CoCl₂·6H₂O, 98%) were purchased from Sigma-Aldrich. Polytetrafluoroethylene aqueous solution (PTFE, 60%) and Nafion solution (5 wt%) were obtained from Shanghai Hesen Inc. Bioethanol was provided by Jiangsu Lianhai biological technology Inc.

2.2. Preparation of catalysts

Pt/CNT and PtCo/CNT were synthesized using the liquid-phase reduction method. For example, PtCo/CNT was typically prepared by first dispersing the corresponding metal salts H₂PtCl₆·6H₂O and CoCl₂·6H₂O with the supporting carbon nanotube (CNT) in ethanol. Then the mixture of sodium borohydride with ethanol, as a reductive agent, was added into the precursor solution, for PtCo NPs depositing on CNT. As the complete reduction was finished, the mixture was then transferred to be centrifuged with a low-speed revolving device followed by washing with prorate water and ethanol. The concentrated liquor was vacuum dried overnight under 50 °C. The resulting product was PtCo/CNT catalyst. As a control, Pt/CNT was synthesized using only H₂PtCl₆·6H₂O as precursor under the same condition.

SD-PtCo/CNT was acquired by subsequent surface dealloying treatment. The as-obtained PtCo/CNT (100 mg) was ultrasonically dispersed into ethanol (200 mL). Then 0.5 M hydrochloric acid (400 mL) ethanol solution was joined to proceed the surface dealloying treatment. After being completely dealloyed, the mixture was centrifuged with a low-speed revolving device followed by washing with 200 mL ethanol. The concentrated liquor was vacuum dried overnight as well under 50 °C and the final SD-PtCo/CNT catalyst was obtained.

2.3. Characterization

The structure and morphology of the as-prepared catalysts were observed by transmission electron microscopy (TEM, JEM 2100F) inductively coupled high angle annular dark field scanning transmission electron microscopy (HAADF-STEM, JEM 2100F). Both TEM and STEM were operated at a voltage of 200 kV. X-ray diffraction (XRD) patterns were collected by a Rigaku Ultima IV diffractometer using Cu Kα radiation (λ = 1.5406 Å) with a filament current of 40 mA and a tube voltage of 40 kV. X-ray photoelectron spectroscopy (XPS) was conducted on Physical Electronics 5400 ESCA. To compensate for charging effects, all the spectra were referenced to C (1s) at 284.5 eV. A plasma atomic emission spectrometry (ICP-AES) was used to identify the elemental composition of the catalysts.

2.4. Electrochemical measurements

All the electrochemical measurements were carried out in a water jacket integrated glass cell at room temperature using a three-electrode system with glassy carbon electrode (GCE) as working electrode, Pt wire as counter electrode, and mercuric oxide electrode (Hg/HgO, MMO for short) as reference electrode controlled by a CHI 760 electrochemistry workstation (Shanghai Chenhua Instruments, Inc.). For the preparation of catalyst ink, 1 mg catalyst was dispersed in 985 µL isopropyl alcohol by ultrasonic-treatment. In order to prevent the catalyst loss from the deposited films, Nafion solution (5%, 15 µL) was added to the dispersion. After obtaining a stable dispersion, a volume of 5 µL was applied to the clean glassy carbon electrode surface followed by drying at room temperature. The catalyst loading was determined as 20 µg cm⁻².

For the electrochemical measurements, the electrolyte solution was always kept under 99.999% N₂ flow during the whole experi-
mental process. An aqueous solution of 2.0 M KOH containing 1.0 M high purity C₂H₂OH served as the supporting electrolyte for the cyclic voltammetry tests (CV, scan rate of 50 mV s⁻¹), linear scanning voltammetry (LSV, scan rate of 1 mV s⁻¹), and chronamperometry (maintain a constant potential of −0.5 V vs MMO). For the control experiments, CV measurements were also performed under N₂-saturated 2.0 M KOH aqueous solution. All potentials were given relative to the MMO.

2.5. Fabrication and testing of fuel cells

The fuel cell tests were performed using an Arbin BT2000 equipment (Arbin Instruments, USA) combined with temperature control system, and the fixture with a 6.25 cm² geometric area was manufactured by Jiansu Yundian Co. The membrane electrode assembly was performed according to the CCM (catalyst coated on the membrane) technique. For anode based electrodes, the as-prepared anode catalysts were first scattered in 1-propanol and then mixed with diluted polytetrafluoroethylene solution (catalyst: PTFE = 9:1 mass ratio), which was subsequently sprayed on a carbon cloth with an MPL (W1S005, Taiwan Co Tech.). The anode catalyst loading was determined as 0.5 mg Pt cm⁻². The cathode electrode was prepared by dispersing commercial 20 wt% Pt/C catalyst with AS-4 ionomer at the catalyst: ionomer mass ratio of 7:3 in 1-propanol. The mixture was then directly sprayed onto an anion exchange membrane (AS01 Tokuyama, 10 μm). The cathode catalyst loading was controlled at 1.0 mg Pt cm⁻².

The membrane coated catalysts were then sandwiched between a carbon cloth anode and carbon paper cathode layer to construct an MEA (Short for Membrane Electrode Assembly). During the tests of the cell with bioethanol and pure oxygen as fuels, the MEA was made to fit the technical fixture with graphite and polar plates to evaluate its performance. After full activation of the cell, the polarization behaviors were measured and potential-current curves were recorded. Specially, the internal resistance of the cell was synchronously monitored.

3. Results and discussion

3.1. Structural characterization of catalysts

In this study, Pt-based bimetallic catalyst and PtCo nanoparticles with surface dealloyed nanostructure loaded on multiwalled carbon nanotubes were prepared using a facile route. Fig. 1 shows the schematic illustration of the preparation for this active catalyst with surface dealloyed nanostructure. As it is shown, the active SD-PtCo/CNT catalyst was prepared via liquid-phase reduction following by surface dealloyed treatment. Compared to the previous in situ voltammetry method, the proposed procedure is simpler and requires no thermal treatment or hazardous surfactant.

The revolved reactions as follows:

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2\text{PtCl}_6^{2-} + 6\text{BH}_4^- + 4\text{H}_2\text{O} \rightarrow 2\text{Pt} + 6\text{B(OH)}_4^- + 8\text{H}^+ + 12\text{Cl}^- \\
\text{Co}^{2+} + 6\text{BH}_4^- + 4\text{H}_2\text{O} \rightarrow \text{Co} + 6\text{B(OH)}_4^- + 8\text{H}^+ \\
\text{Co} + 2\text{H}^+ \rightarrow \text{Co}^{2+} + \text{H}_2 \uparrow
\]

TEM and HRTEM were used to evaluate the size and elemental composition of the as-prepared SD-PtCo/CNT, and the resulting images taken at a different region of the sample surface using various magnifications are shown in Fig. 2(a–d). It can be seen that the PtCo nanoparticles had spherical shape with monodisperse morphology on the carbon nanotubes of about 2.3 nm in diameters (Fig. 2(a–c)). The lattice spacing of 0.135 nm and 0.189 nm illustrated in Fig. 2(d) were assigned to the (220) and (200) facets of Pt, which were 0.004 nm and 0.008 nm smaller than that of Pt/C. The latter revealed the existence of lattice strain. Fig. 2(e) depicts the X-ray diffraction patterns of the as-prepared SD-PtCo/CNT. The comparison of PtCo/CNT, Pt/CNT and commercial Pt/C revealed that the prepared metal particles had face-centered cubic (FCC) structures. Also, a peak shift in PtCo/CNT could obviously be observed when compared with Pt/C and Pt/CNT, demonstrating that PtCo effectively underwent alloying process. This further confirmed the existence of lattice strain. On the other hand, comparison of PtCo/CNT with SD-PtCo/CNT depicted no peak shift. These findings suggested that the present dealloying method did not only generate particles to form rough surface, but also maintained the lattice-strained Pt skeleton structure. According to Debye-Scherrer formula, the mean crystal size of the metal particles in Pt/C (J-M), Pt/CNT, PtCo/CNT and SD-PtCo/CNT catalysts were estimated as 1.9 nm, 2.9 nm, 2.1 nm and 2.2 nm, respectively. The corresponding lattice constants of these catalysts were calculated to be 3.944 Å, 3.918 Å, 3.834 Å and 3.808 Å, respectively.

STEM coupled with EDS was utilized to explore the changes in the composition of Pt and Co in both surface and core of the as-prepared PtCo nanoparticles. Fig. 3(a) shows the STEM image, as well as the corresponding elemental mapping and EDS line scan of a single PtCo/CNT particle. The STEM image of PtCo/CNT clearly depicted that PtCo NPs were tightly anchored on the carbon nanotubes. The corresponding elemental mapping of PtCo/CNT displayed Co atoms gathered around Pt atoms (top right corner of Fig. 3(a)). The line-profile analysis combined with the origin arrow line in Fig. 3(a) was conducted to further analyze the structure of PtCo/CNT nanoparticles. The signals resulting from Pt–L and Co–K are displayed in the lower right corner of Fig. 3(a). The scans across the particle indicated that Pt and Co signals had similar trends of which the highest strengths were observed in the center and lowest edges, where Pt atoms appeared with Co atoms whether at the center or edges of the particles cross-sections, implying that PtCo were well alloyed. By comparison, Fig. 3(b) shows the STEM image with the corresponding elemental mapping and EDS line scan induced from one single SD-PtCo/CNT particle. As can be observed, Co atoms were still present within the area of Pt atoms but with decreased quantities, suggesting that PtCo nanoparticles were still alloyed, but some Co atoms were removed by dealloying. This was observed by STEM and the corresponding elemental mapping shown in Fig. 3(b).

In the corresponding line-profile analysis of SD-PtCo/CNT, the Pt–L and Co–K signals displayed different shapes, demonstrating that distribution of Pt and Co were obviously non-uniform as shown in the PtCo/CNT cross-section. The Pt displayed strong peaks at the center and edges, whereas Co peaks appeared only strong at the center. From the overlapped profiles, it can be noticed that the Pt-strong peaks occurred at the position where the Co peaks were weak. This mismatching in peaks further demonstrated the non-uniformity distribution of Pt and Co atoms on the particles surfaces. The distribution of Pt and Co matched very well the STEM profile and the corresponding elemental mapping, where high contrast regions were roughly located in the middle region between the center and edges of the particle, corresponding to high-intensity peaks at same positions in the line-scan profile of Pt. The latter was characteristic of the porous surface structure of SD-PtCo/CNT nanoparticle, confirming the direct surface dealloying effect.

The EDS results and ICP-AES tests could also manifest the surface Co atoms have been removed successfully. From the HAADF-STEM area scanning mapping and element distribution results of PtCo/CNT and SD-PtCo/CNT (See Figs. S1 and S2), we can infer the surface dealloyed treatment is successfully revealed by the decreasing of Co atomic contents after dealloying treatment. ICP-AES results give that the specific Pt mass ration of PtCo/CNT and SD-PtCo/CNT are 19.6% and 19.5%, respectively. The values are basically in agreement with the Pt precursors demonstrating
the fully reduction. The corresponding atomic ratio Pt:Co were recorded as 54:48 and 69:32, respectively, suggesting the removal of Co atoms at the catalyst surface by the dealloying treatment.

XPS was employed to analyze the surface composition and the oxidation states of the metals on PtCo catalyst surface, and the resulting XPS spectra of PtCo/CNT and SD-PtCo/CNT are gathered, respectively, in Fig. 4(a,b) and Fig. 4(c,d). All Pt-containing samples showed doublets with high energy (Pt4f7/2) and low energy bands (Pt4f5/2) in the Pt4f spectra, indicating the existence of metallic state Pt (Fig. S3 corresponding XPS spectra of Pt/CNT). After proper deconvolution of the spectra, it was found that the peaks at 70.9 eV (Pt 4f7/2), 74.25 eV (Pt 4f5/2), 72.3 eV (Pt 4f7/2) and 75.65 eV (Pt 4f5/2) were assigned to Pt (0) and Pt (II) species. The peaks at 781.7 eV (Co 2p3/2), 796.5 eV (Co 2p1/2), 785.2 eV (Co 2p3/2) and 797.7 eV (Co 2p1/2) corresponded to Co(0) and Co(II) species [22]. The two low-intensity couple peaks in Fig. 4(a,b) originated from the precursors, where the values were consistent with PtCo bimetallic compounds [23]. The change of Co2p spectra illustrated the differences of surface composition between PtCo/CNT and SD-PtCo/CNT. Based on the peak intensity, Co (0) and Pt (0) were found to be the predominant species, revealing that PtCl62− and Co2+ were fully consumed during the synthesis procedure. However, the quantity of Co (II) obviously decreased after the dealloying treatment. Moreover, the atomic concentrations obtained from XPS tests were estimated to (0.85% Pt, 0.78% Co) and (1.01% Pt, 0.61% Co) in PtCo/CNT and SD-PtCo/CNT, respectively. The decline in Co contents after the dealloying treatment also suggested variation in surface composition between the SD-PtCo/CNT and PtCo/CNT catalysts.

3.2. Electrocatalytic analysis of half-cell

Electrochemical measurements were used to clarify the intrinsic catalytic properties of the catalysts towards the ethanol electrooxidation. The electrocatalytic properties closely depend on the electrochemically active surface area (ECSA), normally evaluated by the hydrogen adsorption–desorption peaks of the cyclic voltammograms (CVs) [24,25]. Fig. 5(a) shows the CVs of the as-prepared SD-PtCo/CNT, PtCo/CNT and Pt/CNT in comparison with the commercial Pt/C catalyst. It is well known that higher distribution yields larger ECSA and subsequently leads to elevated electrocatalytic activities [26] As shown in Fig. 5(a), the SD-PtCo/CNT catalysts bearing surface dealloyed nanostructure showed the largest ECSA values, which was mostly ascribed to the highly distributed Pt active NPs and carrier effect from CNT (Fig. S4).

The electrocatalytic oxidation of ethanol using the commercial Pt/C in comparison with the as-prepared catalysts Pt/CNT, PtCo/CNT and SD-PtCo/CNT in 2.0 M KOH aqueous solution containing 1.0 M high purity ethanol at a scan rate of 50 mV s−1, is depicted in Fig. 5(b). It was found that all the voltammometric waves of the catalysts are typical features of the ethanol electrooxidation in alkaline media and are consistent with the literature reports. The peak current densities during the forward scan are used to evaluate the electrocatalytic activities of these catalysts towards the ethanol electrooxidation. The peak current density in the forward scan of SD-PtCo/CNT catalyst was estimated to 0.82 mA µg−1, which was 3.9-, 1.2- and 4.6-folds higher than values obtained with PtCo/CNT (0.21 mA µg−1), Pt/CNT (0.068 mA µg−1) and Pt/C (0.18 mA µg−1) catalysts, respectively. The peak in the reverse scan is ascribed to the removal of carbonaceous species that are not completely oxidized on the forward scan. Compared the reverse peak density of different catalysts in Fig. 5(b), it could be found that it is easiest to the SD-PtCo/CNT catalysts to remove the carbonaceous species resulting in high electrocatalytic activity.

The combined LSV results at scan rate of 1 mV s−1 in Fig. 5(c) revealed that SD-PtCo/CNT had more negative onset potential of ethanol oxidation than PtCo/CNT, Pt/CNT, and Pt/C catalysts. In particular, the onset potential for SD-PtCo/CNT was recorded at about −0.70 V (vs. Hg/HgO), whereas those of PtCo/CNT, Pt/CNT and commercial Pt/C catalysts were located at −0.60 V, −0.59 V and −0.58 V (vs. Hg/HgO), respectively. The lower onset potential indicated that the ethanol oxidation was easier to proceed using SD-PtCo/CNT having a surface dealloyed nanostructure when compared with the other catalysts, demonstrating its superior electrocatalytic activity towards the ethanol electrooxidation [27,28].

Meanwhile the onset potential, peak current density, mass activity and specific activity at −0.5 V (vs. Hg/HgO) shown in LSV curves in Fig. 5(c) indicate clearly that the catalyst activity toward ethanol oxidation is SD-PtCo/CNT > Pt/CNT > PtCo/CNT > Pt/C, which is consistent with results of in half cell fast CV scan. For Pt/CNT, the improvement of the catalytic activity is mainly ascribed to high dispersion result from the CNT support and much

Fig. 1. Schematic representation of the process used to prepare the surface of dealloyed catalyst.
more active Pt atoms exposed on the surface of catalyst [29]. As for PtCo/CNT, roughly half of surface active positions were occupied with Co atoms with relatively lower activity as a result of lower activity, but still higher as compared with Pt/C illustrating the effect of carrier CNT. As to SD-PtCo/CNT, the active positions on the surface occupied by Co atoms were exposed through alloying treatment as well as increasing its roughness resulting in further enlarged ECSA while specific activity is improved by d-band center shift owing to compressed lattice and optimized electronic properties tuned by the sub-layer transitional metal atoms, resulting in much higher mass activity than that both Pt/CNT and Pt/C.

The chronoamperometry (CA) at constant potential performed at −0.5 V (vs. Hg/HgO) in 2.0 M KOH aqueous solution containing 1.0 M high purity ethanol evaluated the durability of these catalysts (Fig. 5(d)). The resting current density after long run testing of SD-PtCo/CNT catalyst was recorded as 24.2 mA µg⁻¹, which was 4.2-folds higher than that of commercial Pt/C catalysts (5.80 mA µg⁻¹). Continuous measurements of SD-PtCo/CNT catalysts for 20,000 s showed that 78% of the initial current was lost with a drop of 50% in the first 2000 s, whereas the current loss of Pt/C reached nearly 100%. This demonstrated the excellent durability of SD-PtCo/CNT catalyst for ethanol electrooxidation. Comparison of PtCo NPs with and without surface dealloying supported on CNT revealed that SD-PtCo/CNT had better stability over PtCo/CNT, implying the positive effect of the surface dealloying treatment. This was mainly attributed to the sub-layer of Co, which

**Fig. 2.** Typical TEM images depicted different regions (a,c) and at various magnifications (a–c) of the sample. Particle size histograms up-left inset in image (c) and HR-TEM image (d) of SD-PtCo/CNT. XRD patterns (e) of Pt/C (J-M), Pt/CNT, PtCo/CNT, and SD-PtCo/CNT (20 wt% Pt loading).
could adjust the electronic structure of Pt surface and prevent reaction intermediate of CO and thus improve the stability of the catalyst. Co atoms can down shift of the d-band center conducts to the formation of occupied antibonding orbitals and, as a consequence, conducts to a weak Pt-OH and/or Pt-O/C0 adsorption strength. In particular, it lowers the adsorption strength of the adsorbed oxygenated species which could remove the generated CO by oxidation resulting in preventing the position of the catalysts [30]. It is worth noting that the CNT loading monometallic Pt NPs in Pt/CNT had a high ECSA and activity when compared with the commercial Pt/C, but obviously was advantageous in terms of stability as very little current attenuation was observed after 20,000 s of continuous polarization. This fully demonstrated the advantages of CNT as carriers.

3.3. Electrocatalytic analysis in single cell

The combination of the electrochemical test results with those from the structural characterization confirmed that the SD-PtCo/CNT catalyst with surface dealloyed nanostructure possessed high intrinsic catalytic activity and excellent durability. The improvement in the catalytic activity was mainly caused by several reasons. First, when compared with traditional monometallic or bimetallic NPs, SD-PtCo/CNT with surface dealloyed nanostructure showed larger surface roughness of the nanoparticles, contributing to superior electrochemical active area. This, in turn, subsequently improved its catalytic activity. Additionally, Co atoms present on the sub-layer may remove intermediates issued from EOR, such as CO, and hence improve the stability of the catalyst by releasing more Pt active sites. Second, SD-PtCo/CNT catalyst with surface dealloyed nanostructure had excellent electronic structure induced by the optimized electronic structure of Pt shell tuned by sub-layer Co atoms. Third, multi-wall CNT as a carrier provided a highly dispersed surface of the catalyst and good electronic transmission, while the multi-wall nanostructure of CNT may anchor nanoparticles and prevent their aggregation.

For practical applications, the evaluation of fabricated single cell towards EOR is essential. Meanwhile, in an attempt to use biomass-derived fuel, bioethanol was applied to fabricate an alkaline membrane direct bioethanol fuel cell using the as-prepared SD-PtCo/CNT, PtCo/CNT and Pt/CNT as anodes and the commercial Pt/C as a control. The performance of the single cell for direct bioethanol fuel cell and the anodic reaction dynamics were then investigated. Fig. 6(a) shows the output performance of the direct
Fig. 4. XPS spectra of Pt 4f and Co 2p of the as prepared PtCo/CNT (a,c) and SD-PtCo/CNT (c,d) catalysts.

Fig. 5. (a) CVs in N₂ purged 2.0 M KOH and (b) CVs, (c) LSVs, (d) CAs in N₂ purged 2.0 M KOH with 1.0 M ethanol of Pt/C, Pt/CNT, PtCo/CNT and SD-PtCo/CNT catalysts at room temperature.
bioethanol fuel cell under 25, 60 and 80 °C. As temperature increased, cell voltage improved, especially peak power density. This could be explained by the elevated temperatures which promoted the reaction kinetics of bioethanol electrooxidation. The optimal temperature to achieve the highest output performance in terms of cell voltage and power density was recorded as 80 °C. The cell voltages of AEM-based direct bioethanol fuel cell based on SD-PtCo/CNT anode operated at 25 °C, 60 °C and 80 °C were recorded as 0.72 V, 0.73 V and 0.74 V, with the respective peak power densities of 68.5 mW cm$^{-2}$, 78.8 mW cm$^{-2}$ and 88.6 mW cm$^{-2}$.

Fig. 6(b) illustrates the performance of the constructed direct bioethanol fuel cell with different anode catalysts under the optimized conditions. The cell voltages were recorded around 0.75 V for SD-Pt-Co/CNT, PtCo/CNT and Pt/CNT anode catalysts, while that of the commercial Pt/C catalyst was 0.79 V. This suggested differences in the dynamics. Due to the robust EOR electrocatalytic activity and structural advantage, AEM-based direct bioethanol fuel cell with SD-Pt-Co/CNT anode catalyst yielded the highest peak power density when compared to the other catalysts. In particular, the peak power density of direct bioethanol/O$_2$ AEMFC with SD-Pt-Co/CNT anode catalyst was estimated as 88.60 mW cm$^{-2}$, which was 47.6%, 121.5% and 195.3% higher than that of PtCo/CNT, Pt/CNT and commercial Pt/C.

It is worth mentioning that the highest mass performance of direct bioethanol/O$_2$ AEMFC was 0.117 W mg$^{-1}$ precious metals per MEA for extremely low Pt loading (only 0.5 mg cm$^{-2}$ for SD-Pt-Co/CNT anode). Therefore, the robust observed catalytic activity and stability in both half-cell and single fuel cell tests strongly suggested that SD-Pt-Co/CNT could be a promising anodic catalyst for direct bioethanol alkaline fuel cells with high performance and low cost. To the best of our knowledge, the resulting high output performance of AEM-DEFC running on bioethanol as fuel and surface dealloyed PtCo nanocomposite as anodic catalyst outperformed that of commercial Pt/C under the same conditions. Also, these data were comparable to those obtained with pure methanol and ethanol ranked into the high performance direct biomass-derived fuel cells [31–35].

4. Conclusions

We have developed a highly active PtCo NPs with surface dealloyed nanostructures supported on carbon nanotubes for efficient ethanol oxidation. The surface dealloyed nanostructure of PtCo catalyst was demonstrated by STEM images and other relevant tests. Based on electrochemical measurements, SD-PtCo/CNT exhibited superior electrocatalytic activity and excellent durability. The improvement in the catalytic property was mainly induced from the high dispersion, good electronic structure, and excellent performance of the carrier. It was also demonstrated for the first time that bioethanol could directly be employed as an efficient fuel for DAFCs, a promising new and low-cost method. Built on the acceleration of surface dealloyed catalysts towards EOR, CNT loading PtCo with surface dealloyed nanostructure were explored as anode catalysts for the direct bioethanol fuel cell. The results suggested very high single cell performance of 88.60 mW cm$^{-2}$ at low Pt loading of 0.5 mg Pt cm$^{-2}$ under 80 °C temperature and ambient pressure. These data outperformed those obtained with commercial Pt/C under the same conditions, while were comparable to pure methanol or ethanol, ranging from high performance direct biomass-derived fuel cells.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2017.02.111.

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