Nanotechnology

PAPER

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To cite this article: Mohammad Fathi Tovini et al 2018 Nanotechnology 29 475401

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Nanohybrid structured RuO₂/Mn₂O₃/CNF as a catalyst for Na–O₂ batteries

Mohammad Fathi Tovini, Bhushan Patil, Cevriye Koz, Tamer Uyar and Eda Yılmaz

Institute of Materials Science and Nanotechnology, National Nanotechnology Research Center, Bilkent University, Ankara 06800, Turkey

E-mail: yilmaz@unam.edu.tr

Received 14 May 2018, revised 29 July 2018
Accepted for publication 7 September 2018
Published 26 September 2018

Abstract

A 3D RuO₂/Mn₂O₃/carbon nanofiber (CNF) composite has been prepared in this study by a facile two step microwave synthesis, as a bi-functional electrocatalyst towards oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). RuO₂ nanoparticles with the mean size of 1.57 nm are uniformly distributed on Mn₂O₃ nano-rods grown on electrospun CNFs. The electrocatalytic activity of the composites are investigated towards ORR/OER under alkaline condition. The ternary RuO₂/Mn₂O₃/CNF composite showed superior ORR activity in terms of onset potential (0.95 V versus RHE) and Tafel slope (121 mV dec⁻¹) compared to its RuO₂/CNF and Mn₂O₃/CNF counterparts. In the case of OER, the RuO₂/Mn₂O₃/CNF exhibited 0.34 V over-potential value measured at 10 mA cm⁻² and 52 mV dec⁻¹ Tafel slope which are lower than those of the other synthesized samples and as compared to state of the art RuO₂ and IrOₓ type materials. RuO₂/Mn₂O₃/CNF also exhibited higher specific capacity (9352 mAh g⁻¹ carbon) than CNF (1395 mAh g⁻¹ carbon), Mn₂O₃/CNF (3108 mAh g⁻¹ carbon) and RuO₂/CNF (4859 mAh g⁻¹ carbon) as the cathode material in Na–O₂ battery, which indicates the validity of the results in non-aqueous medium. Taking the benefit of RuO₂ and Mn₂O₃ synergistic effect, the decomposition of inevitable side products at the end of charge occurs at 3.838 V versus Na+/Na⁺ by using RuO₂/Mn₂O₃/CNF, which is 388 mV more cathodic compared with CNF.

Supplementary material for this article is available online

Keywords: RuO₂/Mn₂O₃/CNF, 3D composite, oxygen reduction reaction, oxygen evolution reaction, Na–O₂ batteries

(Some figures may appear in colour only in the online journal)
poisoning hinder their application as bi-functional electrocatalysts for these reactions [8]. The first row transition metal oxides, like NiO and CoO, are promising alternative catalysts for ORR due to their reasonably comparable catalytic activity to Pt, lower cost, high stability and abundance in the nature [9]. Manganese oxides (MnO x, like α-, β-, γ-, δ-MnO2, Mn2O3 and Mn3O4) have been widely investigated as outstanding ORR catalysts due to several characteristics of Mn including: its oxidation state change between +2, +3 and +4 near the equilibrium ORR potential which facilitates oxygen atoms exchange in relevant potentials, low toxicity, high chemical stability and earth abundance and potential for large scale energy applications [10–13]. However, the poor electronic conductivity and the relatively low OER kinetics of MnO2 limits its application as a bi-functional electrocatalyst and needs to be considered for future applications. To address the low electronic conductivity of MnO x, several researches have been attempted to combine it with highly conductive carbonaceous materials like graphene, carbon nanotubes and porous carbon [14–16]. Among all, electrospun carbon nanofibers (CNF) have been considered as promising backbone for MnO2 to improve the charge exchange due to its high surface area, excellent electrical conductivity, mechanical property and low cost of synthesis [17]. However, to the best of our knowledge, CNF has not been studied as a matrix for MnO2 deposition for ORR/OER application.

In order to deal with the low OER activity of MnO x, composite materials containing MnO2 and metal/oxides (like Au, Ti, TiO2, Co3O4, Fe2O3 etc) have been proposed [18–22]. Ruthenium based oxides (RuO x) have been frequently reported as high electronically conductive catalysts especially for OER based electrochemistry [23–25]. In this regard, Lee et al showed the OER catalytic activity of RuO2 in both acidic and basic media [26]. Also recently, Bhowmik et al confirmed the OER activity of RuO2 nanowires grown on carbon-nitride in all pH values, including acidic (pH = 0), neutral (pH = 7) and alkaline (pH = 14) solutions [27]. For these reasons, the MnO x/RuO2 combination has been achieved by different research groups as a bi-functional catalyst for ORR/OER for diverse applications [28–30]. However, the lack of a rational 3D structure design consisting of a highly electronic conductive path in the core to supply electric charge and maintain the mechanical stiffness of the structure can be realized in these works. Such a design has been extensively investigated for the energy conversion and storage applications. They include 3D carbon/SnO2 [31], CNT/MO (M = Co, Zn, Mn) [32], CNF/Fe3O4 [33], SnO2/Co3O4 nano fiber-coated graphene [34] etc.

Herein, we first optimize a rational 3D design of RuO2/MnO2/CNF (RMC) bi-functional catalyst for ORR/OER in alkaline aqueous media and in the second step, the optimized samples are implemented as the cathode material for Na–O2 batteries. RMC has been prepared through a facile two-step microwave synthesis, in which RuO2 nano-particles were attached on the as synthesized Mn2O3 nano-rods coated electrospun CNF (figure 1). Electrospun CNFs provide an optimal surface for the 3D structure to grow and the electrochemical results confirmed that the 3D RMC exhibits improved ORR/OER catalytic activity compared to its RuO2/CNF (RC) and Mn2O3/CNF (MC) counterparts, which demonstrates that RMC offers a competitive alternative to the already available ORR/OER catalysts.

2. Experimental

2.1. Preparation of Mn2O3/CNF, RuO2/CNF and RuO2/Mn2O3/CNF

In the first step, Mn2O3/CNF (MC) composites were prepared by a facile microwave synthesis method. Typically, 20 mg of electrospun CNF (fabrication details in supplementary information) was dispersed in 20 ml DI water by 10 min sonication. Then, different amounts of KMnO4 were mixed with the CNF dispersion and stirred in the room temperature for 30 min. The above dispersions were added to the vessels and the microwave-assisted hydrothermal reactions were performed at 180 °C for 30 min in the microwave synthesis reactor (Anton Paar Monowave 300). The amount of KMnO4 was adjusted to 0.125, 0.25 and 0.5 mmol to result MC1, MC2 and MC3 samples, respectively. After the reactions were performed, MC samples were washed and centrifuged with DI water and ethanol for several times and dried in an oven at 60 °C for overnight. Finally, the samples were annealed for 1 h in 150 °C in the air atmosphere.

For RMC preparation, 20 mg MC2 was dispersed in 20 ml DI water by 5 min sonication and different amounts of RuCl3.xH2O were mixed with the solution by stirring for 30 min. Then, the resulting mixtures were added into the vessels and put in the microwave synthesis reactor at 180 °C for 20 min. The amount of RuCl3.xH2O was adjusted to 0.01, 0.025 and 0.04 mmol to result RMC1, RCM2 and RMC3 samples, respectively. Figure 1 shows the schematic illustration of RMC samples preparation sequence. During the whole microwave synthesis preparation of MCs and RMCs, the mixers were stirred at 600 rpm. After the reactions were
complete, the products were washed, dried and annealed same as MC samples.

For the preparation of RC, the same procedure as RMC2 was applied, but MC2 was replaced by CNF as the substrate for RuO2 deposition.

2.2. Materials characterization

The morphological and structural evaluations of the samples were performed by using the immersion mode of a focused ion beam-scanning electron microscope (FIB-SEM, FEI 600 Dual Beam) operating at 15 kV and transmission electron microscope (TEM, FEI Tecnai G2 F30) operating at 300 kV. For TEM measurements, samples were randomly dispersed in acetone and dropped on a lacy carbon coated TEM copper grid. Energy dispersive spectroscopy (EDS) was performed in SEM (FEI-Quanta 200 FEG) operating at 15 kV and the average of 6 different points measurements were used for Ru: Mn ratio calculations. The averages of diameter of more than 40 fibers from different SEM images were used for fiber diameter calculations. CHNS elemental analysis of the samples was performed by using a Thermo Flash 2000 elemental analyzer. Crystallographic identifications were performed by a Panalytical (X’pert Pro MPD) instrument and x-ray diffraction (XRD) patterns were collected over the 2θ range of 10°–80° using Cu-kα radiation (λ = 1.54 Å). High resolution x-ray photoelectron spectroscopy (XPS, ThermoScientific K-Alpha, Al K-Alpha radiation) was performed on MC2 and RMCs samples to determine the valence number of Mn and Raman spectra were recorded on a confocal Raman instrument (WITec alpha300).

2.3. Electrochemical measurements

All electrochemical measurements were performed with Biologic SP-150 potentiostat at room temperature. The standard three-electrode electrochemical cell was used with the glassy carbon electrode (GC, 3 mm diameter, 0.070 68 cm² of geometric surface area), Pt spiral wire and Ag/AgCl/KCl sat. as working, counter and reference electrodes, respectively. The electrochemical characterizations were performed in 20 ml 0.1 M KOH solution where prior to each measurement the electrolyte solution was saturated with either N2 or O2 gas (99.999% of purity) at 1.54 Å. High resolution x-ray photoelectron spectroscopy (XPS, Thermoscientific K-Alpha, Al K-Alpha radiation) was performed on MC2 and RMCs samples to determine the valence number of Mn and Raman spectra were recorded on a confocal Raman instrument (WITec alpha300).

2.4. Na–O2 cell assembly and galvanostatic measurements

Na–O2 cells were assembled inside an Ar-filled glovebox (O2 level < 0.5 ppm, H2O level < 0.5 ppm) with metallic Na as anode, Celgard 2500 and GF/GC as the separators and 20 wt% C65 containing CNF, MC2, RC and RMC2 cathodes. 280 μl of 0.5 M NaCF2SO3 in tetraethylene glycol dimethyl ether (H2O amount <10 ppm according to Karl Fischer titration) was used in each cell as the electrolyte. The mass of active materials on cathodes was ~0.5 mg which were drop casted on Ni-foams (~11 mm diameter). Galvanostatic measurements of cells were performed using a battery cycler (Landt Instruments CT2001A) under 1.5 mbar of O2 pressure (40 ml integrated O2 tank). Discharged or charged cathodes were extracted from disassembled cells inside the glovebox and washed with 3 ml acetonitrile (H2O amount <5 ppm) in order to remove residual electrolyte and used for postmortem characterizations.

3. Results and discussions

In order to find the optimum amount of KMnO4 and RuCl3·xH2O precursors, three different batches of MCs and RMCs are prepared and morphological and structural evaluations are performed by SEM (figures 2, S1–S3, available online at stacks.iop.org/NANO/29/475401/mmedia). The as electrosprun CNF exhibits fibrous structure with smooth surface and mean diameter of 255 nm (176–382 nm) (figure 2(a)). However, drastic morphological changes were observed after Mn2O3 deposition on CNF (figures 2(b), S1(b) and S2). Although the CNF framework remains unchanged in MC samples, the deposition of Mn2O3 nano-rod turns the structure to a 3D porous platform, which become quite desirable for RuO2 nanoparticle decoration in the next step. Also, by comparing figures 2(b) and S2, it can be figured out that Mn2O3 coating thickness exhibits a direct relation to KMnO4 precursor amount, resulting in the fibers diameter increase from MC1 (281 nm) to MC3 (464 nm). After RuO2 deposition, the change in Mn2O3 nano-rods diameter can be recognized in SEM images of RMC samples (figures 2(c) and S3) when compared to MC2. Since the least amount of RuCl3·xH2O was used for RMC1 synthesis, its morphology is quite reminiscent of MC2 (figures S3(a) and (b)). On the other hand, some RuO2 agglomerates existing between Mn2O3 nano-rods and accumulating outside of the structure are observed in RMC3 (figures S3(c) and (d)), which results in pore clogging and preventing electrolyte ion accessibility to
the inner pores. Anyhow, the surface morphology of RMC2 in figure 2(c) exhibits no agglomeration of RuO2, showing that the RuO2 nanoparticles were effectively deposited on Mn2O3 nano-rods. In order to realize the function of porous Mn2O3 nano-rods framework in the second hydrothermal step, as electrospun pristine CNF was used for RuO2 deposition to make RC (figure 2(d)). It can be seen that in the absence of Mn2O3 nanorods, RuO2 agglomerates are dominating in this sample. This behavior demonstrates that Mn2O3 nanorods act as trapping network to anchor individual RuO2 nanoparticles which results in the uniform distribution of them in the structure.

TEM has been exploited to further investigate the nanostructure of MC2, RMC2 and RC, as shown in figures 3 and S4. The TEM and high resolution TEM (HRTEM) imaging revealed that a large number of Mn2O3 nano-rods are grown upright on CNF in MC2, making an open porous 3D nano-structure (figures 3(a) and (b) and S4(a)). The selected area electron diffraction (SAED) pattern of MC2 shows the characteristic diffraction rings attributed to the (004), (044) and (226) planes, indicating the crystalline nature of Mn2O3 nano-rods. The TEM images of RMC2 show that RuO2 nanoparticles with the mean size of 1.57 nm are uniformly distributed on Mn2O3 nano-rods without any agglomeration and pore clogging, further confirming the trapping function of Mn2O3 nano-rods in the structure (figures 3(c), (d) and S4(b)). The formation of hierarchical RMC2 was further examined by high angle annular dark field scanning TEM images (figure S4(b)) which yielded a clear contrast between RuO2 nanoparticles and Mn2O3 nano-rods. The elemental EDS line scan results (figure 3(c) inset) show the presence of O, Mn, Ru and C in the structure. The relative positions of these elements indicate that O, Mn and Ru were across the whole structure, therefore, RuO2/Mn2O3 has grown on the CNF core. Furthermore, SAED pattern of RMC2 (figure 3(d) inset) consists of characteristic diffraction rings of (121) and (031) planes attributed to RuO2 and those of Mn2O3. The agglomerating nature of RuO2 nanoparticles was also observed in more detail in TEM images of RC (figures S4(e) and (f)). The crystallinity of the samples was further analyzed by XRD (figures 4(a) and S5(a)). The XRD pattern of CNF shows a broad peak at 2θ = 25° corresponding to the (002) plane of graphitic carbon. In the diffraction patterns of MC and RMC samples, the peaks at 2θ = 33°, 38.2°, 55.4° and 65.8° are corresponding to (222), (004), (044) and (226) planes of Mn2O3 (ICSD 98-003-3647), respectively. It can be realized that Mn2O3 gets more crystalline in RMC samples compared to MC samples which can be owing to the second hydrothermal step for RuO2 deposition. Also, no obvious peaks relating to RuO2 were observed in the patterns of RC and RMC samples which is because of minor amount and small crystal size of RuO2.

Figures 4(b) and S5(b) show the Raman spectra of the samples, in which there are two main peaks of CNF including D band at 1351 cm⁻¹ related to the phonons with A₁g symmetry and G band at 1584 cm⁻¹ corresponding to the E₂g phonon of sp² carbon atoms [35, 36]. The Raman spectra of MC and RMC samples exhibit three bands at 500, 560 and 620 cm⁻¹ which are corresponding to the asymmetric stretching of bridging oxygen species (Mn–O–Mn) and symmetric stretch of Mn2O3 groups [37–39]. The Raman spectrum of RC shows two peaks at 520 and 631 cm⁻¹ which are related to the first order E_g and A_1g phonon bands of rutile RuO2 [40]. However, since the peaks of RuO2 and Mn2O3 coincide in the same spectrum region, there is no obvious peak of RuO2 in RMCs. The presence of RuO2 in the samples is further approved by EDS (figure S6) and XPS high resolution Ru3d spectra (figure S7) and further confirmation about Mn oxidation state of MC2 and RMCs were determined by XPS analysis (figure S5(c)). The Mn 2p spectra of all samples are mainly composed of two peaks located around ~641.1 eV and ~652.7 eV corresponding to Mn 2p₁/₂ and Mn 2p₃/₂ of Mn^{4+}, respectively, and two minor peaks spectra around ~643.4 and ~655.1 eV assigned to Mn^{3+} species [41]. The effect of mixed Mn oxidation state on the electrochemical
behavior will be discussed in the following discussion part for the electrochemical results.

The electrocatalytic ORR activity of the prepared samples was analyzed with RDE measurements from 225 to 1225 rpm with the scan rate of 10 mV s⁻¹ in O₂-saturated 0.1 M KOH aqueous solution (figures 5(a), S8(a) and S9). The Koutecky–Levich plots at the steady state currents were also shown in figures 5(b) and S8(b). The number of electrons involved in the ORR per oxygen molecule was determined from the slope using Koutecky–Levich equitation:

\[ \frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_L} = \frac{1}{j_k} + \frac{1}{(Bw^{1/2})}, \]  

(1)

where \( j \) is the measured current, \( j_k \) is the kinetic current density, \( j_L \) is the Levich current density, \( B = 0.62nFCD^{2/3}v^{-1/6} \), \( n \) is the number of electrons transferred per oxygen molecule, \( F \) is the Faraday constant i.e. 96 485 C mol⁻¹, \( C \) is the dissolved oxygen concentration in the solution (\( 1.26 \times 10^{-6} \text{ mol cm}^{-3} \)), \( v \) is the kinematic viscosity of the solution (\( 1.009 \times 10^{-2} \text{ cm}^{2} \text{ s}^{-1} \)), \( D \) is the diffusion coefficient of oxygen (\( 2.1 \times 10^{-5} \text{ cm}^{2} \text{ s}^{-1} \)) and \( w \) is the rotation rate (rad s⁻¹). Assuming a four-electron reaction and the known geometric electrode surface area, the theoretical slope \( B \) is 2.5 cm² rad⁻¹/² mA⁻¹ 1/².

The kinetic current density was calculated according to the following equation:

\[ j_k = (j \times j_L)/(j_L - j), \]  

(2)

which is further used to estimate the Tafel slopes (figures 5(c) and S8(c)) to find out ORR kinetics of the catalysts. The slope and constant obtained from the straight line of log \( j_k \) versus potential were used to estimate Tafel slope and the exchange current density, respectively. Table 1 summarizes the ORR performance of the materials resulted in figures 5 and S8. The CNF synthesized from PAN in this study generates nitrogen-doped carbon fibers (table S1) which have been demonstrated as one of the suitable catalysts for ORR. It shows the number of electrons involved in ORR as 3.4 with Tafel slope of 133 mV dec⁻¹ and onset potential of 0.87 V. However, poor stability of such carbon in energy applications needs a further coating of secondary material [42, 43].

After Mn₂O₃ coating, ca. 30 mV anodic shift in the onset potential showed further improvement in the ORR catalysis analyzed at the MC1 and MC2 catalysts. Among MC catalysts, electrocatalytic activity towards ORR clearly shows that MC2 is better in terms of most anodic onset potential with lower Tafel slope and higher \( E_{1/2} \) and \( j_k \). Although the number of electrons involved in ORR was less at MC2, better ORR and OER kinetics made it the suitable catalyst for further RuO₂ deposition. After RuO₂ deposition, RMC2 proved as the best ORR catalyst amongst all RMCs, MCs and RC samples and also comparable with Pt/C catalyst.

The Tafel slope of 121 mV dec⁻¹ at RMC2 indicates that first electron transfer is the rate-limiting step. As the RuO₂ amount increases from RMC1 to RMC2, catalysis becomes more efficient thermodynamically and kinetically, however, further increase in RuO₂ turns out to agglomeration (figures S5(c) and (d)) which again decreases the efficiency of catalysis in RMC3. The RC catalyst which showed agglomerated RuO₂ morphology in absence of Mn₂O₃ nano-rods (figures 2(d) and S4(e) and (f)) resulted in the cathodic shift of 70 mV onset potential as compared to RMC2. Thus, the ORR catalysis at RMC2 is proving the synergistic effect of Mn₂O₃ and RuO₂.

From the XPS data (figure S5(c)), it is clear that MC2 and RMC catalysts are composed of both Mn³⁺ and Mn⁴⁺. Although Mn₂O₃ was predicted to be a poor catalyst for ORR [44], it has also been reported that applied potentials can change the oxidation state of manganese [45, 46]. Furthermore, some researchers showed Mn₂O₃ can also enhance ORR catalysis in the presence of another catalyst [44, 47]. Therefore, mediated electron transfer from co-catalyst may enhance the ORR catalytic activity at Mn₂O₃. Based on the earlier studies, it is proposed that ORR on Mn₂O₃ can process through mediation involving the reduction of Mn₂O₃ to MnOOH, followed by electron transfer from Mn³⁺ to oxygen [48, 49]. Takashima et al have reported that Mn³⁺ is stable in alkaline solution at the high potential region of OER [50]. However, in the potential window of ORR, due to applied potentials along with the presence of co-catalyst (i.e. RuO₂), the possibility of disproportionation (i.e. to form Mn²⁺ and Mn⁵⁺) or reduction of the Mn³⁺ state cannot be ruled out [49–51]. Thus, following ORR mechanism can be expected on the MC and RMC catalysts directly at the Mn₂O₃ and disproportionated or reduced Mn⁴⁺ surface [52].

\[
\text{MnO}_2 + \text{H}_2\text{O} + e^- \leftrightarrow \text{MnOOH} + \text{OH}^- \\
2\text{MnOOH} + \text{O}_2 \leftrightarrow (\text{MnOOH})_2 + \text{O}_{2(ad)} \\
(\text{MnOOH})_2 + \text{O}_{2(ad)} + e^- \leftrightarrow \text{MnOOH} + \text{O}_{ad} + \text{OH}^- + \text{MnO}_2 \\
\text{MnOOH} + \text{O}_{ad} + e^- \leftrightarrow \text{MnO}_2 + \text{OH}^-.
\]
A. LSVs measured at a sweep rate of 10 mV s$^{-1}$ in N$_2$-saturated 0.1 M KOH and (b) Tafel plots for CNF, RC, MC2, RMC2 and Pt/C.

Although RuO$_2$ is well known for OER, it does possess ORR catalysis through the mechanism proposed in figure S8d [53]. The different ratios of Mn$_2$O$_3$:MnO$_2$ and change in the active state of Mn$_2$O$_3$ by applied potential are possible rationales for the difference in ORR catalytic activity along with the different amounts and morphologies of deposited Mn$_2$O$_3$ and RuO$_2$ in RMC samples.

The double-layer capacitive region is a precise indicator of an electrochemically active surface area (ECSA). The ECSA of RMCs and RC samples were estimated from the double-layer capacitance ($C_{dl}$) by measuring non-Faradic capacitive current from the CVs measured at different scan rates (figure S10 and figure S10 note). The ECSA was increased from RMC1 to RMC2 due to the higher loading of RuO$_2$ on RMC2 sample, but when the amount of RuO$_2$ was further increased in RMC3, ECSA and RF were decreased compared to RMC2 due to the agglomeration of RuO$_2$ nanoparticles. The effect of ECSA and roughness factor (RF) was in agreement with the electrochemical measurements of ORR and OER.

The electrocatalytic activity of the samples towards OER in 0.1 M KOH aqueous solution was measured via LSV (figures 6(a) and S11(a)) and the overpotential for OER was considered as $\eta = E$ versus RHE$-1.23$ V. Table 2 summarizes all parameters obtained for the samples in this part. As shown, the onset potential of OER at RMC2 ($\eta \sim 0.2$ V) is the most cathodic, indicating best OER catalytic activity among these catalysts and in good agreement with the usual meanings. The lower the value of the Tafel slope, better the catalytic performance with rapid kinetics. The lowest Tafel slope of 52 mV dec$^{-1}$ was achieved for RMC2 indicating better OER kinetics compared to the other samples (table 2). According to the Zeradjanin et al. ‘crack’ RuO$_2$ films exhibited superior OER activity than the ‘crack-free’ structure. In other words, more exposed edges of RuO$_2$ proves better catalytic activity than the plain films [58]. Thus, it proves the importance of morphology of catalysts. Considering this phenomenon, deposition of nanoparticles of RuO$_2$ is preferred in this work so that, the nanoparticle surface acts like the cracked surface of RuO$_2$ film to increase efficient catalytically active sites towards OER. Our results further confirm this hypothesis where RMC2 was superior over RMC3 and RC which have agglomerated RuO$_2$ nanoparticles, thus, reducing the edges or catalytically active sites. In addition, better OER catalysis of RMC2 over RMC1 is expected due to the high amount of RuO$_2$ in RMC2. The overall reaction at the RuO$_2$ is elaborated in figure S11(c) as proposed earlier for the bimetallic composites [55]. Another possibility of the cathodic shift in the onset potential of OER might be due to the contribution from Mn$^{3+}$ which is stable in an alkaline medium which proved to be effective OER catalyst.

The kinetic parameters were measured by plotting overpotential against log ($j$) for all RMCs and RC samples (figures 6(b) and S11(b)), based on the fundamental equation (3):

$$\eta = a + (2.3RT/\alpha nF) \log (j),$$

where $j$ is the current density and other symbols have their usual meanings. The lower the value of the Tafel slope, better the catalytic performance with rapid kinetics. The lowest Tafel slope of 52 mV dec$^{-1}$ was achieved for RMC2 indicating better OER kinetics compared to the other samples (table 2). According to the Zeradjanin et al. ‘crack’ RuO$_2$ films exhibited superior OER activity than the ‘crack-free’ structure. In other words, more exposed edges of RuO$_2$ proves better catalytic activity than the plain films [58]. Thus, it proves the importance of morphology of catalysts. Considering this phenomenon, deposition of nanoparticles of RuO$_2$ is preferred in this work so that, the nanoparticle surface acts like the cracked surface of RuO$_2$ film to increase efficient catalytically active sites towards OER. Our results further confirm this hypothesis where RMC2 was superior over RMC3 and RC which have agglomerated RuO$_2$ nanoparticles, thus, reducing the edges or catalytically active sites. In addition, better OER catalysis of RMC2 over RMC1 is expected due to the high amount of RuO$_2$ in RMC2. The overall reaction at the RuO$_2$ is elaborated in figure S11(c) as proposed earlier for the bimetallic composites [55]. Another possibility of the cathodic shift in the onset potential of OER might be due to the contribution from Mn$^{3+}$ which is stable in an alkaline medium which proved to be effective OER catalyst.

The SEM and TEM images of RMC samples clearly shows that RuO$_2$ forms nanoparticles with partially covering the surface of Mn$_2$O$_3$, in other words, uncovered surface of Mn$_2$O$_3$ can act as the sites for OER catalytic reactions. Takahshima et al. have reported that in the alkaline solution

<table>
<thead>
<tr>
<th>Sample</th>
<th>Onset potential V versus RHE</th>
<th>No. of electrons</th>
<th>Tafel slope mV dec$^{-1}$</th>
<th>$E_{1/2}$ at 400 rpm V versus RHE</th>
<th>$j_k$ at 820 mV mA cm$^{-2}$</th>
<th>$j_k$ at 720 mV mA cm$^{-2}$</th>
<th>$i_0$ mA cm$^{-2}$</th>
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<tbody>
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<td>MC1</td>
<td>0.90</td>
<td>3.81</td>
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<td>0.65</td>
<td>0.525</td>
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<td>0.68</td>
<td>0.536</td>
<td>1.47</td>
<td>5.546</td>
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<tr>
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<td>0.295</td>
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<td>5.163</td>
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<td>1.514</td>
<td>31</td>
<td>7.063</td>
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<tr>
<td>RMC2</td>
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<td>7.178</td>
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<tr>
<td>RMC3</td>
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<td>2.95</td>
<td>134</td>
<td>0.8</td>
<td>0.797</td>
<td>2.95</td>
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<td>0.555</td>
<td>1.22</td>
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<td>119</td>
<td>0.85</td>
<td>5.979</td>
<td>70</td>
<td>8.222</td>
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<tr>
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<td>3.4</td>
<td>133</td>
<td>0.62</td>
<td>0.033</td>
<td>0.365</td>
<td>4.487</td>
</tr>
<tr>
<td>Sample</td>
<td>ESCA/cm²</td>
<td>RF</td>
<td>Onset η/V</td>
<td>η to 10 mA cm⁻²/V</td>
<td>Tafel slope/mV dec⁻¹</td>
<td>TOF/s⁻¹</td>
<td>j at 0.34 V mA⁻¹ cm⁻²</td>
</tr>
<tr>
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</tr>
<tr>
<td>MC1</td>
<td>—</td>
<td>—</td>
<td>0.5</td>
<td>1.13</td>
<td>124</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>MC2</td>
<td>—</td>
<td>—</td>
<td>0.45</td>
<td>0.69</td>
<td>113</td>
<td>0.00358</td>
<td>1.95</td>
</tr>
<tr>
<td>MC4</td>
<td>—</td>
<td>—</td>
<td>0.45</td>
<td>0.919</td>
<td>166</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>RMC21</td>
<td>67.2</td>
<td>950.76</td>
<td>0.25</td>
<td>0.47</td>
<td>63</td>
<td>0.00577</td>
<td>5.57</td>
</tr>
<tr>
<td>RMC22</td>
<td>67.7</td>
<td>957.83</td>
<td>0.2</td>
<td>0.34</td>
<td>52</td>
<td>0.01417</td>
<td>10.05</td>
</tr>
<tr>
<td>RMC23</td>
<td>54.5</td>
<td>771.08</td>
<td>0.27</td>
<td>0.36</td>
<td>55</td>
<td>0.00848</td>
<td>8.87</td>
</tr>
<tr>
<td>RC</td>
<td>56.8</td>
<td>803.62</td>
<td>0.2</td>
<td>—</td>
<td>58</td>
<td>0.00775</td>
<td>1.87</td>
</tr>
</tbody>
</table>
(typically more than pH 9) Mn$^{3+}$ ions are free from the disproportionation reaction and stabilized by a symproportionation reaction at high pH using in situ spectroscopic determination [50]. Furthermore, Browne et al also speculated it might be one of the reasons for OER catalytic enhancement at the Mn/Ru complex [30]. Thus, Mn$^{3+}$ can catalyze OER through the stable symproportionation reaction. Although Mn$^{3+}$ is also acting as OER catalyst, in comparison with MC samples, RMCs show the cathodic shift in the onset potential which clearly shows that contribution of RuO$_2$ nanoparticle edges is higher than the Mn$^{3+}$ catalyst.

Till the date, IrO$_2$ and RuO$_2$ are considered as the most favorable state-of-the-art catalysts for the OER. Note that the overpotential required to achieve 10 mA cm$^{-2}$ of RMC2 (340 mV) is 20 mV anodic to the IrO$_2$ (320 mV) and better than RuO$_2$ (390 mV) [56, 59]. Therefore, overall enhancement in the catalytic activity of RMC samples was expected as the synergistic effect of Mn$_2$O$_3$ and RuO$_2$ towards the ORR and OER.

In the light of practical applications in non-aqueous media and in order to further confirm excellent synergistic effect in RMC sample, the prepared materials were utilized in Na–O$_2$ cells as the cathode electrodes. Galvanostatic discharge/charge tests at 0.05 mA cm$^{-2}$ (figure 7(a)) indicate the higher specific capacity For RMC2 (9352 mAh g$_{\text{carbon}}$$^{-1}$) compared with CNF (1395 mAh g$_{\text{carbon}}$$^{-1}$), MC2 (3108 mAh g$_{\text{carbon}}$$^{-1}$) and RC (4839 mAh g$_{\text{carbon}}$$^{-1}$) at the end of discharge with the cutoff potential of 1.5 V. The following charging profiles consist of two main plateaus at lower (~2.4 V) and higher (~4 V) potentials which are assigned to the decomposition of NaO$_2$ and the side products (mainly Na$_2$CO$_3$), respectively [60]. According to the overall discharge/charge measurements, RMC2 not only exhibits higher specific capacity by promoting the formation and decomposition of NaO$_2$, it also facilitates side products decomposition during charge at lower potential (3.838 V) compared to CNF (4.226 V), MC2 (4.077 V) and RC (3.963 V). In order to have a better understanding of the nature of discharge product, Raman spectroscopy of the samples at the end of discharge was investigated (figure 7(b)). The dominance of the Raman band at 1156 cm$^{-1}$ confirms the deposition of NaO$_2$ as the main discharge product during ORR [4, 61]. However, drastic morphological differences of deposited NaO$_2$ were observed between discharged CNF and the other discharged cathodes (figures 7(c)–(f) and S12). Figures 7(c) and S12 and (e) show that micron-sized cubic NaO$_2$ particles are deposited at CNF cathode after discharge, compatible with the report of Hartmann et al [61, 62]. By incorporating Mn$_2$O$_3$ and/or RuO$_2$ on CNF, no further cubic particle was observed on the discharged cathodes (figures 7(d)–(f) and S12), instead, the samples were buried under a conformal coating of NaO$_2$. This behavior is well understood in Li–O$_2$ batteries in which the morphology of Li$_2$O$_2$ discharge product is transformed from conventional toroidal particles to film coating by introducing catalyst on the surface of carbonaceous backbones [63, 64]. In fact, this change is ascribed to the favored adsorption energy of peroxide and superoxide species on the surface of catalyst as the discharge product nucleation spots and the following growth [65, 66]. Therefore, the catalytic reaction can be performed throughout the entire 3D RMC structure rather than only in some local regions as observed in CNF. There is no precipitate observed in the SEM images of the cathodes after charging, indicating that the cathodes have reversibly recovered their structures at the end of complete discharge/charge cycle (figure S13). All of the above mentioned results confirm that RMC is an efficient catalyst for both aqueous and non-aqueous media.

4. Conclusions

In this study, a highly effective 3D RuO$_2$/Mn$_2$O$_3$/CNF ternary composite has been prepared and used as the bifunctional electrocatalyst for ORR/OER. Three sets of Mn$_2$O$_3$/CNF composites with different Mn$_2$O$_3$ amounts are prepared by a microwave synthesis method and according to the electrochemical results towards ORR/OER, the composite with medium amount of Mn$_2$O$_3$ is selected for RuO$_2$ deposition in the second microwave synthesis step. The RuO$_2$/Mn$_2$O$_3$/CNF composite demonstrated superior ORR/OER activity compared to the other samples prepared in this work and state of the art RuO$_2$ and IrO$_2$ type materials. In order to validate the applicability of the catalyst in non-aqueous media, the catalysts were used as cathode materials in Na–O$_2$ cells and RuO$_2$/Mn$_2$O$_3$/CNF showed 6.7 fold specific capacity as CNF. This enhancement is attributed to the synergistic effect of highly electronically conductive CNF
core and RuO$_2$–Mn$_2$O$_3$ shell, as well as the novel 3D morphology of the composite. The more exposed edges and uniform distribution of RuO$_2$ nanoparticle in RuO$_2$/Mn$_2$O$_3$/CNF is due to the trapping effect of Mn$_2$O$_3$ nano-rods, which is confirmed by TEM and SEM results. The 3D design of Mn$_2$O$_3$–RuO$_2$ which are of mostly known catalysts for ORR and OER, respectively, is introduced for the first time in this work, to achieve highly active bi-functional catalyst for ORR and OER.

Acknowledgments

This study is financially supported by The Scientific and Technological Research Council of Turkey (TUBITAK) with the project No. 115M375.

ORCID iDs

Mohammad Fathi Tovini @ https://orcid.org/0000-0003-4334-4471
Blushan Patil @ https://orcid.org/0000-0003-1659-4715
Tamer Uyar @ https://orcid.org/0000-0002-3989-4481

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