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Supporting Information for

Three-Dimensional Interconnected Ni$_{core}$-NiO$_{shell}$ Nanowire Networks for Lithium Microbattery Architectures

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Experimental

The porous membranes were made using the nuclear track-etched technology in which a polymer film is bombarded by energetic heavy ions (Ar^{9+} , 5.5 Mev/amu) under vacuum (10^{-2} mbar) at room temperature in the Cyclotron Resource Center at Louvain-la-Neuve (Belgium). The interconnected nanoporous templates have been prepared by performing a sequential two-step exposure of energetic heavy ions, at angles (α of + 25° and −25° with respect to the normal of the 20 μm thick polycarbonate (PC) film surface**.**

The latent tracks generated by the heavy ions were chemically etched in a 0.5 M NaOH aqueous solution at 70°C to form nanopores, following a previously reported protocol (E. Ferain - 2003). For the present study, the mean pore diameter was ϕ = 230 nm and the membrane volumetric porosity was ~23%. A Cr (15 nm) / Au (1 μm) bilayer was afterwards evaporated on one side of the membrane to serve as cathode during the electrochemical deposition (ECD) process. Next, Ni NWs have been grown by ECD into the crossed pores PC template from an electrolyte containing 262.8 g/l $NiSO_4$ and 30 g/l H_3BO_3 (pH = 3.4), by applying a constant potential of V = −1.1 V versus a double junction Ag/AgCl reference electrode (KCl saturated, E = 0.197 V), while a Pt foil acted as counter electrode. The ECD process was performed at room temperature and the deposition time was 3500 s to ensure complete pore filling of the 20 μm thick membrane. After Ni ECD, the as-prepared samples were immersed for ~10 min in a KI:I_2 (0.6:0.1 M) etchant mixture to remove the Au cathode.

The PC template was subsequently dissolved in dichloromethane to obtain the robust 3D network architectures made up of self-standing crossed Ni NW arrays. The Ni-NiO interconnected core-shell NWs were obtained by thermal oxidation in air at T = 450°C for various times. The obtained interconnected 3D Ni-NiO core-shell networks were robust and stable to be freely handled with tweezers, and the samples easily withstood also thermal processing, coin-cell crimping as well as disassembly and further manipulation for SEM inspection. After annealing, a thick Cu layer (300 nm) was deposited on one side of the NW network to form the current collector. The same annealing process (at 450°C) of 1 and 16 h was done on commercially available Ni film (Goodfellow) and Ni foam (MTIxtl) to produce the electrochemical reference samples.

The porosity of the 23 μm thick PC template with the pore diameter d = 230 nm is about 23%. The diameter of the core-shell Ni-NiO nanowire increases to approximately 305 nm after the annealing process due to the expansion of the NiO shell. Based on the core-shell nanowires diameter, length and density, the surface area increase is estimated at about 50 compared to a 2D configuration. This large enhancement of the surface area for the 3D NW network is in quantitative agreement with the increase in the capacity values as detailed in Fig.3 (c) of the manuscript (from 0.02 mAh/cm^2 for the 2D material, to about 1 mAh/cm^2 for the 3D NW network).

The same considerations can be used to estimate the weight content. The density for Ni and NiO are considered at 8.9 and 6.67 g/cm3, respectively. For the Ni_{core}-NiO_{shell} 3D NWN configuration, the diameter of the Ni core is estimated at 135 nm whereas the outer diameter was measured of about 305 nm. With these parameters, the volumetric content is 20% for Ni and 80% for NiO corresponding to about 25 wt.% for Ni and 75 wt.% for NiO, in accordance with the experimental mass measure and capacity estimation. For the other configurations (2D thin/thick film and macroporous foam) this estimation was less accurate given the higher mass of the Ni support.

The thickness of the NiO film on Ni foil was also estimated by means of spectroscopic ellipsometry (Sentech SE850). The NiO thickness for the thin-film (annealed for 1 h) 2D configuration was estimated at 73 nm whereas the thick-film (annealed for 16 h) 2D configuration resulted in a NiO film thickness of approximately 580 nm. To be mentioned that variations of ±50 nm were measured on different sample sites/spots for the thick film configuration.

The electrochemical performances were analysed in a half-cell configuration using Li-metal as reference and counter electrode. One sheet of Celgard separator soaked in 1M $LiPF_6$ ethylene carbonate / diethyl carbonate (v/v = 1:1, from Solvionic) electrolyte was placed in between the working electrode and the lithium metal electrode. CR2032 coin-cells were sealed in an Ar filled glove box and analysed using an Arbin BT2043 battery tester. For the post-cycling SEM inspection, the cells were first slowly polarized to 3V (*vs.* Li/Li^+) and held at this potential for 24 h. After the coin-cell disassembly, the NWN electrode was immediately placed in acetonitrile and washed several times. The samples were kept in an Ar atmosphere prior to SEM inspection.

The physico-chemical characterization of the NWN samples was done using an X-ray diffraction equipment operating with Cu $K\alpha_1$ radiation (λ = 1.54056 Å) and a JEOL 7600F field-emission scanning electron microscope (FE-SEM) equipped with an energy dispersive X-ray (EDX) analyser. Ultimately, the magnetic investigations were performed by an Alternating Gradient Magnetometer (AGM) enabling hysteresis loop measurements at room temperature.

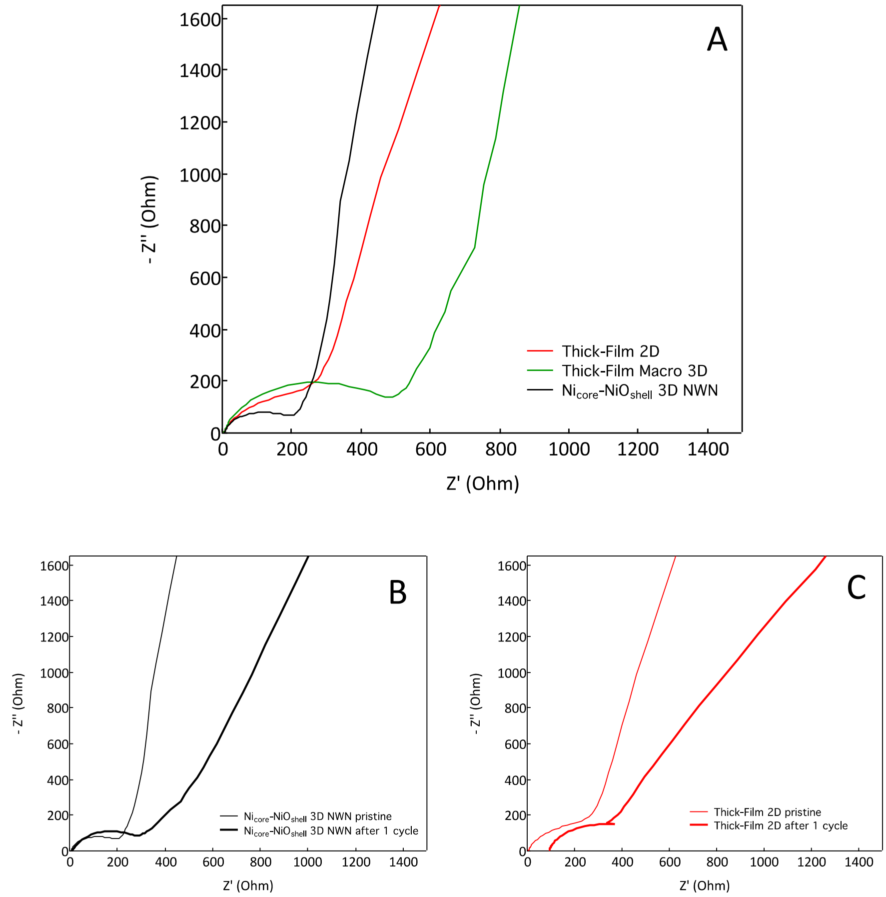

Figure S1. Electrochemical impedance analysis of the representative configurations explored in this work. (A) EIS spectra of the as-assembled cells. All samples were of 1 cm^2. After the assembly, the cells were aged for 12 h before acquiring the EIS spectra. (B, C) Comparison of the EIS after one full lithiation - delithiation cycle. Slow cycling was performed at a current density of 17,5 mA/g$_{NiO}$, equivalent of C/40 rate, in the voltage window of 0.01 - 3V (*vs.* Li/Li$^+$). At the end of the charge, the working electrode was polarized at 3V (*vs.* Li/Li$^+$) for another 24 hours to ensure full delithiation and a stable open circuit potential above 2,6 V (*vs.* Li/Li$^+$). For the samples code, the reader is referred to the legend of Figure 3 of the manuscript.