**The Effects of Morphology, Microstructure and Mixed-valent States of MnO₂
on the Oxygen Evolution Reaction Activity in Alkaline Anion Exchange
Membrane Water Electrolysis**

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Abstract

In this work, we focused on the evaluation of oxygen evolution reaction (OER) activity of three different shapes of α -MnO₂ nanowires (NWs), nanorods (NRs) and nanotubes (NTs) in alkaline anion exchange water electrolyser. We have attempted to separate the effect of shape, surface area, Mn³⁺ content and crystal facets on OER activity and stability. X-ray photoelectron Spectroscopy (XPS) measurements showed that NTs had the highest surface concentration of Mn³⁺ on the as prepared samples with average Mn oxidation state of 3.33. However, after activation an increase in the average oxidation state of all three shapes to 3.9 was confirmed by XPS. X-Ray Diffraction (XRD) showed surface restructuring after testing. MnO₂ NWs showed the highest OER mass activity of 60.6 A g⁻¹ (10 mA cm⁻² at 1.67 V (RHE)) due to the higher surface area of 72.2 m² g⁻¹. While NTs showed the highest specific activity due to highest content of 211 facet, high Mn³⁺ surface concentration /surface defects. Similar trend was observed in electrolyser testing with 2 mg cm⁻² loading. Poor electronic conductivity of MnO₂ resulted in decrease in performance with increased loading to 4 mg cm⁻². All the studied shapes showed good stability over 36 h of electrolyser testing.

Key words: α -MnO₂ nanostructures, alkaline electrolyser, crystal facets, oxygen evolution reaction, turn over frequency, magnetic properties

1. Introduction

Oxygen evolution reaction (OER) is very important process in electrochemical energy conversion and storage technologies such as alkaline electrolyzers, and metal-air batteries [1-8]. OER is an electrochemical oxidation process which will produce molecular oxygen by electrolysis of water. The reaction of oxygen production at the water electrolyser anode is sluggish. As a result of this, it requires a high overpotential to overcome the activation barrier and enhance the reaction rate. Electrocatalysts play a vital role in reducing the overpotential and improve the OER activity. IrO_2 and RuO_2 remain the benchmark catalysts for OER in acidic media [9-12]. Even though they are durable, they have low abundance and high cost. Alkaline media has the advantage over acidic media of faster OER and the ability to use low cost non-precious metal catalyst such as chalcogenides [13, 14], perovskites [15-18], spinels [19, 20], metal oxides [21-24], mixed metal oxides [25], and various combinations of them. Manganese oxides remain very attractive candidate for OER due to their high abundance, eco-friendliness, low-cost and promising OER activity [26-30]. Modification of MnO_x nanomaterial with Au and Pt was reported to lower the overpotential at 10 mA cm^{-2} by 300 – 500 mV and enhance the OER activity [31]. The crystallographic structures of MnO_2 strongly influence both the OER and oxygen reduction reaction (ORR) activities and the activities were reported to follow the order $\alpha\text{-MnO}_2 > \text{amorphous MnO}_2 > \beta\text{-MnO}_2 > \delta\text{-MnO}_2$ [32]. Furthermore, Mn-based non-stoichiometric oxides, perovskites, layered perovskites and bi-nuclear Mn complexes as biological mimicking systems are considered as vital catalysts for water oxidation [33, 34].

In addition, the mixed-valent states of manganese enabled range of catalytic applications in both the crystalline and amorphous forms which could be influenced by doping or inclusion of other elements [35]. However, to the best of our knowledge, the effect of morphology of $\alpha\text{-MnO}_2$

on OER activity and resultant electrolyser performance has not yet been investigated thoroughly. Here, we employed three most distinct α -MnO₂ geometrical-shapes, namely nanowires, nanorods and nanotubes in order to investigate the effects of morphologies on their electrochemical OER activities by using various characterisation techniques including Brunauer-Emmett-Teller (BET), X-ray diffraction (XRD), field-emission scanning electron microscope (FE-SEM), transmission electron microscope (TEM), X-ray photoelectron spectroscopy (XPS), magnetometry and Cyclic Voltammetry studies. The mass activity, surface activity, Tafel slope and the turn over frequencies (TOF) were calculated and compared. Electrolyser testing was also performed using same concentration of NaOH at different temperatures. Our results reveal the influence of morphology, surface area and nature of Mn species on the electrocatalytic activity of α -MnO₂.

2. Experimental

2.1 Materials Used

KMnO₄ (99%, Merck), MnSO₄·H₂O (98%, Merck), HCl (37%≥, Merck), KOH (85% ≥ Merck), NaOH (98%, Merck), H₂SO₄ (98.08%, Fisher Scientific), Ethanol (99.9%, Hayman), and Mn₂O₃ (Sigma Aldrich) were used.

2.2 Preparation of MnO₂ nanostructures

We used hydrothermal method to prepare α -MnO₂ with different morphologies like nanowires (NWs), nanorods (NRs) and nanotubes (NTs). The synthesis of NWs was carried out at 140 °C for 24 h by using 0.47 g of KMnO₄ and 0.50 g of MnSO₄·H₂O in 30 ml distilled H₂O in a 50 ml teflon-lined stainless still autoclave. NRs were prepared by using 0.394 g of KMnO₄ and 0.17 g of MnSO₄·H₂O in 35 ml distilled H₂O at 180 °C for 16 h. To prepare NTs, we treated 0.45

g of KMnO_4 and 1 ml of HCl (37%) in 40 ml distilled H_2O at 140 °C for 12 h. The detailed synthesis procedures were explained in our earlier reports [36, 37].

2.3 Characterization

The phase formation and crystalline structure of the synthesized MnO_2 materials were examined by powder X-ray diffraction (XRD, X'pert Pro, PANalytical) using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) in the 2θ range from 10° to 80° in 0.02° steps and a count time of 0.2 s at each step. The resulting diffraction patterns were refined using Rietveld method [38, 39] using TOPAS Academic V6 [40]. Thermo-gravimetric analysis (TGA) of the MnO_2 nanostructures were carried out using TA instrument (SDT Q600) from room temperature to 800 °C with a heating rate of $10^\circ\text{C min}^{-1}$ in air and is reported in supplementary information (Figure S2). Scanning Electron Microscope (SEM) (BRUKER, VEGA3, TESCAN, Germany) equipped with energy dispersive X-ray (EDX) was used for chemical composition analysis. Field-emission SEM (FE-SEM; Supra 55VP, Carl Zeiss) with an acceleration voltage of 5–30 kV was used to study morphology and surface nature. The size and distribution of MnO_2 samples were examined using a transmission electron microscope (TEM, G² 20, Tecnai) working at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopic (XPS) analysis of the MnO_2 samples was performed using the photoelectron spectrometer (Kratos Axis Supra) with $\text{Al K}\alpha$ (1486.7 eV) source. The Brunauer-Emmett-Teller (BET) surface area of the synthesized samples were analysed by N_2 sorption isotherm at 77 K (Thermo Scientific, Surfer). The conductivity of the powders were measured by making a pellet from the powder by applying a pressure of 4000 kg cm^{-2} . The pellet was then compressed at 1000 kg cm^{-2} and resistance measurements were taken. The magnetic properties of $\alpha\text{-MnO}_2$ nanostructures were measured using physical property measurement system (PPMS,

Dynacool, Quantum Design). The zero field cooled and field cooled magnetization data were collected between 2 and 300 K during warming. The applied magnetic field was 1000 Oe. The M-H measurements were carried out both at 300 and 5 K.

2.4 Electrochemical measurements

Oxygen evolution experiments were carried out using a Gamry potentiostat (model IFC 5000E) and 3 mm gold stationary electrode (BASi®- MF-2114) . 0.275 mg cm⁻² loading mass of the catalyst was dispersed in PTFE (5 wt%) and 1-Methyl-2-pyrrolidone ultrasonically and it was drop casted on gold electrode. Then it was dried naturally at room temperature and used for electrochemical measurements. 1.7 V (RHE) for 30 mins was applied to activate the catalyst surface and then recording 1 mV s⁻¹ linear sweep voltammetry in 0.1 M KOH solution. Electrochemical impedance spectroscopy at 1.7 V (RHE) was also recorded before and after holding at 1.7 V. A Pt mesh was used as a counter electrode and Hg/HgO as a reference electrode. All the potentials in this paper are reported versus the RHE scale (S8).

The turn over frequency (TOF) is defined per metal atom including subsurface metal per second, it is calculated by assuming that every metal atom is involved in the catalysis (lower TOF limits were calculated) [32, 41-44]:

$$TOF = \frac{j \cdot S_{geo}}{4F \cdot n} \quad (1)$$

where, j (mA cm_{geo}⁻²) is the measured current density at $E = 1.7$ V vs RHE, S_{geo} (0.07 cm²) is the geometric surface area of working electrode, F is Faraday's constant and n is the number of moles of metal atom on the electrode. Since several reports in the literature used geometric surface area

current density rather than specific area current density to report TOF for MnO₂ and other metal oxides [32, 41-44], we have also calculated the TOF with respect to the geometric surface area.

2.5 Electrolyser measurements

For the electrolyser single cell testing, titanium was used for the cell body with gold coated serpentine flow fields (active area- 1 cm²) surrounded by O-ring seal. The temperature of the cell was controlled by thermostatically controlled cartridge heaters inserted into the cell body. 300 µm Titanium fibre felt GDL (Bekaert S.A. Fibre Technologies, Netherlands) with 78% porosity was used at the anode. The anode catalyst was sprayed on the Titanium GDL with ionomer (ACTA I2) content of 12.5% wt (30% vol) with catalyst loading of 2 and 4 mg cm⁻².

Non-wet proof carbon GDL with MPL (Freudenberg Germany) was used at the cathode 20% Pt/C, 28 wt.% ionomer (ACTA I2) and isopropanol was mixed and sprayed on the carbon GDL/ with loading of 0.4 mg_{Pt} cm⁻². LDPE-VBC-TMA based alkaline anion exchange membrane was used [45]. The electrolyser cell was assembled by sandwiching the cathode and anode either side of the membrane. ETFE gasket was added to the cathode side to create the required seal. Gamry potentiostat (IFC 5000E) instrument was used to conduct the electrochemical analysis. The experiment was run at a concentration of 0.1 M NaOH by pumping the solution to both anode and cathode separately and a temperature range from 20 °C- 60 °C. Long-term stability of the catalyst was determined by holding at 2 V for 36 h at 40 °C in 0.1 M NaOH solution and recording cyclic voltammetry and impedance at different intervals.

3. Results and Discussions

3.1 Material characterization, morphological and surface analyses

Figure 1. X-ray diffraction patterns of the different MnO₂ nano shapes (a) Pristine, (b) after stability testing in 0.1M NaOH at 40 °C for 36 h.

Figure 1 shows the powder XRD patterns of the synthesized MnO₂ nanostructures. All the reflections can be indexed based on the body-centered tetragonal α -MnO₂ structure (JCPDS No. 044-0141) [46] with crystalline size of 19.6 nm (NWs), 21.4 nm (NTs) and 20 nm (NRs). Rietveld refinement (**Figure S1**) was used to estimate the composition ratio of two polymorphs of

MnO₂, alpha (space group: I4/m) and beta (P42/mnm) within 0.2% error. All three prepared MnO₂ shapes contained over 85% of alpha phase which is reported to be the most active for OER [32, 47]. NRs had 89 and 11% while NWs had 85 and 15% and NTs had 87 and 13%, of α -MnO₂ and β -MnO₂ phases, respectively. The amount of variation of content of α -MnO₂ between all the three samples is small (<5%) to warrant alone a significant difference in the performances. The NWs have slightly different lattice parameter compared to both NTs and NRs which has almost similar parameter for both the phases (**Table 1**).

Table 1. Lattice parameters calculated using Rietveld method from X-ray Diffraction

Sample	α -MnO ₂			β -MnO ₂	
	a (Å)	c (Å)	a/c	c (Å)	c (Å)
Nanowires	9.845	2.859	3.444	4.362	2.988
Nanotubes	9.828	2.859	3.438	4.382	3.028
Nanorods	9.832	2.859	3.439	4.380	3.014

Table 2. Percentage area of the main four facets from XRD for Pristine and aged sample after testing in 0.1M NaOH solution for 36 h.

Facet	Nanowires		Nanotubes		Nanorods	
	Pristine	Tested	Pristine	Tested	Pristine	Tested
(110)	19.57	20.58	19.32	22.69	18.44	21.31
(200)	21.23	18.42	19.67	19.08	21.95	24.89
(310)	32.67	40.74	33.85	38.47	34.08	39.26
(211)	26.52	20.26	27.16	19.76	25.53	14.54

Looking into the microstructure, four main dominant facets (110, 200, 310 & 211) of the XRD diagram were analysed further before and after the electrolyser testing. To study any changes to the content of these facets, peak areas obtained by integration and the content percentage was calculated with respect to these 4 main selected facets (**Table 2**). We have focused content of 310/211 facets ratio as this has been shown to be directly linked to the microstructure and exposed planes on the sidewall surface of the grown NTs/NWs/NRs [48]. While there have been no studies reported so far on the specific activity of these facets towards OER, higher 310 facets content was directly linked to 110 exposed plane of MnO₂ side walls and showed lower capacity for Li intercalation in comparison to the 210 plane which is rich in 211 facet [48]. Furthermore, Selvakumar et.al [36] used Density Functional Theory approach on the above 4 facets and confirmed that the oxygen reduction reaction (ORR) happens more favorably on the 211 facet compared to 310, 200, 110 with 211 facets showing the lowest activation energy of reaction. A study by Jia et.al [49] also suggested that the 211 facet was the most active towards decomposition of ozone compared to 110 and 200.

NWs and NTs had similar 211/310 facets ratio of 0.81 while NRs had lower value of 0.75. Interestingly, the content of the facets changed significantly in the samples after testing with the amount of 211 facets decreasing and the 310 facet increasing by different amount in all the studied samples. The ratio of content of 211/310 changed to 0.5 for NWs, 0.52 for NTs and 0.37 for NRs. This change could suggest either higher dissolution rates of the most active 211 facet or dynamic surface restructuring under OER. Universal correlation has been reported between the oxygen evolution activity and the corrosion of metal oxides [50]. Binninger et. al [51] studied the thermodynamic stability of the metal oxides for OER catalysts and showed that the metal oxides

undergo significant structural changes due to the dissolution of the catalyst and re-deposition on the surface caused by the instability of oxygen anion in the metal oxide lattice.

α -MnO₂ has a tunnel structure with K⁺, Na⁺ or H₃O⁺ ions occupying the tunnel. The Mn/K atomic ratio was found to be $\sim 10 \pm 3\%$ for all samples using EDX (**Table 3**) which testifies the tunnel type α -MnO₂ structure. **Figure S3** represents the FE-SEM (a, c and e) and TEM (b, d and f) images of different MnO₂ shapes prepared in this work. The thickness and length of all the shapes were measured by taking 50 readings using ImageJ and the values obtained are reported as average and range below. Nanowires were grown into average of 2-3 μm in length with an average of 40 ± 8 nm in diameter (**Figure S3a and b**). Similarly, nanotubes composed of a moderate wall thickness with an average value of 35 ± 7 nm and an average inner tube diameter of ~ 20 nm bringing the total diameter to 90 ± 14 nm as can be seen in **Figure S3c and d**. Nanorods display an average length in the range of 1-2 μm with an average diameter of 76 ± 15 nm (**Figure S3e and f**). The SEM figures (**Figure S3 a, c, e**) shows the size range of the all the shapes and the TEM figures (**Figure S3 b, d, f**) shows typical shape profile of the various MnO₂ shapes synthesized in the study. The variation in morphologies e.g tube vs rod, diameter and length of the synthesized materials will result in difference in surface area and consequently differences in mass activity. Theoretical surface area of these shapes are calculated by considering a cylinder and using the average diameter as obtained above using ImageJ and length of 2 μm . The estimated surface area from the average dimension values measured by SEM/TEM is in good agreement with BET measurements shown in **Table 3**.

Table 3. The calculated BET, EDX and XPS structural parameters for as prepared MnO₂ shapes studied in this work.

Sample	BET surface area (m ² g ⁻¹)	Theoretical surface area (m ² g ⁻¹)	Mn atomic %	K atomic %	Atomic ratio Mn/K	XPS $\Delta 2p$ value / eV	Average Oxidation State
Nanowires	72.2	59.4	35.85 ± 0.72	3.58 ± 0.07	10.01 ± 0.20	11.67	3.62 ± 0.25
Nanotubes	21.1	19.5	26.02 ± 0.52	3.18 ± 0.06	8.18 ± 0.16	11.78	3.35 ± 0.25
Nanorods	24.8	16.5	31.42 ± 0.63	3.11 ± 0.06	10.10 ± 0.20	11.61	3.81 ± 0.25

The N₂ adsorption-desorption isotherms of the three α -MnO₂ samples with different morphologies are shown in **Figure S4a**. The BET specific surface area of α -MnO₂ nanowires is the highest by a factor of ca. 3 (72.2 m² g⁻¹) among all the three samples (**Table 3**). There is an inherent link between the prepared shapes and their surface area e.g. the main difference between nanorods and nanowires are the length and diameter and therefore specific surface area.

The surface of the α -MnO₂ samples were studied *ex-situ* using XPS technique (**Figure 2 and S5**). The core-level XPS signal of Mn 2p in all the three α -MnO₂ samples showed the Mn 2p_{3/2} and 2p_{1/2} centered at 642.5 and 654.4 eV, respectively suggesting predominant Mn⁴⁺ [52-54]. However, there was a distinct shoulder present at the lower binding energy which is attributed to Mn³⁺. Peaks were fitted by modifying the model reported by Besieger [55] using mix of Lorentzian and Gaussian line due to asymmetrical peaks. All of the samples contained around 20-21% of Mn³⁺ using the fitting of Mn 2p peaks (**Figure S5a**). However, to get the average oxidation state (AOS) of the different samples, Mn 3s peaks are fitted [56-62] and AOS was calculated using equation 2 [49, 56-58].

$$\text{AOS} = 9.67 - 1.27 \times \Delta E_{3s} \quad (2)$$

where, ΔE s - Difference between peaks of 3s orbital

The AOS for the different shapes as calculated from the Mn 3s peak fitting, are shown in **Figure 2a**, are 3.62 ± 0.25 (NWs), 3.35 ± 0.25 (NTs) and 3.81 ± 0.25 (NRs) by taking into account an error of ± 0.1 eV in the peak positions. This clearly shows that the as prepared nanotubes has higher Mn^{3+} content on the surface compared to other two samples.

Figure 2. XPS fitting on Mn 3s peaks for different shapes of MnO_2 catalysts.

The surface content of Mn^{3+} was measured after electrolyser testing for all three samples. While the Mn 2p spectrum didn't show significant change (**Figure S5**), there was noticeable change in the Mn 3s spectra (**Figure S5**) and the calculated AOS of the materials have increased to around 3.9 for all the samples suggesting the increased amount of higher oxidation states of Mn. This is expected as under OER conditions the higher electrode potential will result in increase in oxidation of Mn^{3+} to Mn^{4+} depending on the applied potential [63]. This is also in good agreement with restructuring of MnO_2 surface after testing seen in XRD analysis above.

Electrical conductivity

Figure S4b shows the effect of applied compression on the electrical conductivity of the as prepared MnO_2 samples with NTs having the highest conductivity among all samples. However, the difference in the two-point probe electrical conductivity while relatively small for

all the powders ($0.0083\text{--}0.0128\text{ S cm}^{-1}$ at 1000 kg cm^{-2}) is still significant, with a factor of 1.5. The overall measured conductivity values for the tested $\alpha\text{-MnO}_2$ is in good agreement with the range of values reported in literature [64–66]. The electrical conductivity for NTs synthesized in the current study was 12.8 mS cm^{-1} (at 1000 kg cm^{-2}) which is in good agreement with the value of 17 mS cm^{-1} reported to provide an optimum trade-off between electrical conductivity and $\text{Mn}^{4+}/\text{Mn}^{3+}$ ratio (defects) for maximum ORR catalytic activity [64], while NW (8.7 mS cm^{-1}) and NR (8.3 mS cm^{-1}) had slightly lower values. While higher electrical conductivity may result in better catalyst utilization and lower charge transfer resistance, it should be stressed that the optimal ratio of $\text{Mn}^{4+}/\text{Mn}^{3+}$ mentioned above in [64] was measured using XPS on as prepared samples and does not necessarily reflect the $\text{Mn}^{4+}/\text{Mn}^{3+}$ in the bulk content which will impact electrical conductivity or does not take into account the mass loading of used MnO_2 catalyst or changes of Mn oxidation state under (increase) OER or (decrease) ORR test conditions [63].

Importantly, under OER conditions and with increase in Mn AOS, decrease in electrical conductivity is expected. This was seen by increase in electronic area specific resistance of catalyst (high frequency resistance) by 8% ($0.37\text{ }\Omega\text{ cm}^2$) for NWs and 10% ($0.59\text{ }\Omega\text{ cm}^2$) for NRs and 27% ($1.37\text{ }\Omega\text{ cm}^2$) for NTs (see section 3.2 below). Interestingly, NTs which showed the highest Mn^{3+} surface content and highest electronic conductivity in as prepared samples showed the largest decrease in electrical conductivity after testing. This suggest after activation the highest electronic conductivity become in the order of $\text{NRs}\approx\text{NTs}>\text{NWs}$ which is in agreement with high frequency impedance intercept recorded in electrolyser tests in inserts in **Figure 5 b, d & f**.

The torque applied of (2 N m^{-2}) to tighten the electrolyser cell will result in low applied pressure/compression on catalyst layer compared to the force applied here in ex-situ conductivity

measurement and hence it is expected that lower electrical conductivity of the different powders will be seen in operating electrolyser.

The conductivity values of MnO_2 are also similar to the ionic conductivity range of membranes and ionomers used for the alkaline electrolyzers when using de-ionised water as circulating electrolyte and lower if using supporting electrolyte of 0.1M NaOH or higher [45, 67, 68]. The poor electrical conductivity of unsupported MnO_2 will affect significantly the catalyst utilization and the current distribution in the cell particularly at high catalyst loadings (thicker electrodes) and higher current densities. The higher ionic conductivity of the ionomer in comparison to that of electronic conductivity of the catalyst will result in higher utilization of the catalyst layer away from membrane and towards the current collector.

Magnetometry

We used magnetometry to obtain further information on the nature of MnO_2 and Mn oxidation state in the bulk materials of the as prepared samples. The electron spin plays a fundamental role in determining the kinetics, enthalpy and entropy of electron transfer reactions, and these correlations are recently summarised as “spintro-catalysis”, mainly for the OER and ORR catalysts [69-71]. Magnetometric studies has recently revealed the implications of surface uncompensated spins over $\alpha\text{-Mn}_2\text{O}_3$, the presence of Mn_3O_4 and interplay between Mn^{3+} and Mn^{2+} states on the catalytic activities of nanostructured mesoporous manganese oxides [35].

Figure 3. (a) The zero field cooled (ZFC) and field cooled (FC) magnetization results of α -MnO₂ nanowires, nanotubes and nanorods. The applied field was 1000 Oe. The insets show the ZFC results in a narrow temperature range to clearly see the peaks and χ^{-1} vs. T plots in each case. (b) M-H results measured at 300 and 5 K of the same samples are compared.

Figure 3a shows the zero field cooled (ZFC) and field cooled (FC) magnetisation of as prepared α -MnO₂ NWs, NTs, and NRs between 300 and 2 K. All these samples exhibited a bifurcation between the ZFC and FC magnetisation at ~55 K. The ZFC data of NWs in the narrow temperature range reveal a peak at 18 K and a shoulder at ~40 K whereas NTs exhibit a broad peak at 26 K and NRs reveal two well separated peaks at 52 and 13 K (insets in **Figure 3a**). The Néel temperature of bulk α -MnO₂ is 25 K and depending on the particle size and morphology, a shift towards lower temperatures is already known [72, 73]. The observed magnetisation behavior of NRs is similar to the one reported for α -K_xMnO₂ in which the low temperature peak at 20 K was attributed to the spin glass transition [74]. The χ^{-1} vs. T plots show the Curie-Weiss behavior above 100 K and the Curie constant (C) and Weiss temperature (θ) were deduced by fitting the data (insets of **Figure 3a**). It is inferred from the more negative Weiss temperature (-454 K) that the antiferromagnetic interaction is the strongest for the as prepared NRs among all three samples, while it was similar for the NTs and NWs case. It has been shown that MnO₂ samples had lower

Weiss temperature of -621 K when they had high 310 facet content, while -166 K has been reported for high 211 facet content [48]. This is in line with the XRD analysis above on the pristine materials showing higher 310 facet content in NRs compared to NTs and NWs. From the M-H measurements carried out at 5 K, it was found that all the three samples show a ferromagnetic-like behavior (**Figure 3b**). The highest coercive field (H_c) of 10.15 kOe was observed for NRs when compared to those of NWs (6.8 kOe) and NTs (7.8 kOe). This suggests that the presence of ferromagnetic-like phase is dominant in NRs that contribute to the observed highest H_c . It was reported that at low concentrations of K^+ in α - MnO_2 , the ferromagnetic contribution is higher and this originates from the electron charge transfer by K^+ doping and the Mn^{3+} related Jahn-Teller distortion [71].

In our study, the presence of ferromagnetic phase is seen in all three samples with predominant contribution in NRs. The magnetic moments were calculated from the obtained Curie constant using the following relation and are listed in **Table 4**.

$$\mu_{eff.} = \sqrt{8C} \mu_B \quad (3)$$

Table 4. The obtained Curie constant, Weiss temperature (θ), and calculated effective magnetic moment ($\mu_{eff.}$) of α - MnO_2 NWs, NTs and NRs. The coercive fields (H_c) measured from the M-H data at 5 K of these samples are also listed.

Sample	C (emu K mol ⁻¹ Oe ⁻¹)	θ (K)	$\mu_{eff.}$ (μ_B)	H_c (Oe) @ 5 K
Nanowires	1.735	-282	3.73	6800
Nanotubes	1.823	-296	3.82	7700
Nanorods	2.299	-454	4.29	10150

The calculated magnetic moment for Mn^{4+} ion is $3.87 \mu_{\text{B}}$ suggesting the presence of predominately Mn^{4+} in the bulk of NWs and NTs. The experimental μ_{eff} for the as prepared MnO_2 NRs is $4.29 \mu_{\text{B}}$ suggesting the presence of higher content of Mn^{3+} in the bulk and doping by K^+ in comparison to NWs and NTs. However, this was not reflected in electrical conductivity data above where NRs and NWs had similar conductivity values. This behavior could also be due to the presences of different $\angle \text{Mn-O-Mn}$ bond angles and the uncoupled surface spins in NRs in comparison to what was observed with $\alpha\text{-MnO}_2$ nanowires [75]. Li et.al [48] also studied the effect of facet engineering on the magnetic properties of the $\alpha\text{-MnO}_2$ by using magnetometry and DFT calculations. The magnetic moments calculated above and reported in **Table 4** was obtained from Curie constant. Li et.al [48] has shown that MnO_2 samples despite containing only Mn^{4+} (albeit measured only on the surface and not bulk by XPS), they had large variation in Curie's constant. Samples rich in 310 facet (110 side wall plane) had Curie constant of $2.608 \text{ emu K mol}^{-1} \text{ Oe}^{-1}$ while samples that are rich with 211 facet (210 side wall plane) had Curie constant of $1.816 \text{ emu K mol}^{-1} \text{ Oe}^{-1}$ [48]. This is in good agreement with our XRD data obtained for the as prepared samples where NWs and NTs had similar 211/310 facet ratios and Curie's constant value. While NRs sample had lower 211/310 ratio (higher 310 content) and higher Curie's constant value.

3.2 Electrochemical oxygen evolution studies on different MnO_2 shapes

Figure 4a shows the IR corrected linear sweep voltammograms at 1 mV s^{-1} in 0.1 M KOH for three as-prepared MnO_2 electrocatalysts. The electrode potentials at 1 mA cm^{-2} were 1.61 V (NWs), 1.61 V (NTs), and 1.62 V (NRs) vs. RHE with NRs having the highest overpotential of 0.39 V . The NWs performed slightly better when compared to NTs at higher current densities. The electrode potentials at 10 mA cm^{-2} were 1.672 V (NWs), 1.688 V (NTs) and 1.706 V (NRs) vs.

RHE. This can be explained by the higher surface area of MnO₂ NWs and consequently higher mass activity since a constant mass loading of all three catalyst was applied and compared in this test. The catalyst activation of these shapes was evaluated by holding the potential at 1.7 V vs RHE and recording the change in the current density (**Figure 4b**).

Figure 3. a) IR corrected Linear sweep voltammograms at a scan rate of 1 mV s⁻¹, b) Chronoamperometry at 1.7 V (RHE), c) Nyquist plot at 1.7 V (RHE), d) IR Corrected Tafel curve of various MnO₂ nano shapes on Au electrode in 0.1 M KOH solution.

The voltammograms (**Figure 4a**) have been recorded after the activation step of 30 mins (**Figure 4b**). Within the 30 min activation the three catalysts showed a stable current density with minor changes seen in NTs from (5.42 to 4.48 mA cm⁻²). This can be explained by the largest

decrease in electrical conductivity as discussed above in section 3.1 and further below. The effect of catalyst activation can also be further analysed by comparing the impedance spectra before and after the activation step and it is shown in **Figure 4c**. For all the samples, the high frequency intercept and consequently the electronic resistance has increased which can be due to the possible increase of AOS of Mn i.e. oxidation of Mn^{3+} to Mn^{4+} and higher oxidation states as confirmed by XPS after the activation. For the NWs and NRs, the charge transfer resistance shown by the difference between low and high frequency intercepts (with Z'' axis) decreased from 4.20 to 4.03 $\Omega \text{ cm}^2$ (NWs) and 8.90 to 8.55 $\Omega \text{ cm}^2$ (NRs) after 30 min activation. This was counter balanced by increase in electronic resistance of catalyst (high frequency resistance) by 0.37 $\Omega \text{ cm}^2$ (NWs) and 0.59 $\Omega \text{ cm}^2$ (NRs) assuming that the ionic conductivity of the solution remained unchanged. However, the area specific charge transfer resistance and electronic area specific resistance for NTs increased from 6.18 $\Omega \text{ cm}^2$ to 7.50 $\Omega \text{ cm}^2$ and 4.94 to 6.31 $\Omega \text{ cm}^2$ explaining the seen slow decrease of current density of the sample in the 30 min activation step. The increase in electrical resistivity of MnO_2 can be explained by increase of Mn oxidation state in OER potential window as discussed above e.g. E° is 1.43V vs RHE for $\text{Mn}^{4+}/\text{Mn}^{6+}$ and $\text{Mn}^{4+}/\text{Mn}^{7+}$ in alkaline media.. One plausible explanation behind decrease of activity of NTs with activation in comparison to the increase seen in NWs and NRs is the higher initial content of Mn^{3+} which decreased significantly after activation due to oxidation as discussed above decreasing below the optimal level of conductivity. Moreover, decrease in electrical conductivity will result in lower catalyst utilization. The results also suggests that the trade-off between electrical conductivity and defects in MnO_2 reported for ORR [64] might not apply for OER after activation with higher operating voltages/and higher Mn oxidation states and where improvement in activity were seen (reduction in charge transfer resistance) despite decrease in electrical conductivity.

Table 5. The observed electrochemical kinetic parameters for various MnO₂ materials studied in this work using three electrode cell setup.

Catalyst	Potential (E) at $j = 10 \text{ mA cm}^{-2}$ (mV)	Specific Surface Activity at 1.70 V (A m^{-2})	Geometric Activity at 1.7 V ($\text{A m}^{-2}_{\text{geo}}$)	Mass activity at 1.70 V (A g^{-1})	Tafel slope at low j (mV dec^{-1})	Tafel slope at high j (mV dec^{-1})	TOF at 1.70 V ($\times 10^{-2} \text{ s}^{-1}$)	j_0 ($\times 10^{-14} \text{ A cm}^{-2}$)
<i>Nanowires</i>	1.672	0.84	167	60.60	28 ± 3	58 ± 4	1.36 ± 0.12	0.002
<i>Nanotubes</i>	1.688	2.07	120	43.70	36 ± 4	75 ± 5	0.98 ± 0.25	2.19 ± 0.40
<i>Nanorods</i>	1.702	1.31	89	32.50	39 ± 2	78 ± 4	0.73 ± 0.12	3.24 ± 0.20

Figure 4d shows the IR corrected Tafel plots from 0.1 to 1 mA cm^{-2} (low j) and 1 mA to 10 mA cm^{-2} (high j). **Table 5** lists all the electrochemical parameters calculated from three electrode cell testing. The Tafel slope values follows the order NRs ($39 \pm 2 \text{ mV dec}^{-1}$) > NTs ($36 \pm 4 \text{ mV dec}^{-1}$) > NWs ($28 \pm 3 \text{ mV dec}^{-1}$) for low current density region and similarly for higher current density region NRs ($78 \pm 4 \text{ mV dec}^{-1}$) > NTs ($75 \pm 5 \text{ mV dec}^{-1}$) > NWs ($58 \pm 4 \text{ mV dec}^{-1}$). The low Tafel slope in region of 30-35 mV dec^{-1} could suggest that (along with reaction order with respect to $\text{OH}^- > 0$) rate determining step is ($\text{SOOH} + \text{OH}^- \rightarrow \text{SOO}^- + \text{H}_2\text{O}$) with the increase in the Tafel slope value from ca. 30 mV dec^{-1} to ca. 60 mV dec^{-1} possibly due to the increase in the surface coverage of the reaction intermediates formed > 0.6 [76] with increase in overpotential and current density. However, since j is plotted vs geometric current density then electrode with highest roughness (NW) will have lowest current density per catalyst unit area and therefore the potential range and current density at which we transit from low to high coverage or Tafel slope regions will occur at higher values as can be seen in **Figure 4d**. The NWs showed the highest mass activity of (60.6 A g^{-1}) compared to the NTs (43.7 A g^{-1}) and NRs (32.7 A g^{-1}) as expected with NWs highest

surface. The specific activity based on surface area obtained from BET for NWs (0.84 A m^{-2}) is lower than that of NTs (2.07 A m^{-2}) and NRs (1.31 A m^{-2}). It should be mentioned that specific activity doesn't always scale linearly with surface area for example: it has been widely reported that the ORR surface specific activity of the Pt is best around 2-3 nm particle size and it does not increase if we lower the particle size further [77, 78]. So it is not necessary that with the decrease in particle size or increase in surface area, the mass activity will linearly increase. In other words, tripling the surface area will not necessarily triple the mass activity. Therefore, NTs and NRs with a third of the surface area of NWs will show higher specific activity to that of NWs when converting from mass to specific activity.

Since NRs and NTs had similar surface area, a direct comparison of their specific activity is relevant. Given the thin catalyst layer used and IR correction of electronic/ionic losses it is unlikely the electronic conductivity will have any significant effect on the measured specific activities. However, this will become pronounced in electrolyser with higher catalyst loading and when IR correction is not applied. The higher specific activity of NTs in comparison to NRs could be attributed to higher ratio of the more active 211 facet i.e. higher 211/310 facet ratio which is maintained even after activation and testing (**Table 2**). Additionally, NTs sample had the highest Mn^{3+} concentration (XPS) at the surface which is linked to highest defects, however this has changed after testing where both NRs and NTs samples had similar AOS of 3.9 on the surface.

The highest TOF value of $1.36 \times 10^{-2} \text{ s}^{-1}$ was obtained for NWs which can be explained by its higher specific surface area as the study used fixed mass loading of catalyst, which is slightly higher than that of NTs ($0.98 \times 10^{-2} \text{ s}^{-1}$) and NRs ($0.73 \times 10^{-2} \text{ s}^{-1}$) as shown in **Table 5**. These values follow the same trend as the mass activity and geometric activity based on the geometric surface area. The values used for the above calculation of TOF is the IR corrected at 1.7 V obtained

from the LSV curves in **Figure 4a**. Recently, Meng et al. [32] studied various MnO₂ nanostructures (α -MnO₂, β -MnO₂, δ -MnO₂ and amorphous) as electrocatalysts for ORR/OER reactions in alkaline media and found that α -MnO₂ possess the highest electrocatalytic activity [32]. They reported TOF values in the range of 0.08- 0.047 $\times 10^{-2}$ s⁻¹ in 0.1 M KOH solution at 1.68 V vs RHE using the geometric surface area [32]. These values are much lower than the TOF values obtained for all the samples in the current study. Similarly, the highest mass activity values reported of 23.4 A g⁻¹ [32] is lower than the lowest value obtained in this study for NRs of 32.5 A g⁻¹. The overpotential to reach a current density of 10 mA cm⁻² was 0.49 V [32] and 0.6 V [79] as compared to 0.44-0.47 V for the catalysts in current study.

We believe that the higher mass activity observed for NWs in the present study is mainly arisen from its higher surface area and higher potential values when switching from low to high Tafel slope as discussed above. Moreover, it has been reported that nanoscale transition metal oxides not only possess higher surface to volume ratios but also result in a significant shift in oxidation–reduction equilibrium, making them quite different from their respective bulk material [80].

3.3 Electrolyser performance in 0.1 M NaOH

Figure 5a shows the polarisation curves for MnO₂ catalysts in 0.1 M NaOH solution at 20 °C. The cell voltage to reach a current density of 100 mA cm⁻² were 1.88 V (NWs), 1.91 V (NRs) and 1.95 V (NTs). This shows a voltage shift of around 30-70 mV for NWs compared to other shapes. This is in agreement with the performance obtained for these materials using three electrode-cell experiments above. In contrast, the performance of NRs at high current densities (**Figure 5a** and **5c**) showed better j-V slope than that of NTs which can be explained by higher

electrical conductivity after activation as can be seen from the lower high frequency intercept from inset in **Figure 5b, 5d & 5f** and **Figure 6b & 6d**.

Figure 4. a) Polarisation at 20 °C, b) Nyquist plot at 1.7 V at 20 °C, c) Polarisation at 40 °C, b) Nyquist plot at 1.7 V at 40 °C, e) Polarisation at 60 °C and f) Nyquist plot at 1.7 V at 60 °C of various MnO₂ nano shaped catalysts in 0.1 M NaOH solution (Anode Loading: 2 mg cm⁻²)

As the amount of catalyst loading is much higher in the case of electrolyser testing compared to three electrode cell testing by a factor of 7.2, and the j-V data of the electrolyser is

not IR corrected, the performance variation in the case of NRs vs NTs at high current densities can be explained by the significant effect of catalyst electrical conductivity at high current densities and consequently different catalyst utilization and current distribution in electrode as will be discussed further below in section 3.5.

The overpotential of NWs in 0.1 M NaOH at 100 mA cm^{-2} at 20°C is very similar (20 mV higher) to that obtained with NiCo_2O_4 albeit with much lower surface area of $\sim 5 \text{ m}^2\text{g}^{-1}$ for the later [45] at the same temperature and pH conditions. The area specific resistance (ASR) (**Table 6**), as calculated from the impedance spectra shown in **Figure 5b**, of the electrolyzers using NWs anode is the highest compared to those of NRs and NTs at the same conditions. Measured ASR were $178 \text{ m}\Omega \text{ cm}^2$ (NWs), $142 \text{ m}\Omega \text{ cm}^2$ (NRs), and $155 \text{ m}\Omega \text{ cm}^2$ (NTs). As the membrane ASR is around $100 \text{ m}\Omega \text{ cm}^2$, the estimated ASR of the catalyst layer will be $78 \text{ m}\Omega \text{ cm}^2$ (NWs), $42 \text{ m}\Omega \text{ cm}^2$ (NRs) and $55 \text{ m}\Omega \text{ cm}^2$ (NTs). The contribution from the variation of the ASR at 100 mA cm^{-2} will be only 7.8 mV (NWs), 4.2 mV (NRs) and 5.5 mV (NTs) and thus the main contribution to the performance variation is due to the surface area of the catalyst. However, it should be highlighted that the effect of change in electrical conductivity on catalyst utilization and current distribution can be significant as will be discussed below. While it cannot be ruled out that the small differences measured in ASR especially between NRs and NTs is not caused by small variation in used membranes, the fact that the same ASR order was obtained in **Figure 6** (double loading) makes this unlikely.

Table 6. Area specific resistance of different catalyst at different temperatures in 0.1 M NaOH solution (Loading 2 mg cm⁻²).

Sample	20 °C (Ω cm ²)	40 °C (Ω cm ²)	60 °C (Ω cm ²)
Nanowires	0.178	0.160	0.136
Nanotubes	0.155	0.134	0.115
Nanorods	0.142	0.124	0.109

3.4 Effect of temperature on the Electrolyser performance

Figure 5c and **5e** shows the polarisation curves for MnO₂ samples in 0.1 M NaOH solution at 40 and 60 °C respectively. All the catalysts showed improved performance with temperature increase as expected. At 1.75 V, the NWs showed the highest increase with the current density rising from 56.6 (20 °C) to 76.6 (40 °C) to 96.6 (60 °C) mA cm⁻². The current density increased at 1.75 V for NTs from 42.8 (20 °C) to 55.5 (40 °C) to 72.6 (60 °C) mA cm⁻² and for NRs from 45.8 (20 °C) to 53.8 (40 °C) to 65.7 (60 °C) mA cm⁻². One factor which plays a role in the improvement of the performance is the ASR calculated from **Figures 5d and 5f** and shown in (**Table 6**). ASR have decreased for all sample with the increase in temperature and thus contributing to the improved performance of the electrolyser. Electrolyser ASR changed with the temperature increased from 20 to 40 to 60 °C from 178 to 160 to 136 m Ω cm² in NWs, 142 to 124 to 109 m Ω cm² in NRs and 155 to 134 to 115 m Ω cm² in NTs, respectively. However, as can be seen from **Figure 5**, at the studied cell voltage of 1.7 V, the charge transfer resistance is the dominant factor and it decreased as expected with temperature. As discussed above the higher surface area NWs had lower charge transfer resistance for fixed 2 mg cm⁻² loading electrodes by ~ 2-3 Ω cm² compared to the NTs and NRs across the temperature range of 20 - 60 °C.

3.5 Effect of Anode Loading on the electrolyser performance

Figure 5. a) Polarisation at 20 °C, b) Nyquist plot at 1.7 V at 20 °C, c) Polarisation at 40 °C, and d) Nyquist plot at 1.7 V at 40 °C of various MnO₂ nano shaped catalysts in 0.1 M NaOH solution (Anode Loading 4 mg cm⁻²).

Figure 6a shows the polarisation curves for MnO₂ catalysts with a loading of 4 mg cm⁻² in 0.1 M NaOH solution at 20 °C. The performance of all the catalysts decreased with the increase in the catalyst loading. However, the performance of electrolyser with NTs anode is worse than that based on NWs and NRs anodes, which exhibited similar performances. This can be explained by the trade-off of high surface area/activity of NWs and high electrical conductivity/catalyst utilization of NRs in the thick catalyst layer. NTs with lower electrical conductivity after activation than NRs and lower surface area than NWs performing the worst. The current density at a cell voltage of 1.75 V decreased by a factor of 4-5 from 56.6 to 10 mA cm⁻² (NWs), 45.8 to 11.8 mA

cm^{-2} (NRs) and 42.8 to 10.7 mA cm^{-2} (NTs) when the loading was increased from 2 to 4 mg cm^{-2} for MnO_2 while maintaining the cathode loading. This shows the importance of optimization of catalyst layer to balance the ionic (ionomer), electronic (MnO_2) and mass transport (bubble and water diffusion) energy losses. It also shows that only a small fraction of the catalyst layer is active. The ASR (**Figure 6b**) for the catalyst layer increased significantly with the increase in loading from 2 to 4 mg cm^{-2} i.e. 178 to 252 $\text{m}\Omega \text{ cm}^2$ (NWs), 142 to 217 $\text{m}\Omega \text{ cm}^2$ (NRs), 155 to 217 $\text{m}\Omega \text{ cm}^2$ (NTs). Since the membrane ASR is 100 $\text{m}\Omega \text{ cm}^2$, the calculated change in the ASR for the catalyst layers for the different MnO_2 shapes is 78 to 152 $\text{m}\Omega \text{ cm}^2$ (NWs), 42 to 127 $\text{m}\Omega \text{ cm}^2$ (NRs) and 55 to 127 $\text{m}\Omega \text{ cm}^2$ (NTs). This shows the resistance of the catalyst layer has increased by a factor of 2-2.5 with the increase of the loading from 2 to 4 mg cm^{-2} . The estimated catalyst layer thickness has increased to $\sim 17.6 \mu\text{m}$ from $\sim 8.8 \mu\text{m}$ with the increase in the loading, as calculated by using the loading of 2 and 4 mg cm^{-2} , density of MnO_2 (5.03 g cm^{-3}), 30% by volume of ionomer and 25% porosity. Gupta et.al [45] showed that even after increasing the catalyst loading for the more electrically conductive NiCo_2O_4 to 10 mg cm^2 (catalyst layer thickness $\sim 29 \mu\text{m}$), the performance of the electrolyser still improved. But in the studied case, the utilization of the anode catalyst layer of MnO_2 has decreased by high factor than the factor of 2 of increasing the catalyst loading due to the higher electrical resistance of the materials. As the catalyst layer is composed of around 30% ionomer by volume and with the use of 0.1M NaOH electrolyte the effective ionic conductivity is significantly higher by factor of 3-4 than electrical conductivity of MnO_2 and is not the limiting factor as seen in the case of NiCo_2O_4 . A similar behavior was observed when the cell temperature was increased to 40 $^\circ\text{C}$. Increase in temperature will improve slightly the anode catalyst layer utilization with decrease in charge transfer resistance and ionic conductivity but will have negligible effect on electrical conductivity. The polarisation curves for the different catalysts

with a catalyst loading of 4 mg cm^{-2} at 40°C in 0.1 M NaOH solution are shown in **Figure 6c**. The overall performance of all the catalysts was 3-4.5 times lower with the higher loading of 4 mg cm^{-2} when compared to the lower loading of 2 mg cm^{-2} . At 1.75 V , the current density has decreased significantly from 76.6 to 16.45 mA cm^{-2} (NWs), 53.8 to 18.68 mA cm^{-2} (NRs), and 55.5 to 14.65 mA cm^{-2} (NTs) when loading is increased from 2 to 4 mg cm^{-2} . This is due to the very high resistance of the anode catalyst layer as can be seen in the EIS data in **Figure 6d**. It can be seen that the ASR values have increased significantly for all the catalysts from 160 to $200 \text{ m}\Omega \text{ cm}^2$ (NWs), 124 to $169 \text{ m}\Omega \text{ cm}^2$ (NRs) and 134 to $175 \text{ m}\Omega \text{ cm}^2$ (NTs) at 40°C when loading was increased from 2 to 4 mg cm^{-2} . The lower catalyst utilization, the dominating factor in lower performance seen, can be seen from the significant increase by ca. factor of 2 of charge transfer resistance when increasing the loading from 2 to 4 mg cm^{-2} for the studied catalyst (**Figure 6b** and **6d**). This suggests that if higher loading of MnO_2 is desired a conductive support or doping needs to be introduced.

3.6 Stability testing of MnO_2 in AEM electrolyser

The stability of all three catalysts with a loading of 4 mg cm^{-2} were tested at 40°C in 0.1 M NaOH by holding the cell voltage at 2 V and running polarisation curves and EIS at regular intervals. **Figure 7a** shows the chronoamperometry graph of these catalyst at 2 V and 40°C . Polarisation curves and EIS were done at time intervals of 12 , 24 and 36 h causing small spikes in the presented data. All the catalysts showed an initial drop in current density during the first 6 h of testing but then remained almost constant over the remaining duration of the test. The drop in current density over the initial 6 h of stability was 78.44 to 61.53 mA cm^{-2} (27% for NRs), 78.45

to 65.15 mA cm^{-2} (20%, NWs) and 64.22 to 51.76 mA cm^{-2} (22%, NTs) with NRs showing the largest change.

Figure 6. a) Chronoamperometry at 2 V, b) Polarisation comparison and c, d) Nyquist plot comparison at 1.7 V of various MnO_2 nano shaped 0.1 M NaOH solution at 40°C (Anode Loading 4 mg cm^{-2}).

During the three electrode measurements (section 3.2), the increase of electrical resistance of catalyst, attributed to increase in average Mn oxidation state, didn't influence significantly the seen activity over short period of time since catalyst layer/loading was very low. The same anticipated increase in electrical resistivity of MnO_2 catalyst at OER potentials will become more pronounced with catalyst layer using much higher loading e.g. 4 mg cm^{-2} resulting in significant

decrease in catalyst utilization and increase in charge transfer resistance seen in **Figure 7c** and as discussed above for the case of increasing catalyst loading from 2 to 4 mg cm⁻². All three shapes showed increase in charge transfer resistance from initial value to 12 h but then almost remained unchanged from 12 to 36 h (**Figure 7c and 7d**). The initial drop and then stabilization can also be caused by the rearranging of the surface, dissolution and redeposition of the oxide and change of the oxidation of the Mn from lower to higher oxidation state as confirmed by both XPS and XRD of the aged electrodes discussed earlier. **Figure S7** shows the Nyquist plots every 12 hours during the stability test. NRs showed the highest increase ca. 20% in the low frequency intercept. XRD analysis before and after testing (**Figure 1**) has shown the change in the ratio of some of the facets which can explain this finding where the proportion of the higher activity (211) facet decreased in all the three shapes with NRs losing the most (lowest content) as discussed above. However, it should also be considered that under electrolyser operation with high catalyst loading and low catalyst utilization (low electrical conductivity) any changes in current distribution e.g. bubbles blocking will have pronounced effect on the seen current density. **Figure 7b** shows the polarisation curve of these catalysts before and after the 36 h of stability test and **Figure S6** shows the behavior every 12 hours. The NWs showed a slight recovery in performance after 36 h in comparison to 12 h but still lower than initial performance. The charge transfer resistance has remained almost same for the NWs from 14.48 to 14.80 Ω cm² whereas the charge transfer resistance increased considerably for NRs (14.36 to 17.69 Ω cm²) and NTs (18.50 to 22.23 Ω cm²). The NRs and NTs showed a decrease in the performance with NTs being the poorest after 36 h of testing even though the performance loss rate of NRs was much higher than others in the first 6 h. The current density of these catalysts at 1.75 V changed from 16.45 to 19.04 mA cm⁻² (NWs), 18.68 to 15.72 mA cm⁻² (NRs), 14.65 to 13.21 (NTs) after 36 h of testing. Similarly, at 2 V, the current density changed

from 77.26 to 66.99 mA cm⁻² (NWs), 80.65 to 59.69 mA cm⁻² (NRs), and 64.75 to 52.18 mA cm⁻² (NTs). Overall, after some initial changes to all three shapes, a good stability was seen up to 36 h of testing.

Conclusions

In this work, we adapted a simple, easily scalable, and shape-controlled synthesis of MnO₂ nanostructures we reported previously to prepare three distinct morphologies namely nanotubes (NTs), nanowires (NWs) and nanorods (NRs). The materials obtained are in a good crystallographic purity and morphological homogeneity. The influence of the shapes of manganese oxide on the water oxidation activity in alkaline electrolyte was evaluated. The as prepared NRs, NWs and NTs exhibited different specific surface areas, average Mn oxidation states on the surface, electrical conductivity, and 211 and 310 facets contents. Additionally these properties changes under OER testing.

The electrolysis process is dynamic and the surface as well as the bulk is continuously changing as evident from the XPS, XRD and conductivity measurements before and after electrolyser testing. XPS study was able to separate the content of Mn³⁺ from Mn⁴⁺ from the surface with NTs having the highest Mn³⁺ on the surface in the as prepared samples. However, the content of Mn⁴⁺ increased after OER testing with average oxidation state increased to 3.9 for all samples. XRD studies before and after testing supported the hypothesis that there is surface restructuring under the OER environment with considerable change in the content of the different facets after testing. Change in electrical conductivity after testing was also confirmed by impedance spectroscopy. The higher mass activity seen for NWs of 60.6 Ag⁻¹ at 1.7 V (RHE) was due to the much higher surface area (>2.5) of these shapes compared to NTs and NRs. It was

observed that the electrode coated with MnO₂ nanowires attains 10 mA cm⁻² current density at a potential of 1.672 V (RHE) compared to 1.688 V(RHE) for Nanotubes and 1.702 V (RHE) for Nanorods. There is also evidence that higher 211 facet content result in better specific activity towards OER.

The full electrolyser tests also revealed the importance and trade-off between surface area and electrical conductivity on performance. The best performance was achieved by the Nanowires anode at all studied temperatures at 2 mg cm⁻² loading. A decrease in electrolyser performance with increased loading from 2 to 4 mg cm⁻² was attributed to poor electronic conductivity of MnO₂. With higher loading electrical conductivity become more important to achieve good catalyst utilization and the performance of NRs and NWs become similar. While NTs with lower electrical conductivity after activation than NRs and lower surface area than NWs performing the worst.

All the samples showed good stability over the 36 h of testing at 40 °C in 0.1 M NaOH solution after an initial drop in performance during the initial stage of testing.

Conflicts of interest

There are no conflicts to declare.

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