Assessment of nickel nanofoam as a novel material to be used as a current collector for supercapacitors

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Abstract

Porous current collectors offer a conductive network for a fast electron transport and a porous environment through which the electrolyte can wet the active material. In supercapacitors and other energy storage devices, this may be a great advantage over the commonly used metal foil current collectors. The objective of this work is to produce a supercapacitor electrode based on manganese dioxide supported onto a nickel nanofoam current collector without using insulating binders to fix the manganese dioxide on the current collector. Two approaches are attempted and compared to produce the manganese dioxide: electrodeposition and combustion synthesis.

Abbreviations

BET: Brunauer, Emmett and Teller CV: Cyclic voltammetry EDX: Energy-dispersive X-ray spectroscopy ESEM: Environmental scanning electron microscopy

Introduction

The shift from non-renewable to renewable sources of energy, energy efficient vehicles and buildings, has to be a paradigm of the future in order to avoid the climate and economic disasters that would be originated from the prolonged use of fossil fuels. The increase of the global temperature leads to more frequent weather disasters and threaten life on Earth as we know it. A fossil fuel shortage, such as the peak oil, can tighten the relationship between different nations and become a trigger for military conflicts. Electric and hydrogen vehicles use electricity to power the engine, the energy is stored in a battery in the case of the electric vehicle and hydrogen is stored in a container and eventually transformed into electricity with the fuel cell. The energy efficiency of this electric and hydrogen vehicles is around 60% while in an internal combustion engine which uses fossil fuels is around 20% [1][2].

Hybrid, electric and hydrogen vehicles (HEHV) share some traits to maximize mileage and energy efficiency: they use the start-stop technology so that they stop the engine when the vehicle stops in traffic lights. They also use regenerative braking to absorb electric energy when braking -the motor spins in the opposite direction acting as a generator so the kinetic energy is transformed into electric energy- and the stored energy is used afterwards for acceleration. The drawback is that this generates a continuous high power microcycling of the battery/fuel cell and diminishes its life. The above-mentioned characteristics open the possibility of pairing the battery/fuel cell with a supercapacitor unit able to absorb and release the energy from regenerative braking and restart the engine after it has stopped. Supercapacitors are electrochemical energy storage devices that can be recharged hundreds of thousands of times, offer high power density but low energy density. This makes them ideal for the power-assisting unit of HEHV, a fact that places them

HEHV: Hybrid, electric and hydrogen vehicles NiNF: Nickel nanofoam SCE: Saturated calomel reference electrode XRD: X-Ray diffraction

in a strategic point in the market since they can be paired with both electric and hydrogen vehicle technologies [2]. Supercapacitors contain different parts. There are two electrodes, the cathode which works at high voltage and the anode which works at low voltage. Each electrode has a porous active material able to store electrical charge and a current collector -a highly conductive material- that facilitates the electron transport between the electrodes. The electrical conductivity of the active material is rather low so conductive additives such as carbon black are added to improve the performance of the supercapacitor. The active material and the conductive additive are attached to the current collector with a binder, which usually is an insulating polymer like polytetrafluoroethylene or carboxymethyl cellulose. The electrodes are separated by an insulating porous membrane known as the separator and all the mentioned components are soaked in an electrolyte, which can be aqueous or organic [3][4]. An scheme of a supercapacitor can be seen in Figure 1.



Figure 1: Scheme of a supercapacitor or ultracapacitor. https://gigaom.com/2011/07/12/how-ultracapacitors-work-and-why-they-fall-short/

When the supercapacitor is charged, a voltage is applied between the two electrodes and electrons are forced to flow from the cathode to the anode. Therefore, the voltage becomes more negative in the anode, where the electrons arrive, and more positive in the cathode, where the electrons come from. The ions in the electrolyte move towards the surface of the electrodes to compensate the charge. The supercapacitor can hold the charge as long as there is not an external circuit connecting the electrodes because they are separated by an insulating separator, when the electrodes get electrically connected the supercapacitor starts discharging and releases the stored energy.

In commercial supercapacitors, there is not a homogeneous contact between the active material and the current collector because the active material is casted as a thick film of several micrometers on the collector. Since the active material is usually a semiconductor and the binder an insulator, a high internal resistance arises from the active material film hindering the power capabilities of the supercapacitor. Therefore, porous current collectors are an interesting option because they offer a porous conductive network on which the active material can be grown to maximize the contact between the two materials, the liquid electrolyte and avoid the use of binders [5].

There is a wide variety of active materials for supercapacitors such as activated carbon, transition metal oxides and conductive polymers [6][7]. One of the most promising materials among them is manganese dioxide in the form of birnessite. Manganese dioxide is inexpensive, non-toxic, relatively environmentally friendly and stable at higher voltages in aqueous electrolytes than other metal oxides. However, manganese dioxide has a low conductivity and needs to be paired with a conductive support.

Composites of manganese dioxide with carbon nanotubes or graphene have emerged as promising materials for supercapacitors thanks to the combination of the high capacitance of manganese dioxide and the conductivity of the carbon nanostructures. Unfortunately, conductive carbon nanotubes and graphene are still hard to produce industrially leading to a prohibitive cost of the material. Therefore, less expensive conducting supports need to be developed for this application. Furthermore, the composites are usually in the form of a powder that must be mixed with a binder and coated on a foil-type current collector, which lead to problems of high internal resistance [8–10].

Metal nanofoams offer a porous architecture through which the electrolyte can easily diffuse and a continuous conducting network for the electrons to flow, reducing the internal resistance and improving the power capabilities of the supercapacitor. Between the variety of metallic nanofoams available, nickel has been chosen because it is an abundant metal in the Earth's crust and it has been extensively used as a current collector in the form of nickel foil. This suggests that the use of nickel as a nanofoam could be superior to the foil [11,12].

Since in this work we focus on materials for energy efficient vehicles, the objective of this master thesis is to develop a novel composite material, based on manganese dioxide and a nickel nanofoam, to be used as a supercapacitor electrode for electric and hydrogen vehicles. The central endeavour is to produce the material without using binders, which are insulating polymers that hinder the supercapacitor's performance. For this, two synthesis approaches to grow manganese dioxide on the nanofoam are attempted, one based on electrodeposition and the other is a solution combustion approach, and their viability as supercapacitor materials is extensively studied.

Experimental section

Chemicals and materials

Nickel(II) nitrate hexahydrate (99%) and 2-methoxy ethanol (99.5%) were purchased from Acros Organics. Anhydrous manganese(II) sulfate (98%), potassium sulfate (99%), manganese(II) nitrate tetrahydrate (98%), hexaamineruthenium(III) chloride (98%) and potassium chloride (99%) were purchased from Sigma-Aldrich. Nitric acid (69.5% w/v) was purchased from Scharlau. All solutions were prepared using water purified through a

Milli-Q system with a resistance of $18.2 \text{ M}\Omega \cdot \text{cm}^{-1}$.

DropSens[®] 250BT chips with a gold working electrode were used to perform the electrochemical measurements.

Synthesis of the nickel nanofoam

The nickel nanofoam (NiNF) was synthesized using a solution combustion method according to previous studies in the literature [12] [13]. A certain amount of nickel nitrate hexahydrate was dissolved in 50 ml of 2-methoxy ethanol in a 250 ml beaker to form a clear green solution. Unless stated otherwise, the initial concentration of nickel nitrate hexahydrate in the solution was 1 M in 2-methoxy ethanol. The solution was kept at 80 °C for two hours without stirring to evaporate the water that was initially present with the hydrated salt. The solution is ready to be ignited when it thickens enough to form bubbles at 80 °C. At this point, the temperature of the agitator was set to 370 °C to start the combustion. When the mixture is about to burn, large quantities of nitrous oxides are released, eventually leading to a fast and self-sustained combustion of the solution that forms a foamy grey powder of elemental nickel. The Ni²⁺ is reduced to metallic Ni by the CO produced during the combustion, acquiring a foamy structure thanks to the copious amounts of gases released.

The material was collected with a magnet and washed one time with distilled water, one time with ethanol and one time with acetone. Eventually, the material was dried in a vacuum oven and stored in a desiccator under dry silica.

Sintering of the nickel nanofoam

When the nickel nanofoam is obtained from the combustion, it is a grey powder. In order to make the electrodes, the powder was cold pressed to cause the sintering of the metal and improve its mechanical properties.

However, cold pressing is not enough to produce a robust material and hot pressing was also investigated. The previously cold pressed electrodes were placed in a hot press and kept under a force of 1000 kg/m² and 250 °C for 20 min.



Figure 2: Sintering of the NiNF powder. As synthesized NiNF can be seen to the left and a sintered NiNF can be seen to the right.

Synthesis of the manganese oxide nanofoam

1 g of manganese(II) nitrate tetrahydrate was dissolved in 6 ml of 2-methoxy ethanol in a 50 ml beaker. The solution was kept still at 80 °C. After one hour the solution changed in colour from pale pink, from the manganese(II) ions, to yellow, probably due to the formation of manganese oxide nanoparticles, and eventually became black due to the formation of larger aggregates of manganese oxide particles. When the solution started bubbling, the temperature dial of the agitator was set to 370 °C to start the combustion. The combustion is less energetic and proceeds slower than in the case of the nickel nanofoam combustion.

Synthesis of the manganese oxide - nickel nanofoam

A certain amount of nickel(II) nitrate hexahydrate and manganese(II) nitrate tetrahydrate were dissolved in 8 ml of 2-methoxy ethanol in a 50 ml beaker. The solution was kept still at 80 °C until it started forming bubbles. At this point, the temperature dial of the agitator was set to 370 °C to start the combustion. The combustion proceeded similarly to the nickel nanofoam combustion, however, if the concentration of manganese nitrate was high; manganese oxides started to precipitate before the combustion.

 Table 1: Reagents used to prepare manganese oxide – nickel nanofoam composites

Sample name	Ni(NO ₃) ₂ ·6H ₂ O (g)	Mn(NO ₃) ₂ ·4H ₂ O (g)	2- methoxyethanol (ml)
Mn _x O _y	-	0.97	8
Mn _x O _y /Ni	2.06	1.00	8
MnO/Ni	0.54	2.11	8

Electrodeposition of manganese dioxide

Cold pressed nickel nanofoam electrodes weighing between 2 and 10 mg were fixed on the gold working surface of a DropSens® 250BT chip by using a small magnet. The gold surface, which acted as the working electrode, was placed in a 15 ml electrolytic cell along with a saturated calomel reference electrode (SCE), four pieces of carbon cloth (National Centre for Biotechnology Education) of 1×3 cm acting as the counter electrode and 10 ml of a 0.4 M manganese(II) sulfate aqueous solution as the electrolyte. Manganese dioxide was deposited on the nickel nanofoam by applying a constant potential of 1.2 V (vs SCE) for a certain period of time with stirring (300 rpm) at room temperature.

Characterization

Electrochemical characterization

All electrochemical measurements were performed on a DropSens® 250BT chip in a three electrode setup using a CHI660 potentiostat (CH Instruments Inc). The chips were only used once for each sample and were electrochemically cleaned before use by 50 potential cycles between 0 and 1.2 V vs SCE at 100 mV/s in 0.5 M sulfuric acid. Since all samples were magnetic, a small magnet was placed on the back of the chip by means of a double- sided sticky tape in order to ensure a good contact between the sample and the gold surface of the working electrode. The sample was placed on the gold surface which acted as the working electrode, the platinum counter electrode of the chip was used as the counter electrode and an external SCE was used as the reference. A 100 μ L the electrolyte was poured on top of the chip so it could wet all the electrodes.



Figure 3: Electrochemical characterization setup

Electrochemical area measurements

The electrochemical area of the samples, that is the area of the sample accessible by the electrolye, was calculated using the Randles-Sevcik equation in 1 mM hexaamineruthenium (III) chloride + 0.1 M potassium chloride solution [14]:

$$i_n = 2.69 \cdot 10^5 A D^{1/2} C n^{3/2} v^{1/2} \tag{1}$$

Where i_p is the intensity of the peak in A, A is the electrochemical area in cm², D is the diffusion coefficient of the hexaamineruthenium(III) ion in 0.1 M KCl electrolyte in cm²/s [15], C is the concentration of hexaamineruthenium(III) in mol/cm³, n is the number of electrons exchanged in the reaction (in this particular case is 1 because ruthenium is oxidised and reduced between the +2 and +3 oxidation states) and v is the scan rate in V/s.

 i_p was plotted against the square root of the scan rate and the electrochemical area was calculated from the slope of the curve.

Capacitance measurements

The capacitance was calculated with cyclic voltammetry in a 1 M sodium sulfate electrolyte in a three electrode system.

The samples were cycled at a scan rate of 50 mV/s for 20 cycles before recording the voltammograms used to calculate the capacitance in order to ensure that the equilibrium was reached. If the cyclic voltammogram is rectangular, the following formula can be used to calculate the capacitance:

$$C = \frac{\int_{V_1}^{V_2} i(V) dV}{2 \cdot v |(V_2 - V_1)|}$$
(2)

Where the numerator is the area enclosed between both scans of the cyclic voltammogram, v is the scan rate, V_2 and V_1 are the highest and lowest potentials of the cyclic voltammogram [16][17]. The value of the integral was calculated using the Origin version 7 software.

X-Ray diffraction measurements

XRD (X-ray diffraction) measurements were made using a Siemens D5000 diffractometer (Bragg-Brentano parafocusing geometry and vertical θ - θ goniometer) fitted with a curved graphite diffracted-beam monochromator, incident and diffracted -beam Soller slits, a 0.06° receiving slit and scintillation counter as a detector. The angular 2 θ diffraction range was between 5 and 70°. The data were collected with an angular step of 0.05° at 3s per step and sample rotation. Cu_{ka} radiation was obtained from a copper X-ray tube operated at 40 kV and 30 mA. The identification of the cristalline phases of the samples were matched with WIN FIT 1.2 software.

Nitrogen physisorption measurements

BET areas were calculated from the nitrogen adsorption isotherms at 77 K and the pore size distribution was calculated with the BJH method using the data from the same isotherms. The samples were grinded with an agate pestle and mortar for 5 minutes and degassed overnight at 353 K with a Flovac Degasser (Quantachrome instruments) in order to remove all adsorbed gases. Eventually nitrogen was injected to the samples to provide an atmosphere free of contaminants. The degassed samples were weighed and immediately placed into a Quadrasorb SI (Quantachrome instruments) nitrogen physisorption instrument along with Dewar flasks full of liquid nitrogen to perform the nitrogen physisorption experiments.

Environmental scanning electron microscopy

Environmental scanning electron microscopy (ESEM) was recorded in a Quanta 600 microscope (FEI Company, Inc.) under high vacuum at 25 kV. Samples were analyzed at a 10 mm working distance.

Atomic absorption spectroscopy

Atomic absorption spectroscopy with was performed with an atomic absorption spectrophotometer 3110 coupled with a Co-Cr-Cu-Fe-Ni-Mn lamp (Perkin Elmer) with a current of 30 mA to know the amount of nickel and manganese in the samples. All experiments were done with an airacetylene flame with a ratio air/acetylene of 2.5. Ni was analyzed at a wavelength of 253 nm and the calibration curve was linear in the concentration range between 5 to 30 mg/l, while for Mn the wavelength was 279 nm and the calibration curve was between 0.5 to 4 mg/l. The weighted samples were dissolved in hot concentrated nitric acid and were brought to a volume of 10 ml. The resulting solutions were diluted as needed in order to fit into the linear range of the calibration curve of the spectrophotometer.

Results

Nickel nanofoam sintering

The NiNF had an open and porous structure as can be seen in Figure 4. The material was in the form of a powder which consisted in aggregates of foamy nickel. A closer look into the material in Figure 4B reveals that it is not homogeneous and some parts are completely solid, while others are full of pores ranging from 20 to 400 nm.





Figure 4: ESEM images of the NiNF.

The inhomogeneity of the NiNF is mainly attributed to the lack of control over the reaction parameters that are involved in the combustion synthesis. Since the material is formed during the combustion, its final morphology depends on the path that the nickel atoms take when they are propelled by the gases produced, hence, combustion synthesis a process difficult to control and the final morphology of the product is random.

Energy-dispersive X-ray spectroscopy (EDX) was performed on the samples to know the composition of their surface. The composition of the sample turned out to be 97.8% Ni and 2.2% O by weight, confirming that the product of the reaction yields mainly metallic nickel. The EDX results were confirmed by the XRD of the NiNF in which only NiO and Ni related peaks were found. The oxygen content of the sample is attributed to the natural passivation of nickel under air atmosphere.



Figure 5: X-Ray diffractogram of the NiNF. - Bunsenite – NiO, A Ni.

In order to assess the viability of the material as a selfstanding current collector the NiNF powders were cold pressed. Under pressure, nickel particles tend to aggregate by a sintering mechanism and the material can be easily shaped into a self-standing pellet.

However, cold pressing did not produce enough sintering regardless of the time the sample spend under pressure and the NiNF pellets produced were dusty and broke easily.

We decided to increase the pressure over the sample and the temperature to favour the sintering process by using a hot press. After hot pressing the NiNF pellets became stronger and were not dusty, however they were not flexible as a thin nickel foil. ESEM was used to confirm that even though the sintering was produced the samples remained porous, as can be seen in Figure 6.



Figure 6: ESEM image of a sintered NiNF. The material remains porous after the sintering.

MnO₂ electrodeposition on NiNF

In this step, an intimate contact between the manganese precursor and the porous NiNF is very important. Therefore, the time required to wet the nickel nanofoam was assessed by means of electrochemical area measurements. The electrochemical area of the same piece of nickel nanofoam was tested in two different conditions: less than 5 min of contact with the electrolyte at room temperature and 1 min of sonication + 3 days of contact with the electrolyte at room temperature.

Wetting time	Electrochemical area (cm ² /g)
Less than 5 min	84.5
3 days	86.3

As can be seen in Table 2, the electrochemical area only increased in 2.1% for the nanofoam in contact with the electrolyte for several days; therefore the samples were

soaked in the electrodeposition bath for about 5 min prior to the electrodeposition.

X-ray measurements were performed on the samples to assess the nature of the manganese oxide deposited. However, it was not possible to detect any crystalline phase of manganese oxide so we assumed the manganese oxide was nanocrystalline and its signal was lost in the background of the X-ray diffractogram. Nevertheless, the material behaved in a capacitive way suggesting it is some form of manganese dioxide as can be seen in Figure 7.

The evolution of the capacitance with deposition time was tested in order to determine the optimum deposition time, the results are shown in

Figure 7 and Table 3.



Figure 7: CV in 1 M Na_2SO_4 of a NiNF with MnO_2 deposited during different amounts of time. Scan rate: 50 mV/s.

Table 3: Composition and capacitance of electrodeposited MnO₂

Deposition time (s)	% wt. Mn	Specific capacitance (F/g Mn)	Specific capacitance (F/g electrode ^a)
200	1.5%	807	12
1200	5.3%	112	5.9

^a Electrode weight includes Mn, O and Ni.

The capacitance increases proportionally with the deposition time up to 200 s. Longer deposition times lead to a capacitance decrease even though the amount of active material is higher. This phenomenon can be explained by two factors: firstly, as the thickness of the manganese dioxide film increases the path that the electrons have to travel to reach the nickel substrate becomes longer. Since manganese dioxide is a wide band gap semiconductor with a poor electrical conductivity the manganese dioxide layer behaves as an insulator preventing the electrons to reach the nickel nanofoam. Secondly, as the manganese dioxide layer becomes thicker it is increasingly harder to wet with the electrolyte, thus, limiting the ion transport through the material and hindering its capacitive behaviour because most of the capacitive charge storage occurs at the Helmholtz double layer created on the surface [18,19]. A representation of the phenomena is shown in Figure 8.



Figure 8: A) Optimal MnO2 film thickness, all the material is wetted by the electrolyte and the electron path is short. B) Thick MnO2 layer, it is too thick to get wetted and the extra unwetted material only produces resistance to the electronic flow leading to a capacitance loss.

The fact that there is an optimum layer thickness for MnO_2 is commonly reported in the literature. However, the most usual way to report the capacitance is by means of specific capacitance normalizing it against the weight of only the active material, which is the manganese dioxide in this case. This can lead to confusing results, in which a thin film of the active material is deposited over a conductive substrate and a very high specific capacitance is reported. Indeed, the active material possesses a high capacitance but when the capacitance is normalized against the total weight or volume of the electrode it becomes rather modest.

Misleading results can be seen for instance in references 8, 20 and 21 and are summarized in Figure 9 and Table 4.



Figure 9: A) Bare carbon fibers that act as the current collector. B) Carbon fibers coated with a thin film of manganese dioxide. C) Manganese dioxide coated on carbon nanotubes grown by chemical vapour deposition on a steel mesh current collector. A and B are from [20] and C is from [8].

 Table 4: Composition and performance parameters of some reported supercapacitors.

Active material content	Capacitance	Active material film thickness	Reference
18.41 MnO ₂ % wt.	1000 F/g MnO ₂	70 nm	[21]
15.52 MnO ₂ % wt.	515 F/g MnO ₂	300 nm	[20]

In these papers a thin film of manganese dioxide is grown on top of a macroporous current collector and the capacitance is referred to the weight of manganese dioxide, therefore, the capacitance appears to be very high. However, since the maximum thickness of the film is limited to a few nanometers, the loading of manganese dioxide is very low as can be seen in Table 4. In commercial electrochemical devices with metal oxide active materials, the active material usually accounts for 50 - 60% of the total weight of the device, including the current collectors and packaging. Furthermore, large voids in the structure of the macroporous current collector lead to a vast "dead volume" (Figure 9C), that has to be filled with electrolyte and is not active in the energy storage process. Ideally the voids should be filled with active material in order to minimize the "dead volume" and maximize the energy density. Unfortunately these details are commonly ignored in the literature and misleading results are published.

The same happens when manganese dioxide is directly electrodeposited on nickel nanofoam; if the capacitance is reported against the weight of the active material it approaches its theoretical value of 1370 F/g and the results seem to be promising, however, if the capacitance is reported against the total weight of the electrode it turns out that the material produced would never reach a real application because the capacitance is far too low, as can be seen in Table 3.

In order to overcome the ion and electron transport issues originated on thick manganese dioxide films, simultaneous combustion synthesis of nickel and manganese nitrates was studied as a possible approach to produce a material for supercapacitor or electrocatalysis applications. Three samples with different Mn/Ni ratios were prepared and, the composition was evaluated with atomic absorption spectroscopy and is shown in Table 5.

Sample name	Mn% wt.	Ni% wt.
Mn _x O _y	73.1	-
Mn _x O _y /Ni	51.3	29.8
MnO/Ni	19	75.5

 Table 5: Composition of NiNF/MnxOy composites

The X-ray diffraction patterns of Mn_xO_y revealed that the manganese in the sample was a mixture of MnO, Mn_3O_4 and Mn_2O_3 being MnO the predominant oxide. In the case of Mn_xO_y/Ni , the most oxidized form of manganese, Mn_2O_3 , could not be detected. Manganese was found as MnO, Mn_3O_4 and as a solid solution with nickel oxide while most of the nickel is in the form of metallic nickel and a small portion as NiO. The sample MnO/Ni was found to only contain MnO and metallic nickel.

The XRD spectra revealed that none of the materials contained manganese dioxide.



Figure 10: X-Ray diffractograms of the Mn_xO_y/NiNF composites.

Hausmannite (Mn₃O₄), → Manganosite(MnO), Ni-Mn-O solid solution,
 Bunsenite (NiO), ▲Ni, ◆ Bixbyite (cubic-Mn₂O₃).

Even though manganese was present in the mixture, Ni^{2+} could be reduced to metallic nickel as if it was a combustion of a pure nickel nitrate salt. However, there was a significant difference in the composition of the manganese oxides between the samples. The difference is attributed to the precipitation of Mn_3O_4 and Mn_2O_3 during the evaporation stage of the combustion synthesis which occurred in Mn_xO_y/Ni and Mn_xO_y . When the mixture started the combustion, the reducing environment produced lead to the formation of Mn_3O_4 and Mn_2O_3 were detected with XRD whereas for the sample Mn_2O_4 and Mn_2O_3 were detected with XRD whereas for the sample MnO/Ni, in which there was no precipitation during the evaporation stage, all the manganese formed MnO.

The nitrogen adsorption isotherms seen in Figure 11A can be matched with a type IV isotherm characteristic for macroporous materials [22]. The presence of a hysteresis loop indicates that the materials also contain mesopores. The pore size distribution was calculated with the BJH method to confirm the presence of mesopores, the results can be seen in Figure 11B. All samples show a sharp peak at a pore radius of 1.6 nm which can be classified as micropores. For MnO/Ni and Mn_xO_y/Ni the vast majority of small pores have a radius of 1.6 nm, however, Mn_xO_y presents a bimodal distribution of pores; displaying a peak at 1.6 nm and a broad peak between 2-20 nm. Even though there is a presence of micro and mesopores in the samples, all of them have the type IV isotherm which suggests that the porosity contribution from this kind of pores is rather low.



Figure 11: A) Nitrogen adsorption isotherms (right vertical axis is for the isotherm of Mn_xO_y). B) Pore size distributions of the Mn_xO_y /NiNF composites.

The BET surface area, shown in Table 6, confirmed the results obtained from the isotherms and the BJH pore distribution, all the samples have a poor BET surface area as is expected for macroporous materials. Furthermore, the BET surface area decreases as the content of nickel in the composite increases. The surface area of the samples that contained nickel was so low that any possibility of using it as catalyst was discarded because the catalyst activity was expected to be very low [23–25].

Table 6: BET surface area of the Mn_xO_y/NiNF composites.

Sample	BET area (m ² /g)
Mn _x O _y	18.358
Mn _x O _y /Ni	4.124
MnO/Ni	2.103

The only material with a surface area high enough to perform catalysis would be Mn_xO_y , however, since it is a mixture of oxides and its composition could not be reproduced the option was also discarded.

A manganese oxide with a homogeneous composition was found in MnO/Ni, however, it had a poor surface area because of the high amount of nickel present during the combustion. Nevertheless, a MnO foam free of nickel and with a high surface area could be an interesting catalyst. For this reason we attempted to produce a pure MnO foam by dissolving the same quantity of manganese nitrate in 2methoxyethanol as in the sample MnO/Ni but without nickel nitrate. Unfortunately, it was impossible to start the ignition of the mixture while avoiding the precipitation of the manganese oxides mentioned earlier and the synthesis of the pure MnO foam could not be achieved.

Conclusions

Nickel nanofoam was used as a current collector for manganese dioxide based supercapacitor electrodes. Two synthesis methods were used to deposit the manganese dioxide on the nickel nanofoam: electrodeposition and combustion synthesis.



Figure 12: Representation of A) binder-free MnO₂ grown on NiNF B) MnO₂ nanoparticles embedded in the pores of the NiNF and fixed by a binder. \bigcirc MnO2, \bigcirc NiNF, \bigcirc Electrolyte, \bigcirc Binder.

Electrodepostion turned out to be a bad option to produce the electrode because manganese dioxide capacitive behaviour is limited by the thickness of the manganese dioxide layer. Therefore, the final electrode contains an insufficient quantity of manganese dioxide to be used in real applications. A possible option to use the nickel nanofoam as a current collector for energy storage applications would be to fill the pores in the nanofoam with nanoparticles of the active material using binders (Figure 12). If the content of the active material is be comparable to the one used in commercial applications with foil-type current collectors, the nanofoam is expected to perform better thanks to the porous and conductive environment it offers. Another possibility would be to attempt the electrodeposition in a nanofoam with larger pores, although the mechanical properties of the metallic collector should be carefully monitored.

Combustion synthesis was not a good option either as the originated environment reducing from the 2methoxyethanol combustion prevents the formation of manganese dioxide and the materials showed no capacitive behaviour. Furthermore, the materials produced do not look appealing for catalysis uses because their mesoporosity and the BET surface area are low. In this case, the use of less reducing organic ligands/solvents in the combustion synthesis, together with an optimization of the reaction parameters such as the precursor salt concentrations may lead to better results

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References

- A. Chu, P. Braatz, Comparison of commercial supercapacitors and high-power lithium-ion batteries for power-assist applications in hybrid electric vehicles, *J. Power Sources.* 112 (2002) 236–246. doi: 10.1016/S0378-7753(02)00364-6
- [2] S.G. Stewart, V. Srinivasan, J. Newman, Modeling the Performance of Lithium-Ion Batteries and Capacitors during Hybrid-Electric-Vehicle Operation, *J. Electrochem. Soc.* 155 (2008) 664–671. doi:10.1149/1.2953524.
- G.Z. Chen, Supercapacitor and supercapattery as emerging electrochemical energy stores, *Int. Mater. Rev.* 62 (2017) 173–202. doi:10.1080/09506608.2016.1240914.
- [4] L. Yu, G.Z. Chen, High energy supercapattery with an ionic liquid solution of LiClO₄, *Faraday Discuss*. 190 (2016) 231–240. doi: 10.1039/C5FD00232J.
- J. Yan, Q. Wang, T. Wei, Z. Fan, Recent Advances in Design and Fabrication of Electrochemical Supercapacitors with High Energy Densities, *Adv. Energy Mater.* 4 (2014). doi:10.1002/aenm.201300816.
- [6] G. Wang, L. Zhang, J. Zhang, A review of electrode materials for electrochemical supercapacitors, *Chem. Soc. Rev.* 41 (2012) 797. doi:10.1039/c1cs15060j.
- [7] D.O. Carlsson, A. Mihranyan, M. Strømme, L. Nyholm, Tailoring porosities and electrochemical properties of composites composed of microfibrillated cellulose and polypyrrole, *RSC Adv.* 4 (2014) 8489. doi:10.1039/c3ra47588c.
- [8] Y. Wang, H. Liu, I. Zhitomirsky, Manganese dioxide carbon nanotube nanocomposites for electrodes of electrochemical supercapacitors, *Scr. Mater.* 61 (2009) 1079–1082. doi:10.1016/j.scriptamat.2009.08.040.
- [9] S. Hwang, S. Ryu, S. Yun, J. Myoun, K. Man, K. Ryu, Behavior of NiO – MnO₂ / MWCNT composites for use in a supercapacitor, *Mater. Chem. Phys.* 130 (2011) 507–512. doi:10.1016/j.matchemphys.2011.07.022.
- [10] S. Chou, J. Wang, S. Chew, H. Liu, S. Dou,

Electrodeposition of MnO₂ nanowires on carbon nanotube paper as free-standing, flexible electrode for supercapacitors, *Electrochem. Commun.* 10 (2008) 1724–1727. doi:10.1016/j.elecom.2008.08.051.

- [11] W. Ni, H. Bin Wu, B. Wang, R. Xu, X. Wen, D. Lou, One-Pot Synthesis of Ultra-Light Nickel Nanofoams Composed of Nanowires and Their Transformation into Various Functional Nanofoams, *Small.* 8 (2012) 3432– 3437. doi:10.1002/smll.201201678.
- [12] Y. Fu, Z. Yang, X. Li, X. Wang, D. Liu, D. Hu, L. Qiao, D. He, Template-free synthesized Ni nanofoams as nanostructured current collectors for highperformance electrodes in lithium ion batteries, *J. Mater. Chem. A.* 1 (2013) 10002–10007. doi:10.1039/c3ta11753g.
- [13] D. Gao, G. Yang, Z. Zhu, J. Zhang, Z. Yang, Z. Zhang, D. Xue, One-step synthesis of open-cell Ni foams by anneling the Ni²⁺ -based precursor in air, *J. Mater. Chem.* 22 (2012) 9462–9465. doi:10.1039/c2jm30548h.
- [14] A.M. Debela, M. Ortiz, V. Beni, C.K.O. Sullivan, Surface functionalisation of carbon for low cost fabrication of highly stable electrochemical DNA sensors, *Biosens. Bioelectron.* 71 (2015) 25–29. doi:10.1016/j.bios.2015.03.076.
- Y. Wang, J.G. Limon-petersen, R.G. Compton, Measurement of the diffusion coefficients of [Ru(NH₃)₆]³⁺ and [Ru(NH₃)₆]²⁺ in aqueous solution using microelectrode double potential step chronoamperometry, *J. Electroanal. Chem.* 652 (2011) 13–17. doi:10.1016/j.jelechem.2010.12.011.
- [16] C. Peng, S. Zhang, X. Zhou, G.Z. Chen, Unequalisation of electrode capacitances for enhanced energy capacity in asymmetrical supercapacitors, *Energy Environ. Sci.* 3 (2010) 1499–1502. doi:10.1039/c0ee00228c.
- [17] F. Zhang, C. Yuan, J. Zhu, J. Wang, X. Zhang, X. Wen, D. Lou, Flexible Films Derived from Electrospun Carbon Nanofibers Incorporated with Co₃O₄ Hollow Nanoparticles as Self-Supported Electrodes for Electrochemical Capacitors, *Adv. Funct. Mater.* 23 (2013) 3909–3915. doi:10.1002/adfm.201203844.
- [18] S.W. Zhang, G.Z. Chen, Manganese oxide based materials for supercapacitors, *Energy Mater.* 3 (2008) 186–200. doi:10.1179/174892409X427940.
- [19] C.D. Lokhande, D.P. Dubal, O. Joo, Metal oxide thin film based supercapacitors, *Curr. Appl. Phys.* 11 (2011) 255–270. doi:10.1016/j.cap.2010.12.001.
- [20] Z. Zhu, X. Hu, X. Wei, W. Wei, S. Qin, H. Cheng, Y. Zeng, B. Wang, Hierarchical Manganese Dioxide/Poly(3,4-ethylenedioxythiophene) Core – Shell Nano flakes on Ramie-Derived Carbon Fiber for High-Performance Flexible All-Solid-State Supercapacitor, ACS Sustain. Chem. Eng. 4 (2016) 1201–1211. doi:10.1021/acssuschemeng.5b01263.
- [21] B. Anothumakkool, S. Kurungot, Electrochemically grown nanoporous MnO₂ nanowalls on a porous carbon substrate with enhanced capacitance through faster ionic and electrical mobility, *Chem. Commun.* 50 (2014) 7188–7190. doi:10.1039/c4cc00927d.
- [22] K.S. Sing, Reporting physisorption data for gas/solid

systems with special reference to the determination of surface area and porosity (Recommendations 1984), *Pure Appl. Chem.* 57 (1985) 603–619.

- [23] E. Byambajav, Y. Ohtsuka, Cracking behavior of asphaltene in the presence of iron catalysts supported on mesoporous molecular sieve with different pore diameters, *Fuel.* 82 (2003) 1571–1577. doi:10.1016/S0016-2361(03)00094-2.
- [24] V.R. Choudhary, S.K. Jana, B.P. Kiran, Highly Active Si-MCM-41-Supported Ga₂O_a and In₂O₃ Catalysts for FriedeI-Crafts-Type Benzylation and Acylation Reactions in the Presence or Absence of Moisture, *J. Catal.* 192 (2000) 257–261.
- [25] M.J. Climent, A. Corma, S. Iborra, J. Primo, Use of Mesoporous MCM-41 Aluminosilicates as Catalysts in the Preparation of Fine Chemicals A New Route for the Preparation of Jasminaldehyde with High Selectivity, J. Catal. 175 (1998) 70–79.