Synthesis and characterization of multiwalled carbon nanotubes supported La$_x$Ca$_{1-x}$MnO$_3$ ($x = 0.2, 0.3$)

Anees-ur Rahman, Sana Sabahat, Muhammad Arshad, Rizwan Raza and Ghazanfar Abbas

1 Department of Physics, COMSATS University, Islamabad, Pakistan
2 Department of Chemistry, COMSATS University, Islamabad, Pakistan
3 Nanoscience and Technology Department, National Centre of Physics, Islamabad, Pakistan
4 Department of Physics, COMSATS University, Islamabad, Lahore Campus, Pakistan

E-mail: s.sabahat@comsats.edu.pk

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Abstract

Multiwalled carbon nanotubes (MWCNTs) supported La$_x$Ca$_{1-x}$MnO$_3$ ($x = 0.2, 0.3$) were synthesized via wet impregnation method, calcined at 450 °C and under vacuum oven at 200 °C for six hours. The x-ray diffraction (XRD) analysis inferred the presence of carbon within parent crystal orientation of LaCaMnO$_3$ in synthesized MWCNT/La$_x$Ca$_{1-x}$MnO$_3$ ($x = 0.2, 0.3$). Compositional analysis and binding energies profile of elements presents in synthesized samples was studied via x-ray photoelectron spectroscopy (XPS). Maximum output power density of La$_{0.2}$Ca$_{0.8}$MnO$_3$/MWCNTs and La$_{0.3}$Ca$_{0.7}$MnO$_3$/MWCNTs was found to be 277 mW cm$^{-2}$ and 151 mW cm$^{-2}$ at 600 °C observed from fuel cell data.

1. Introduction

Carbon nanotubes (CNTs) contains high-surface area, good electronic conductivity, strong mechanical properties and high-chemical stability. Due to these versatile properties, CNTs are widely used as support material for electrocatalysts. Studies show that the deposition of nanoparticles onto the surface of CNTs not only protect particles from aggregation, but also improve the catalytic activities [1]. However, the inertness of the CNT walls refrains the effective attachment of the metal catalysts remains a challenge, especially for the solution-based methods for the preparation of metal deposited CNTs (metal/CNTs) [2]. In comparison to the traditional electrocatalysts support such as carbon black, CNTs have shown more corrosive resistance under the simulated fuel cell operation conditions [3]. Multiwalled carbon nanotubes (MWCNTs) consists of several coaxially arranged graphene sheets rolled into a cylinder, the arrangement of carbon atoms (p-orbitals) across valence ($\pi$) and conduction ($\pi^*$) bands promotes fast electron transport. The versatile properties of MWCNTs may due to the strength of C–C bonds of nanotubes [4].

For MWCNTs the conduction is mainly due to the outer shells. They possess active surface area, high chemical inertness and mechanical strength [5]. MWCNTs show different orbital interactions, $\pi$- and $\sigma$-covalent bonds with nanostructures [6]. MWCNTs has been explored as suitable catalysts for energy storage [7], transistor and capacitors [8, 9] and electrochemical devices [10]. Asgari et al [11] investigated that durability and potential cycling stability of MWCNTs supported electrocatalysts for proton exchange fuel cell is stronger as compared to SWCNTs supported materials. Thiele et al [12] inferred that MWCNTs supported electrode produced better fuel cell performance as compared to electrocatalysts and acetylene black. Due to versatile catalytic properties of MWCNTs, they have been selected for the proposed study.

Perovskite (ABO$_3$) are functional materials which are cost effective and earth-abundant [13]. Because of their compositional diversity and tunable chemical and physical properties, perovskite materials/electrocatalysts attain great attention especially for energy storage materials [e.g., solid oxide fuel cells (SOFCs) electrode materials; La$_x$Ca$_{1-x}$MnO$_3$ etc] [14–18].
LaMnO$_3$ belongs to manganites class which possess good electrical-electronic, structural [19] and magnetic properties [20]. On doping with rare earth metal Ca$^{2+}$, parent LaMnO$_3$ (La$_x$Ca$_{1-x}$MnO$_3$) underwent dynamic John-Teller effects. In La$_x$Ca$_{1-x}$MnO$_3$ with $x$ ranges from 0–1, the mixed ionic and electronic conductivity increases when Ca$^{2+}$ content is above 0.5 [21]. We had synthesized whole range of Ca doped LaMnO$_3$ in our laboratory, we had obtained some promising results (related to structural, electrical and electronic conduction) which also concluded that improved conductivity profile of Ca doped LaMnO$_3$ was obtained with La$_{0.3}$Ca$_{0.7}$MnO$_3$ and La$_{0.2}$Ca$_{0.8}$MnO$_3$.

LaMnO$_3$/MWCNTs exhibited extraordinary photocatalytic properties as compared to LaMnO$_3$ [22]. Literature infers that MWCNTs had contributed to improve fuel cell performances when supported with pervoskite materials/electrocatalysts. On behalf of our previous research findings and literature information, we have selected La$_{0.5}$Ca$_{0.5}$MnO$_3$ and La$_{0.5}$Ca$_{0.5}$MnO$_3$ to be supported by MWCNTs.

In the present study, modified wet impregnation method has been adopted for successful synthesis of MWCNT supported ternary electrocatalysts (i.e., La$_x$Ca$_{1-x}$MnO$_3$ where $x = 0.2$ and 0.3). Structural and morphological analysis reveals the presence of MWCNTs within the parent crystal structure of La$_x$Ca$_{1-x}$MnO$_3$. Interestingly, MWCNT’s supported La$_{0.2}$Ca$_{0.8}$MnO$_3$ attained good fuel cell activity.

2. Materials and methods

2.1. Chemicals

Lanthanum(III) nitrate hexa-hydrate La(NO$_3$)$_3$·6H$_2$O, (Sigma Aldrich), Calcium nitrate tetra- hydrate CaNO$_3$·4H$_2$O, Cobalt(II) Nitrate hexa-hydrate Co(NO$_3$)$_2$·6H$_2$O, (Sigma Aldrich), Nickel(III) nitrate hexa-hydrate Ni(NO$_3$)$_3$·6H$_2$O, (Sigma Aldrich), Manganese(II) nitrate tetra-hydrate Mn(NO$_3$)$_2$·4H$_2$O, (Sigma Aldrich), Ethylene Glycol (Sigma Aldrich), Multi wall Carbon Nanotubes, Main range of diameter: <2 nm, de-ionized water, sulphuric acid (H$_2$SO$_4$), nitric acid (HNO$_3$) silver paste of analytical grades were used in this experimental work.

Structural analysis of synthesized ternary electrocatalysts was carried out using PANalytical, Model name: X’Pert PRO ‘XRD’ with Cu K$_{α}$ radiation ($\lambda = 1.5418$ Å), 35 kV voltage and 30 mA current at room temperature. Morphological analysis was done by Scanning Electron Microscopy [(SEM/EDX) (Hitachi, Model number: SU-1500)].

Fuel-Cell testing was carried out by fabricating three layers of cells using synthesized MWCNT supported Calcium doped Lanthanum manganite as cathode, Sodium Samarium Doped Ceria (NSDC) as electrolyte and LiNiCuZnO as anode material. Pallets of 13 mm were prepared and pressed using dry press technique. Thickness of the pallet was controlled by 0.2 mm cathode, 0.3 mm electrolyte and 0.2 mm anode. Silver paste was used on both side of the cell to make electrical contacts. The fuel cell performance was measured by using hydrogen as fuel at anode side and air as oxidant at cathode. The flow of hydrogen gas was controlled at a rate of 100 ml min$^{-1}$ under 1 atm pressure at room temperature. The data of open circuit voltage (OCV) at 600 °C was observed. Power density was calculated from I–V and I–P curves.

XPS measurements were carried out using a Scienta-Omicron XPS instrument equipped with a micro-focused monochromatic Al K–Alpha x-ray source. The source was operated at 15 KeV with about 700-micron spot size, constant analyzer energy (CAE) 100 eV for survey scan and 20 eV for detailed scans. The data acquisition was performed with Matrix software and data analysis was performed with Igor pro along with XPS fit procedures. The Curve fitting of spectra was done using Gaussian-Lorentzia line shape after performing the shrilly background corrections.

2.2. Experimentation

2.2.1. Functionalization of MWCNTs

Functionalization of multiwalled carbon nanotubes (MWCNTs) were carried out by adopting following steps [23]. A mass of 100 mg MWCNTs were mixed in stoichiometric ratio (3:1) of H$_2$SO$_4$ and HNO$_3$ and subjected to ultrasonic vibration for 6 h. The resulting mixture was washed repeatedly with distilled water until the pH of the filtrate turned neutral, and then dried in an oven for 12 h at 100°C.

2.2.2. Synthesis of supported ternary electrocatalysts

Modified wet-impregnation method [24–26] was used for synthesis of supported ternary electrocatalysts. A volume of 10 ml ethylene glycol (C$_2$H$_4$O$_2$, EG) was added in molar solutions of La(NO$_3$)$_3$·6H$_2$O, Ca(NO$_3$)$_2$·4H$_2$O, Mn(NO$_3$)$_2$·6H$_2$O. A mass of 1 gm of functionalized MWCNTs were then mixed in the above solution. The temperature of mixture was set to 100 °C for 3 h for its complete dryness. The dried powder was first annealed in box furnace at 450 °C for 2 h and then finally in vacuum oven at 200 °C for 6 h to attain the sample morphology. Final dried black colored sample was attained.
3. Results and discussion:

3.1. Structural analysis of supported ternary electrocatalysts, La$_{x}$Ca$_{1-x}$MnO$_3$ ($x = 0.2$ and $0.3$)

Figure 1 shows the XRD pattern of La$_{0.3}$Ca$_{0.7}$MnO$_3$/MWCNTs. In La$_{0.3}$Ca$_{0.7}$MnO$_3$/MWCNTs, the diffraction peaks appeared at $23^\circ$, $27^\circ$, $31^\circ$, $41.5^\circ$, $43.5^\circ$, $47.5^\circ$, $54^\circ$, $61^\circ$, $69^\circ$, and $79^\circ$ referred to scattering from (111), (002), (121), (022), (100), (202), (301), (240), (400) and (402). XRD patterns of supported La$_{x}$Ca$_{1-x}$MnO$_3$ attain perovskite type structure representing orthorhombic structure of La$_{x}$Ca$_{1-x}$MnO$_3$. It was observed that introduction of MWCNTs into pure La$_{x}$Ca$_{1-x}$MnO$_3$ does not affect the structure of La$_{x}$Ca$_{1-x}$MnO$_3$. The peaks appeared at $27^\circ$ and $45^\circ$ are indexed as (002) and (100) respectively, related to MWCNTs. With MWCNTs as carrier, the LaMnO$_3$ particles showed nucleation and growth [22]. Without MWCNTs, in parent La$_{0.3}$Ca$_{0.7}$MnO$_3$ crystal structure, the substitution of lanthanum with calcium may causes change in the cell parameters due to different ionic radii of the substitute cation like Ca$^{2+}$ (ionic radius 0.99 Å), and the substituted La$^{3+}$ (ionic radius 1.15 Å) [21, 27]. The XRD measurement of La$_{0.3}$Ca$_{0.7}$MnO$_3$/MWCNTs was carried out by JCPDS-00-051-1586. The crystallite size ($D_\beta$) was calculated from line-broadening peaks of XRD patterns using Scherer’s equation:

$$ D_\beta = \frac{0.9 \lambda}{\beta \cos \theta (2\theta)} $$

Where $\lambda$ and $\beta$ are wavelength and full width half maximum (FWHM), respectively. The average particle size of La$_{0.3}$Ca$_{0.7}$MnO$_3$/MWCNTs was found to be 30 nm.

3.2. SEM and EDX analysis of La$_{0.2}$Ca$_{0.8}$MnO$_3$/MWCNTs

Surface morphology of synthesized nanoparticles is shown in SEM images of La$_{0.2}$Ca$_{0.8}$MnO$_3$/MWCNTs. The nano-sized La$_{0.2}$Ca$_{0.8}$MnO$_3$ particles were well dispersed and uniformly deposited on the surface of MWCNTs. EDX analysis showed the elemental profile and relative abundance of synthesized sample (La$_{0.2}$Ca$_{0.8}$MnO$_3$/MWCNTs). It can be inferred that most of the surface of the synthesized sample is covered by La$_{0.2}$Ca$_{0.8}$MnO$_3$. Presence of CNTs (supporting element for La$_{0.2}$Ca$_{0.8}$MnO$_3$) was also noticed, this confirms successful synthesis of supported electrocatalyst [28].

3.3. XPS Analysis of La$_{0.3}$Ca$_{0.7}$MnO$_3$/MWCNTs:

XPS spectra collected from La$_{0.3}$Ca$_{0.7}$MnO$_3$/MWCNTs as shown in figure 3. The survey scan reveals the presence of carbon (C), oxygen (O), manganese (Mn), calcium (Ca) and lanthanum (La) only. The high resolution (HR) spectra of C1s, O1s, Mn2p, Ca2p and La3d were received to investigate chemical combination and surface oxidation states. The atomic% concentrations of C, O, Mn, Ca, and La are 33.68, 40.93, 14.51, 7.59 and 3.26 respectively. The HR C1s spectrum deconvoluted into five sub peaks as shown in figure 3(b). The first peak at 284.6 eV is assigned to sp2 configuration of carbon, whereas the peak at 285.6 is attributed to C–OH bonded carbon. The other peaks located at 287.3 eV and 289.3 provides the indication of C–O–C and Ca–O/C=O functional groups present on the surface of the sample correspondingly. The peak appeared at higher binding value at 291.1 eV is associated with shakeup satellites due to the CNTs [29]. The HR spectrum of O1s is also resolved into five sub peaks which are located at 528.8 eV, 531.2 eV, 532.8 eV, 535.2 eV and 537.2 eV. The O1s peaks resolved at 529.8 eV and 531.7 eV typically shows the presence of Mn–O–Mn and Mn–OH bonding whereas the peak at 532.8 eV is correlated with oxygen bonded with Ca and peaks at higher binding energy represents C–O/COOH species [30].
The Mn2p3/2 peak deconvoluted into three sub peaks placed 640.6 eV and 642.3 eV, which characterize the Mn (II) and Mn (IV) oxidation states respectively. The peaks at 647.6 eV corresponds to shakeup satellite structures indication of Mn (II). The quantitative analysis shows that Mn (II) and Mn (IV) exist 1:1 (50% each) on the surface [31, 32]. The Ca2p spectra, figure 3(e) is comprised of five deconvoluted peaks in which two peaks lying at 345.78 eV and 349.25 eV are typical signature of spin–orbit splitting and are associated with Ca2+ [33]. The other peaks at 347.86 and 351.12 are due to the presence of CaCO3 on the surface. The La3d3/2 core level is resolved into sub peaks a shown in figure 3(f). The first two peaks positioned at 834.4 eV and 835.9 eV are corresponding to La3+ in La2O3 and La/Ca respectively while peaks at high binding energy level at 837.8 eV and 839.2 eV are associated with La2CO3/La(OH)3 which also indicates that La is reactive. The peak at 840.8 eV may also be assigned to LaH2 species. The calculated binding energies \(\text{BE (eV)}\) profile of 1s CNTs, 2p Ca, 1s O, 2p Mn, 3d La were found as 284.6, 349, 541.1, 649.9 and 853.

3.4. Fuel cell performance of supported electrocatalysts

From Fuel cell experimental data, Open Circuit Voltage (OCV) and maximum power density of La0.3Ca0.7MnO3/MWCNTs and La0.2Ca0.8MnO3/MWCNTs was found to be 0.949 V (0.781 V for unsupported La0.3Ca0.7MnO3) & 151 mWcm\(^2\) (149 mW cm\(^{-2}\) for unsupported La0.3Ca0.7MnO3) and 0.825 V & 277 mWcm\(^2\) (213 mW cm\(^{-2}\) for unsupported La0.2Ca0.8MnO3) at 600 °C using hydrogen as fuel at anode. The IV & IP profile of La0.2Ca0.8MnO3/MWCNTs is shown in figure 4.

The comparative data analysis of supported and unsupported electrocatalysts revealed that the support of MWCNTs improved the fuel cell performance of supported electrocatalysts. The participation of Ca\(^{2+}\) within the parent crystal structure produces oxidation changes in Mn. This may result in increase in fuel cell performance, conduction and durability of synthesized electrocatalysts [34, 35]. Literature studies show that MWCNTs increases the overall performance of fuel cell. In our case study, we have observed the same scenario.

4. Conclusion

Ternary supported electrocatalysts, La0.2Ca0.8MnO3/MWCNT and La0.3Ca0.7MnO3/MWCNT were successfully synthesized using wet impregnation method. Crystallinity was attained in every synthesized samples confirmed via XRD analysis. SEM depicts good crystallinity and morphology of synthesized compounds. The nano-sized La0.2Ca0.8MnO3 and La0.3Ca0.7MnO3 particles were well dispersed and uniformly deposited on the
surface of MWCNTs. The successful insertion of LaCaMnO$_3$ on MWCNTs was confirmed via EDS analysis and XPS survey scans. The chemical combination and surface oxidation states of C1s, O1s, Mn2p, Ca2p and La3d was studied via HR XPS spectra. The atomic% concentrations of C, O, Mn, Ca, and La were found to be 33.68, 40.93, 14.51, 7.59 and 3.26 respectively. Fuel cell results inferred that MWCNTs attained good fuel cell activity. The maximum power density of LaxCa$_{1-x}$MnO$_3$/MWCNTs (x = 0.2 and 0.3) was calculated to be 0.825 V &
277 mWcm$^{-2}$ and 0.949 V & 151 mWcm$^{-2}$ at 600 °C using hydrogen as fuel at anode. Considering all results, synthesized supported electrocatalysts can be tuned for low temperature SOFCs.

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Conflict of interest

There is no conflict of interest.

ORCID iDs

Sana Sabahat https://orcid.org/0000-0002-8787-3212

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