The improvement of methanol oxidation using nano-electrocatalysts

Zahra Yavari, Meissam Noroozifar and Mozhgan Khorasani-Motlagh

Department of Chemistry, University of Sistan and Baluchestan, Zahedan, Iran

ABSTRACT
In this study, a nano-scale perovskite LaMnO$_3$ (LaMnO$_3$NPs) was synthesised by a rapid microwave-assisted co-precipitation method and characterised by X-ray powder diffraction, Fourier transform infrared, scanning electron microscopy and energy dispersive X-ray techniques. A modified glassy carbon electrode with Pt nanoparticles (PtNPs), functionalised multi-walled carbon nanotubes (CNTs) and LaMnO$_3$NPs as multifunctional catalyst was prepared and furthermore, its catalytic activity toward methanol oxidation was investigated. Based on the electrochemical studies, the PtNPs–CNTs–LaMnO$_3$NPs nanocomposite showed considerable activity for methanol oxidation in comparison to PtNPs, PtNPs–CNTs and PtNPs–LaMnO$_3$NPs. The results displayed the adding of CNTs and LaMnO$_3$NPs into PtNPs catalyst and the use of a more porous matrix of chitosan can improve the anode performance for methanol oxidation. The transition metals presence at catalyst structure caused to catalyse the methanol dehydrogenation. The decreasing the poisoning rate of the PtNPs with intermediates and by-products of anodic reaction was observed due to the bi-functional effect electrical and oxygen ion conductive perovskite. Direct methanol fuel cell (DMFC) was designed, assembled and tested with suggested PtNPs–CNTs–LaMnO$_3$NPs nanocomposites as anodic catalyst at variety conditions. The effect of experimental factors such as temperature and methanol concentration on DMFC performances was investigated and optimised.

Keywords
- direct methanol fuel cell;
- perovskite;
- nano-electrocatalysis;
- cyclic voltammetry;
- methanol catalytic oxidation

1. Introduction
Direct methanol fuel cells (DMFCs) are extensively considered as clean energy and potentially greatly efficient systems. In spite of significant advances in recent years, a number of

Highlights
- LaMnO$_3$ nanoparticles were synthesised and characterised.
- Dispersed Pt, Pt–LaMnO$_3$ and Pt–CNTs–LaMnO$_3$ in chitosan were prepared.
- Their catalytic activity toward methanol oxidation was investigated.
technical barriers still exist in the development of the anodic catalysts for methanol oxidation. To solve this barrier, an enormous effort has been devoted toward the catalysts development.[1,2] These catalysts have contained platinum and platinum-based alloys. They have shown the high activity for catalysis of methanol oxidation in acidic medium, but the platinum surface has been readily poisoned by the CO intermediates formed during this reaction.[3] Perovskite type complex oxides are favourable materials for application as exhaust gas sensors in automobiles,[4] membranes for separation processes and the catalytic materials in fuel cell. Among them lanthanum-transition metal perovskites (LaMO₃) have been studied widely.[5] The electrocatalytic activities of noble metals-based catalysts depend on some factors, the main factor being the supporting materials. Catalyst supports with high surface area are assigned to reduce metal loading while keeping the high activity of the catalyst. Special attention has been given to alternative carbon materials among multi-walled carbon nanotubes (MWCNTs) as anodic catalyst supports for DMFCs.[6] In previous studies, we perused electrocatalytic methanol oxidation on Pt-chitosan [7] and Pt-functionalised CNTs-chitosan [8] and described the addition of chitosan into noble metal containing catalysts can noticeably improve the catalyst performance for methanol oxidation. Chitosan has exhibited great advantages due to its non-toxicity and appropriate adhesion in nanocomposite. Polymers like chitosan are considered as a good host material for the catalytic nanoparticles such as noble metals and oxides.

In this study, diverse approaches for the improvement of an effective, low-cost, multifunctional anodic catalyst for direct methanol-based fuel cells followed. We investigated methanol electrocatalytic activity over a hybrid Pt catalyst consisting of LaMnO₃ nanocrystals and CNTs and presented detailed electrochemical results on the catalysts with different composition, and the individual role of each composition was proposed. In order to provide more effective reaction sites for the catalysis, LaMnO₃ catalysts were synthesised as nano-meter particles (LaMnO₃NPs). The activity of PtNPs in the presence of functionalised CNT and LaMnO₃NPs for methanol oxidation was evaluated by using a glassy carbon (GC) electrode. Here, based on the importance of multifunctional catalysts, incorporating effect of LaMnO₃NPs and CNTs to PtNPs catalyst for methanol oxidation has been studied. Multifunctional nanocatalysts, PtNPs, PtNPs—LaMnO₃NPs and PtNPs—CNT—LaMnO₃NPs dispersed in chitosan (CH) were successfully prepared and their catalytic activity toward methanol oxidation was compared with each other. The effect of experimental factors on the anodic current density and the potential of methanol oxidation were studied and the optimum conditions were suggested. Finally, the functions of PtNPs—CNTs—LaMnO₃NPs—CH nanocomposites were investigated in stack and assembled DMFC as anodic catalysts. The fuel cell polarisation curves were plotted for mentioned DMFC.

2. Experimental

2.1. Materials

The lanthanum chloride, manganese sulphate, H₂PtCl₆ aqueous solution, octanoic acid and NaBH₄ were purchased from Merck. One per cent of acetic acid (CH₃COOH) solution was prepared with doubly distilled water. A natural polymer, chitosan, ([2-amino-2-deoxy-(1-4)-β-D-glucopyranose]), with medium molecular weight of 400,000 Da was
purchased from Fluka. MWCNTs with nanotube diameters, outer diameter = 20–30 nm, wall thickness = 1–2 nm, length = 0.5–2 μm and purity >95% were purchased from Aldrich. All solutions were prepared by doubly distilled water. The carbon cloth-diffusion layer (CC-DL) and Nafton117 membrane were purchased from Asian Hydrogen New Science Company (H₂ Engine Company), manufacturing and development Isfahan science and technology town, Isfahan, Iran.

2.2. Instrumentation

Electrochemical measurements were carried out with a potentiostat/galvanostate SAMA500 Electroanalyser (SAMA Research Center, Iran) controlled by a personal computer. All electrochemical experiments were carried out in a conventional three-electrode cell. The working electrode substrate was GC electrode with 0.0314 cm² surface area. A platinum electrode and a saturated calomel electrode were used as the counter and reference electrodes, respectively. All potentials were measured with respect to this reference electrode. The electrolyte was a mixture of sulphuric acid and the corresponding alcohol with a known concentration. All experiments were performed at room temperature. X-ray powder diffraction (XRD) analysis was conducted on a Philips analytical PC-APD X-ray diffractometer with graphite monochromatic CuKα radiation (λ = 1.54056 Å) to verify the formation of products. The Fourier transform infrared (FT-IR) spectra of the samples were taken using a JASCO-460 FT-IR spectrometer. The surface morphology and the status of the sample were observed with scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis, which was equipped with an SEM instrument (SEM-Philips XL30). Transmission electron microscopy (TEM) image of produced nanocomposite was taken by a Philips CM120 transmission electron microscopy with 2.5 Å resolution. An air brush kit model MBD-116C was employed for spray nanocatalyst ink on CC-DL. An infrared dryer: Mega Max, MH-2000 TURBO model, AC 220–240 V, 800 W, 50/60Hz was used for preparing the catalyst layers on the electrode surface.

2.3. Preparation of LaMnO₃ nanocrystalline (LaMnO₃NPs)

Aqueous solutions of manganese sulphate 0.1 M (10 mL) and lanthanum chloride 0.1 M (10 mL) were prepared separately and mixed together in 1:1 molar ratio. Two millilitres of octanoic acid was added to the solution as a surfactant. The solution was stirred followed by adding NaOH (1.5 M) drop by drop to keep the pH at 7–8. After complete precipitation, the oily precipitate was transferred to the microwave infrared irradiation (900 W/180 °C) for 6 min. After cooling at room temperature, the resulting products were centrifuged for 15 min at 403 RCF and washed with distilled water and ethanol several times to remove the excess surfactant from the solution. The product was calcinated at 800 °C for 5 h to let the product self-ignite and burn off the organic compound in the material.

2.4. Preparation of nanocomposites

A chitosan solution (2 mg mL⁻¹) in 1% acetic acid solution was prepared, due to the poor solubility of the polymer, the mixture was stirred to dissolve entirely and kept for 24 h,
and the solution was then filtrated to remove any impurity before use. Twenty-five micro-
liters of H\textsubscript{2}PtCl\textsubscript{6} aqueous solution (0.5 M) was mixed with a known amount of chitosan
solution using a rotary aperture (100 rpm) for 45 min. Functionalised CNTs were first
subjected to the oxidative pre-treatment by vigorously stirring in a mixture of concen-
trated sulphuric acid and nitric acid with the volumetric ratio of 3:1 at room temperature
for 24 h. This pre-treatment removes impurities and generates sufficient functional groups
on the surface of CNTs [9,10]. The treated CNTs were filtered by centrifugation (806
RCF) and washed with double distilled water until the pH of the filtrate reached 7. The
precipitate was dried at 90 °C for 7 h. Then, 1 mg of the functionalised CNTs was dis-
persed into the appropriate amount of CH solution with stirring, resulting in uniform carbon
ink. The prepared carbon ink was added to the Pt—CH mixture and stirred for
another 60 min. Then, 50 μl of freshly prepared aqueous solution of 2.5 M NaBH\textsubscript{4} was
added to the blend. It was kept stirring for 60 min to achieve complete reduction of Pt
nanoparticles (PtNPs).

\[
6\text{NaBH}_4 + \text{H}_2\text{PtCl}_6 \rightarrow \text{Pt} + 6\text{NaCl} + 3\text{B}_2\text{H}_6 + 4\text{H}_2 \tag{1}
\]

One milligram LaMnO\textsubscript{3}NPs was mixed with 0.5 mL CH solution using an ultrasonic bath
for 30 min. These materials were added to PtNPs—CNTs—CH mixture and mixed
together using the rotary aperture (100 rpm) for 90 min. The obtained nanocomposite
was denoted as PtNPs—CNTs—LaMnO\textsubscript{3}NPs—CH.

2.5. Electrode preparation

The GC electrode with 0.0314 cm\textsuperscript{2} surface area was polished with 0.05 μm alumina slurry
to a mirror finish surface and was then, rinsed with distilled water. It was subsequently
sonicated in a mixture of water:ethanol (9:1 v/v) for 3 min. The GC electrode was cleaned and
activated in an electrochemical cell containing 1 M H\textsubscript{2}SO\textsubscript{4} solution by using cyclic voltammetry (CV)
technique between −1.5 and +1.5 V at a scan rate of 100 mV s\textsuperscript{−1} until a stable cyclic voltammetric profile (∼15 times) was obtained. For electrode modification, 10 μL of PtNPs—CNTs—LaMnO\textsubscript{3}NPs—CH nanocomposite was spread by a pipette onto
the prepared GC electrode and was then put under infrared radiation for fast drying. Dur-
ing this period, the solvent evaporation led to the formation of a deposited catalyst layer
on the GC electrode surface. The catalyst film was fixed onto the GC substrate by chitosan
polymer. This modified GC electrode was denoted as GC/PtNPs—CNTs—LaM-
\textsubscript{nO\textsubscript{3}}NPs—CH. Similarly, the same method was used for the preparation of GC/PtNPs—
CH, GC/PtNPs—LaMnO\textsubscript{3}NPs—CH and GC/LaMnO\textsubscript{3}NPs—CH electrodes.

2.6. Fuel cell operation

The anode catalyst loading was (2 mg cm\textsuperscript{−2}) PtNPs — (1 mg cm\textsuperscript{−2}) LaMnO\textsubscript{3}NPs — (0.6
mg cm\textsuperscript{−2}) functionalised CNTs onto the CC-DL (PtNPs—LaMnO\textsubscript{3}NPs—CNTs/CC-DL),
whiles the active surface area of the single cell was 5 cm\textsuperscript{2}. This suspension were sprayed
onto CC-DL using the air brush kit. The CC-DL with prepared PtNPs—CH (4 mg.cm\textsuperscript{−2})
was used as cathode. The Nafion117 membrane was pretreated by successive dipping in
5% wt H\textsubscript{2}O\textsubscript{2} solution, doubly distilled water, 8% wt H\textsubscript{2}SO\textsubscript{4} solution and finally in doubly
distilled water again, at 80 °C and 30 min each step. The diffusion layers based on carbon cloths with prepared catalyst layers on the anode and the cathode sides and membrane in the middle were formed the single cell. The anode and cathode layers were hot-pressed onto both sides of a Nafion 117 membrane at 140 °C and 200 psi for 4 min. Finally, the membrane electrode assembly (MEA) was cooled down to room temperature and assembled in the single cell for performance evaluation. The flow rate of methanol as a fuel was controlled using a peristaltic pump. I–V curves were obtained galvanostatically with an electronic load, EL200P, Daegil and controlled via a personal computer.

3. Result and discussion

3.1. Characterisation of LaMnO$_3$NPs

The FT-IR spectra of octanoic acid (a), the product before calcination (b) and LaMnO$_3$NPs perovskite after calcination (c), in the frequency range from 4000 to 400 cm$^{-1}$, have been displayed in Figure 1(A). In Figure 1(A) (a), the 2500–3400 cm$^{-1}$ broad band is attributed to the O–H stretching vibration of octanoic acid. The absorptive peaks at 3004 and 2700–3000 cm$^{-1}$ are attributed to =C–H and the C–H aliphatic group, respectively, while the peak at 1711 cm$^{-1}$ is the typical band of the carbonyl group. The bands at 1465 and 1378 cm$^{-1}$ are associated with the bending of CH$_2$ and CH$_3$ bonds, respectively. The absorption peaks detected at 1285 and 938 cm$^{-1}$ were attributed to the stretching of C–O and out of plane bending of the O–H group, respectively. The peaks at 700–800 cm$^{-1}$ arose from out of plane bending of the =C–H group. For precursor, all

![Figure 1.](image-url) (A) FT-IR spectra of (a) octanoic acid, (b) the product before calcination and (c) the product after calcination, (B) XRD, (C) SEM and (D) EDX of LaMnO$_3$NPs.
infrared bands of octanoic acid are observed but shift to a lower wave number as seen in Figure 1(A) (b). The FT-IR spectrum of the final product (Figure 1(A) (c)) displays 2 strong absorptive bands at about 629 and 544 cm$^{-1}$ which corresponded to $\text{M}/\text{CO}_\text{O}$ stretching vibration and $\text{O}/\text{M}/\text{CO}_\text{O}$ bending vibration of LaMnO$_3$NPs.

Figure 1(B) shows the XRD pattern of perovskite. The XRD analysis only shows the corresponding pattern of the perovskite-type LaMnO$_3$ (JCPDS File no. 23-0484), which was crystallised in the hexagonal system with a main diffraction peak at $d = 2.75$ Å $((1 \ 1 \ 0)$ plane). The sharpening of the peaks was due to the enhanced crystallinity of the nanoparticles and any characteristic peaks of impurities were not detected at the XRD pattern. The broadening of the peaks shows that the particles were nano-size. The characteristic peaks of LaMnO$_3$NPs have been presented and can be seen in Table 1. The lattice parameters were considered by Equation (2) [11]:

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

while $d$ is the distance between crystalline planes with Miller indices $(h \ k \ l)$, $a$, $b$, and $c$ are the lattice parameters. The mean size of the LaMnO$_3$NPs ($D$) was estimated by XRD line broadening using the Debye–Scherrer equation [12]:

$$D = \frac{0.89 \times \lambda}{B \times \cos \theta}$$

where $\lambda$ is the wavelength of the X-ray radiation (1.54056 Å), $\theta$ is the Bragg angle and $B$ is the breadth of the observed diffraction line in its half intensity maximum. The mean crystallite size of the LaMnO$_3$NPs has been arranged in Table 1. To investigate the morphology and size of the particles, SEM was also used.

The SEM image of the particles is shown in Figure 1(C). The mean sphere-like particle size is approximately 72 nm. The SEM image shows that there are some small holes inside the product, which indicate that it can be used in catalysis. In the SEM image, the presence of holes showed perovskite as a porous material. This could lead to a suitable support for the PtNPs with dispersion improvement of PtNPs at composite due to having a higher surface area. It is clear that the surface area is an important parameter in heterogeneous catalysis. Also, holes in perovskite and CNT develop fuel storage for consumption on the catalyst surface. EDAX was performed for the samples (Figure 1(D)) and shows the presence of La and Mn as the only component elements.

| $2\theta$ (degree) | Size (nm) | $B$ (degree) | $h$ | $k$ | $l$ | Average size (nm) |
|-------------------|-----------|--------------|-----|-----|-----|------------------|
| 23.05             | 50.7      | 0.16         | 2   | 0   | 1   | 53.1             |
| 32.58             | 46.0      | 0.18         | 0   | 1   | 1   |                  |
| 32.89             | 59.2      | 0.14         | 4   | 0   | 1   |                  |
| 40.23             | 60.4      | 0.14         | 2   | 0   | 2   |                  |
| 46.88             | 54.1      | 0.16         | 4   | 0   | 2   |                  |
| 58.22             | 47.9      | 0.19         | 1   | 0   | 3   |                  |

**Table 1.** The calculation of average particle size of LaMnO$_3$NPs with Miller indices and using of XRD pattern.
3.2. Characterisation of GC/PtNPs–CNTs–LaMnO₃NPs–CH electrode

Figure 2(A) presents the TEM image of PtNPs–CNTs–LaMnO₃NPs–CH composite. It can be seen from Figure 2(A) that PtNPs with sizes of 10–15 nm are uniformly distributed and well attached to the CNTs, whereas after the modification of CNTs–PtNPs with LaMnO₃NPs nanoparticles no longer coat the CNTs but are distributed in the surrounding solution.

Electrochemical behaviour of the GC/PtNPs–CNTs–LaMnO₃NPs–CH was studied by CV in 1 M H₂SO₄ at a scan rate of 50 mV s⁻¹ with amount of platinum loading: 0.51 mg cm⁻². As seen in Figure 2(B), current peaks are appeared at −433 mV (c₁) and −371 mV (c₂) in the cathodic and at −420 mV (a₁) and −232 mV (a₂) in the anodic directions associated with the adsorption and desorption of hydrogen atoms on the PtNPs surface.

\[
Pt - H_{\text{ads}} \rightarrow Pt + H^{+} + e^{-}
\]  

Figure 2. (A) TEM image of PtNPs–CNTs–LaMnO₃NPs–CH and (B) cyclic voltammogram of GC/PtNPs–CNTs–LaMnO₃NPs–CH electrode in 1 M H₂SO₄ at 50 mV s⁻¹ scan rate with 0.51 mg cm⁻² Pt loading.
Commonly, as for Pt catalyst, the potential region of H adsorption and desorption was about $-0.2$ to $-0.1$ V vs. saturated calomel electrode (SCE) [7]. With incorporation LaMnO$_3$NPs, potentials were shifted toward the negative direction. The catalytic activity of LaMnO$_3$NPs tends to decrease in potential that of the corresponding single base metal oxides and their thermal stability also correlates with that of individual parent oxides. The oxygen over-stoichiometric LaMnO$_{3.48}$ more frequently reveals the highest activity. [5] The broad and weak anodic peak at 578 mV ($a_3$) and cathodic peak at 299 mV ($c_3$) were related to the formation and reduction of platinum oxides, respectively. [13] The consistent of Figure 2(B) cyclic voltammogram with the literature results confirms the PtNPs synthesis, properly. [14]

The electrochemical surface area (EAS) of PtNPs is an important factor for the determination of catalytic activity, especially for an oxidation reaction as a surface reaction. This parameter can be calculated by CV techniques. The voltammogram of H$_2$ adsorption/desorption was used to determine EAS amount of the GC/PtNPs—CNTs—LaMnO$_3$NPs—CH electrode (Figure 2(B)).

The columbic charge ($Q_H$) for hydrogen adsorption/desorption was employed for calculating the platinum EAS of the modified electrodes. The $Q_H$ value is considered as the mean value between the amounts of charge exchanged during the electrochemically adsorption and desorption of H$_2$ on PtNPs sites. [15] It was calculated by measuring the area under the peak at potential range of hydrogen adsorption/desorption ($-0.47$ to $-0.1$ V) on modified electrodes. The EAS amount for PtNPs was calculated electrochemically using $Q_H$ and Equation (5) [16]:

$$
EAS = \frac{Q_H}{0.21 \times L}
$$

where $L$ is the PtNPs loading (mg cm$^{-2}$) that was 0.51 mg cm$^{-2}$ for the modified electrodes and 0.21 is a parameter relating the charge to area. This represents the charge required for the oxidation of a H$_2$ adsorbed monolayer on Pt particles. Table 2 shows the calculated EAS on modified electrodes with similar PtNPs loading.

The EAS amounts were almost the same for GC/PtNPs—CH and GC/PtNPs—LaMnO$_3$NPs—CH electrodes. The perovskite presence at nanocomposite catalyst had a poor effect on hydrogen adsorption/desorption on catalyst surface. This negligible effect was attributed to Tejuca’s study. [17] He expressed that on oxides with cations more oxidised metal centres should be involved in hydrogen adsorption. During the forward scans on catalysts containing perovskite, the current density was raised along the entire investigated potential range that this caused higher EAS for GC/PtNPs—LaMnO$_3$NPs—CH electrode. [18] The electrochemical active surface area (ESA) amount for GC/PtNPs—CNTs—LaMnO$_3$NPs—CH electrode was higher than GC/PtNPs—CH and GC/PtNPs—LaMnO$_3$NPs—CH electrodes when compared per same PtNPs loading. This

### Table 2. The values of EAS and $D_{Pt}$ obtained from CV curves the modified electrodes in 1 M H$_2$SO$_4$ at 50 mV s$^{-1}$ with 0.51 mg cm$^{-2}$ Pt loading.

| Electrode | EAS (m$^2$ g$^{-1}$) | $D_{Pt}$ |
|-----------|----------------------|----------|
| GC/PtNPs—CH | 7.65                 | 0.010    |
| GC/PtNPs—LaMnO$_3$NPs—CH | 12.00              | 0.016    |
| GC/PtNPs—CNTs—LaMnO$_3$NPs—CH | 43.61              | 0.058    |
improvement in the electrocatalytic performance of the GC/PtNPs–CNTs–LaMnO3NPs–CH electrode was attributed to the presence of CNTs supports with unique structural and electrical properties that reduced resistances associated with charge transfer.[19] The unique electrical and structural properties of CNTs were the main parameter for the higher activity in this study. The high dispersion of the PtNPs on the CNTs supports was achieved through this mechanism: surface functional groups such as hydroxyl, carboxyl and carbonyl groups on the CNTs were effectively produced during the chemical oxidation treatment and they had assisted at the ion adsorption and metal deposition by serving as specific nucleation sites for PtNPs.[20] The PtNPs dispersion ($D_{Pt}$) was termed as the fraction of surface-active Pt atoms in all of Pt atoms can be achieved $[21]$:

$$D_{Pt} = \frac{EAS}{M_{Pt} \times (N_A \times 4\pi \times r_{Pt}^2)} \quad (6)$$

where $M_{Pt}$ is the relative Pt molecular weight (195.08 g mol$^{-1}$), $N_A$ is Avogadro number ($6.023 \times 10^{23}$) and $r_{Pt}$ is Pt atomic radius (0.139 nm). The $D_{Pt}$ values were calculated and reported for modified electrodes in Table 2. The PtNPs dispersion on the surface of modified electrodes was improved at CNTs presence. The high dispersion of PtNPs on the CNTs as support through the production of uniformly metal particles, in which the functionalised CNTs surface had allowed uniform adsorption of the PtNPs produced due to surface functional groups.[19]

### 3.3. Methanol oxidation on different modified electrodes

Figure 3 represents the cyclic voltammograms of methanol oxidation on different electrodes such as the GC, GC/CH, GC/LaMnO3NPs–CH, GC/PtNPs–CH, GC/PtNPs–LaMnO3NPs–CH and GC/PtNPs–CNTs–LaMnO3NPs–CH in 0.8 M methanol solution and 1 M H$_2$SO$_4$ at a scan rate of 50 mV s$^{-1}$. Based on Figure 3(a), GC and GC/CH electrodes do not show any peaks for the oxidation of methanol. It has been known that GC and GC/CH cannot have any electrocatalytic activity for methanol oxidation. The

![Figure 3. Cyclic voltammograms of methanol oxidation on (a) GC and GC/CH, (b) GC/LaMnO3NPs–CH, (c) GC/PtNPs–CH, (d) GC/PtNPs–LaMnO3NPs–CH and (e) GC/PtNPs–CNTs–LaMnO3NPs–CH electrodes in 1 M H$_2$SO$_4$ and 0.8 M methanol at scan rate of 50 mV s$^{-1}$.](image-url)
existence of the peak of methanol oxidation for GC/LaMnO3NPs—CH confirmed the catalytic activity of perovskite nanoparticles (Figure 3, curve b) but the positive potential peak ($E_p = 1.4$ V vs. SCE) was not suitable for quick start-up of fuel cell. As seen from Figure 3 curves c to e, 2 oxidation peaks are on the Pt-contained electrodes, which were associated to the oxidation of methanol ($J_f$) and the corresponding produced intermediates ($J_b$). Table 3 indicates the electrochemical data of the cyclic voltammograms on the GC/PtNPs—CH, GC/PtNPs—LaMnO3NPs—CH and GC/PtNPs—CNTs—LaMnO3NPs—CH electrodes for methanol oxidation. The amount of the onset potential for the anodic reaction is important in the DMFCs. The change in the onset potential relates to an improvement in the kinetic reaction.[22]

According to Table 3, the GC/PtNPs—CNTs—LaMnO3NPs—CH electrode has the value lowest of onset potential. It was concluded that the incorporation LaMnO3NPs and CNTs improve the kinetic reaction. The current density on GC/PtNPs—CNTs—LaMnO3NPs—CH electrode ($J_f = 43.84$ mA cm$^{-2}$) is comparable with the GC/PtNPs—CH and GC/PtNPs—LaMnO3NPs—CH electrodes ($J_f = 12.76$ and $25.12$ mA cm$^{-2}$, respectively) and also, others containing noble metals or perovskite electrodes at similar concentration of methanol as electro-active material [23,24]. These results explain that the PtNPs—CNTs—LaMnO3NPs—CH nanocomposite have superior activity for methanol oxidation in acidic media. The forward and reverse peak currents ratio is used to compare the activity of synthetic catalysts for the oxidation of methanol which is determined as $I_f/I_b$ in Table 3. This has been used to determine the tolerance of such catalysts to CO, an intermediate oxidation alcohol; with larger values regarded as a positive sign that the material synthesised is an excellent CO resistant catalyst.[25] The increase in $I_f/I_b$ ratio could be attributed to the removal of CO poisoning on the Pt surface by the surface oxygen of the nanoparticles of LaMnO3 perovskite that is in adjacency of metal particles.[24]

It is clear that both the synergistic effect between platinum nanoparticles and structure effects of the LaMnO3 enhanced the catalytic activity of the presented nanocomposite for methanol oxidation. The current density increasing of the methanol oxidation may be attributed to the removal of CO poisoning on the noble metal surface nanocatalyst. The lattice oxygen of perovskite in LaMnO3 oxide could be considered as active oxygen to remove the intermediates of methanol oxidation reaction. It is clear that the metals with the higher oxidation number have the more power for the oxidising of methanol. The oxidation number of manganese in the LaMnO3 perovskite was +2, while lanthanum has been presented in this compound with +3 oxidation number. The higher oxidation number of lanthanum facilitated the oxidation of methanol. The surface oxygen of the LaMnO3 nanoparticles in adjacency of metal particles removed the CO poisoning on the surface of the platinum nanoparticles.

The addition effect of functionalised CNTs to GC/PtNPs—LaMnO3NPs—CH electrode on the current density of methanol oxidation has been studied by chronomperometry

### Table 3. Electrochemical data for methanol oxidation on GC/PtNPs—CH, GC/PtNPs—LaMnO3NPs—CH and GC/PtNPs—CNTs—LaMnO3NPs—CH electrodes for 0.8 M methanol in 1 M H2SO4 at 50 mV s$^{-1}$.

| Electrode                   | Onset potential (V vs. SCE) | $E_f$ (V vs. SCE) | $I_f$ (mA cm$^{-2}$) | $E_b$ (V vs. SCE) | $I_b$ (mA cm$^{-2}$) | $I_f/I_b$ |
|----------------------------|-----------------------------|-----------------|---------------------|-----------------|---------------------|----------|
| GC/PtNPs—CH               | -0.08                       | 0.63            | 12.76               | 0.39            | 10.74               | 1.19     |
| GC/PtNPs—LaMnO3NPs—CH     | -0.12                       | 0.62            | 25.12               | 0.38            | 11.45               | 2.19     |
| GC/PtNPs—CNTs—LaMnO3NPs—CH| -0.25                       | 0.48            | 43.84               | 0.22            | 33.88               | 1.29     |
technique for a 0.8 M methanol concentration solution (Figure 4). The amounts of current density was obtained 41.64, 53.16 and 56.95 mA cm\(^{-2}\) for the GC/PtNPs/C\(_0\)CH, GC/PtNPs/LaMnO\(_3\)NPs/C\(_0\)CH and GC/PtNPs/CNTs/LaMnO\(_3\)NPs/C\(_0\)CH electrodes at start time (\(t = 0.00\) s), respectively. It was increased when the nanocomposite changed from GC/PtNPs/LaMnO\(_3\)NPs/C\(_0\)CH to GC/PtNPs/CNTs/LaMnO\(_3\)NPs/C\(_0\)CH. Therefore, the composite of CNTs containing showed the higher activity catalytic for methanol oxidation and is a suitable candidate for anodic catalyst in DMFCs. The results of chronoamperometry technique were consistent with obtained previous consequences of CV technique.

3.4. Effect of different parameters toward methanol oxidation on GC/PtNPs/CNTs/LaMnO\(_3\)NPs/CH electrode

We investigated the methanol oxidation on the GC/PtNPs/CNTs/LaMnO\(_3\)NPs/CH electrodes at the different conditions such as: the methanol concentration, scan rate, temperature and the H\(_2\)SO\(_4\) aqueous solution as electrolyte.

3.4.1. Methanol concentration

We investigated the effect of increasing the methanol concentration on the potential and the current density of methanol oxidation at positive and negative sweep on the GC/PtNPs/CNTs/LaMnO\(_3\)NPs/CH electrode in 1 M H\(_2\)SO\(_4\) at \(-0.25\) to +1 V vs. SCE the potential range and 50 mV s\(^{-1}\) scan rate (Figure 5(A)). Obviously, it can be observed that increasing the methanol concentration up to 0.95 M increases the anodic current density and the current density of methanol oxidation did not have any considerable increase in methanol concentrations higher than 0.95 M. This effect could be due to the saturation of active sites on the surface of the catalyst. Moreover, the oxidation reaction of methanol on GC/PtNPs/CNTs/LaMnO\(_3\)NPs/CH electrode is controlled by the diffusion process of methanol toward the catalysis surface. As seen in Figure 5(A), while the methanol concentration increases, the \(E_f\) and \(E_b\) shift toward the positive direction. This may be attributed to the poisoning of Pt catalyst when increasing the methanol.
concentration and the oxidative removal of the adsorbed intermediates which would shift to a more positive potential. Plots of the logarithm of current density ($\log J$) vs. the logarithm of concentration ($\log C$) give the overall reaction order with respect to the initial concentration of methanol (Figure 5(B)). The reaction order, derived from the slope of the straight line was 0.586 for the positive and 1.411 for the negative sweep. It is clear at Figure 5(A) that the slope of current density increasing in the lower methanol concentrations was higher compared with the upper methanol concentration.

### 3.4.2. Scan rate

For kinetic characterisation of methanol oxidation on the GC/PtNPs–CNTs–LaMnO$_3$NPs–CH electrode, the CV curves of methanol oxidation were recorded in 0.8 M methanol and 1 M H$_2$SO$_4$ at various sweeping rates in the range of 25−400 mV s$^{-1}$. The plots of the peak potential ($E_p$) vs. $\ln (\nu)$ (Figure 6(A)) and the anodic peak current density ($J$) of methanol oxidation vs. the square root of the sweeping rate ($\nu^{1/2}$) (Figure 6(B)) were represented. According to Figure 6(A), the peak potential of methanol oxidation ($E_p$) increases with increasing the scan rate, and a linear relationship was obtained between $E_p$ and $\ln (\nu)$. It shows that the oxidation of methanol is an irreversible

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**Figure 5.** Plot of the (A) effect of methanol concentration on peak potential ($\Delta$) and current density ($\Delta$) of methanol oxidation and (B) peak current dependence vs. the logarithm of methanol concentration at forward (solid) and backward (hollow) sweep on the GC/PtNPs–CNTs–LaMnO$_3$NPs–CH electrode in 1 M H$_2$SO$_4$ and 50 mV s$^{-1}$ scan rate.

**Figure 6.** The plot of (A) the anodic peak potential vs. $\ln \nu$ and (B) the anodic peak current density of methanol oxidation vs. $\nu^{1/2}$ on the GC/PtNPs–CNTs–LaMnO$_3$NPs–CH electrode in 0.8 M methanol and 1 M H$_2$SO$_4$ at different scan rates: 25−400 mV s$^{-1}$. 

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*Note: The diagrams are not included in the text.*
charge transfer electrode process. The plot of $E_p$ and ln ($\nu$) has been a straight line with a slope (Equation (7)) [14]:

$$\text{Slope} = \frac{R \times T}{(1 - \alpha) \times n \times F}$$ (7)

where $\alpha$ stands for the electron transfer coefficient, characterising the effect of electrochemical potential on the activation energy of an electrochemical reaction. The slope of $E_p$ vs. ln ($\nu$) was $\delta E_p/\delta(\ln \nu) = 62.80$ mV. The $\alpha$ value was calculated as 0.93 (giving $n = 6$ and $T = 23\,^\circ\text{C}$) which is close to 1. This indicates that the methanol oxidation on the GC/PtNPs-LaMnO$_3$NPs-CH electrode has super kinetics. It is clear from Figure 6(B) that by increasing the applied sweeping rate, the $J$ of methanol oxidation has been increased. The linear relationship between the $J$ and $\nu^{1/2}$ estimates further the control of the overall methanol oxidation reaction via the mass transport of the methanol from the bulk solution to the electrode surface.[26]

### 3.4.3. Temperature

The effect of temperature on the electrochemical activity of GC/PtNPs–CNTs–LaMnO$_3$NPs–CH electrode toward the methanol oxidation was investigated by CV using temperature levels ranging from 20 to 70 °C. The results showed that when the temperature had been changed from 20 to 70 °C, the $J$ was increased from 39.90 to 126.49 mA cm$^{-2}$ with an increment factor of more than 3.17. At the same methanol concentration, the higher current density indicated that the fine structure of the catalyst possess more available Pt active sites to participate in the electrochemical reaction. The relatively higher incremental factor of the $J$ with temperature increment verifies that the highly ordered pores and the very good three-dimensional interconnection in CNTs could provide GC/PtNPs–CNTs–LaMnO$_3$NPs–CH electrode with easier mass transport and consequently superior performance, which suggests that the carbon materials with ordered structure are suitable and attractive for the use as catalyst support materials in fuel cells.[27] Activation energies were determined by studying the oxidation of methanol at different temperatures between 20 and 70 °C on GC/PtNPs–CNTs–LaMnO$_3$NPs–CH electrode. Arrhenius plots of logarithm of peak current density ($\log J_p$) vs. the reciprocal of temperature ($1/T$) provided the apparent activation energy from the slope of linear fitted as shown in Figure 7(A). Activation energies were calculated from the slope of the Arrhenius plot for certain potential values by applying Equation (8):

$$\frac{\partial \ln J_p}{\partial (1/T)} = -\frac{E_a}{R}$$ (8)

The apparent activation energy of methanol at GC/PtNPs–CNTs–LaMnO$_3$NPs–CH electrode was 8.45 kJ mol$^{-1}$. Seiler et al. [28] obtained the activation energy for methanol oxidation on PtRu/C catalyst about 45 kJ mol$^{-1}$; that is lower activation energy for methanol oxidation on PtNPs–CNTs–LaMnO$_3$NPs–CH nanocatalyst. The decreasing activation energy led to faster reaction kinetics for methanol oxidation reaction.
3.4.4. Electrolyte concentration

The methanol oxidation was done on the GC/PtNPs–CNTs–LaMnO₃NPs–CH electrode in different concentrations of H₂SO₄ solution in the range of 0.25 to 1.5 M and the corresponding results have been shown at Figure 7(B). The best result including the high current density and the lowest anodic peak potential for the same amount of PtNPs, CNTs and LaMnO₃ were obtained for a 1 M H₂SO₄ solution as supporting electrolyte. This is because CH can be considered a strong base as it possesses primary amino groups with pKₐ = 6.30. The presence of the amino groups indicates that pH substantially alters the charged state and properties of CH. At low pH, these amines get protonated and become positively charged. This makes CH a water-soluble cationic polyelectrolyte. As the pH increases above 6, chitosan’s amines become deprotonated and the CH loses its charge and becomes insoluble.

3.5. Single cell performances

Finally, single cell performance was tested only for PtNPs–CNTs–LaMnO₃NPs–CH nanocomposite as an anodic catalyst. In order to investigate the improved performance of the PtNPs–CNTs–LaMnO₃NPs–CH catalyst (2.0%Pt–0.6%CNT/CC-DL) in the presence of 1.0% LaMnO₃NPs, as an oxygen storage component, single cell tests were carried out for the MEA made as the anode, and the PtNPs–CH (4 mg cm⁻²) catalyst as the cathode for CH₃OH/O₂. The performance of the proposed single cell system depends on the efficiency of the electrochemical reaction at the interface between the solid phase of electrodes (anode and cathode) and liquid and gas phases in anode and cathode sides, temperature of the fuel cell and methanol concentration of carrier stream has major effects and has to be optimised.

In order to study the temperature effect on the performance of the fuel cell, various temperatures ranging from 60–90 °C were tested while keeping [methanol] constant at 1 M with a flow rate of 1.43 ml min⁻¹ for methanol solution as a fuel and [PₐO₂] 2 bar. The results have been shown in Figure 8(A). The open circuit voltages of the single cells at the different temperatures were 0.32 V at 60 °C, 0.47 V at 70 °C, 0.51 V at 80 °C and 0.71 V at 90 °C.
0.56 V at 90 °C. The increasing temperature enhanced the open circuit voltages. After polarisation loss, the potentials of single cells were stabled at 0.17 V for 60 °C, 0.35 V for 70 °C, 0.23 V for 80 °C and 0.30 V for 90 °C. Also, the observed maximum power density of single cells was 29.73, 161.92, 91.20 and 104.39 mW cm$^{-2}$ at the 60, 70, 80 and 90 °C temperature, respectively. From the $I$–$V$ characteristics, maximum power density of the single cells using the 2.0%Pt–0.6%CNT–1.0%LaMnO$_3$NPs/CC-DL anode was obtained at 70 °C. It is observed that the increasing of temperature was caused the enhancing of the open circuit voltage (OCV) of single cells. It can be due to the faster kinetics of methanol oxidation and oxygen reduction at the higher temperature.

The methanol concentration as a fuel has a significant effect on electrical performances such as cell voltage and power density, as one would expect. The polarisation curves of the single cell system were obtained for various methanol concentrations. Figure 8(B)
shows the results for PtNPs—CNTs—LaMnO$_3$NPs—CH catalyst in the DMFC as an anode in 1, 2 and 3 M methanol concentrations. The open circuit voltages of the single cells were 0.47, 0.51 and 0.53 V for the 1, 2 and 3 M methanol solutions, respectively. The effect of the methanol concentration was positively and negligibly on the OCV. After polarisation loss, the potentials of single cells were stabled at 0.35 V for 1 M, 0.36 V for 2 M and 0.28 V for 3 M methanol solution. The observed maximum power density of single cells was 161.92, 178.86 and 92.36 mW cm$^{-2}$ at the 1, 2 and 3 M methanol solutions, respectively. It is clear that the increasing concentration of methanol solution as a fuel increased the single cell performance; but at higher methanol concentration, the performance of single cell was decreased due to the increasing methanol crossover. The OCV was enhanced with concentration increasing of methanol as a fuel that it can be due to the large number and desaturation of catalytic sites.

4. Conclusion

Effectively, modified GC/PtNPs—CH, GC/PtNPs—LaMnO$_3$NPs—CH and GC/PtNPs—CNTs—LaMnO$_3$NPs—CH electrodes were prepared. The GC/PtNPs—CNTs—LaMnO$_3$NPs—CH electrode was proposed as active catalysts for methanol oxidation. The results showed the adding of LaMnO$_3$NPs and CNTs into PtNPs catalyst and the use of a more porous matrix of CH can significantly improve the electrode performance for methanol oxidation. The transition metals presence (La and Mn) at catalyst structure caused to catalyse the methanol dehydrogenation. Lessening the poisoning rate of the PtNPs with intermediates and byproducts of anodic reaction was observed due to the bi-functional effect electrical and oxygen ion conductive perovskite. According to the anodic peak potential and onset potential of methanol oxidation, the activity of GC/PtNPs—CNTs—LaMnO$_3$NPs—CH electrode for methanol oxidation was higher than GC/PtNPs—CH and GC/PtNPs—LaMnO$_3$NPs—CH electrodes. The factor influencing PtNPs utilisation in the methanol oxidation reaction is intrinsically related to PtNPs formation but using LaMnO$_3$NPs helps in enhancing the DMFC performance with low Pt loading. Also, the reaction order was calculated 0.586 for methanol oxidation and 1.411 for intermediate oxidation. The electron transfer coefficient was obtained as 0.93 for methanol oxidation on GC/PtNPs—CNTs—LaMnO$_3$NPs—CH electrode which is close to 1. This indicates that the methanol oxidation on the GC/PtNPs—LaMnO$_3$NPs—CH electrode has super kinetics.

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