

Electronic Supplementary Information

**O₂ selective membranes based on dextrin-nanosponge (NS) in
PVDF-HFP polymer matrix for Li-Air Cells.**

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The Supporting Information for:

- 1. Synthesis of the nanosponge, description of the membrane preparation and characterization.**
- 2. Pd CNF synthesis, description of the cathode preparation and cell assembly.**
- 3. Electrochemical testing procedure.**

1. Synthesis of the nanosponge, description of the membrane preparation and characterization.

The dextrin-based nanosponge (NS) was prepared by cross-linking Kleptose® Linecaps 17 Lab 4118 (LC, Roquette Frères, Lestrem, France. Mw = 12000 Da) and a small fraction (10 % w/w with respect to LC) of β -cyclodextrin (β -CD, Roquette Frères, Lestrem, France) with an excess of citric acid. LC is a novel highly soluble food-grade starch, derived from pea starch via partial hydrolysis and characterized by a considerable amount of amylose (around 40 % by weight). More specifically, the NS was synthesized by solubilizing 21.00 g of LC, 2.10 g of β -CD, 5.00 g of sodium hypophosphite monohydrate (Sigma-Aldrich) and 71.00 g of citric acid (Sigma-Aldrich) in 50 mL of deionized water. Then, the solution was placed in an oven (Mettler VO500) and heated at 90 °C for 30 h and, finally, at 110 °C for further 40 h, under low pressure (30 mbar). The so-obtained hyper-cross-linked polymer was ground in a mortar, washed with an excess of deionized water and rinsed with acetone (Sigma-Aldrich), through Buchner filtration. After drying, a fine yellow powder was collected.

The PVDF-HFP membranes with the dextrin-nanosponge were prepared via non-solvent induced phase separation using alcohol and water as coagulant bath. In the synthesis, an amount equal to 2.0 g of PVDF-HFP (average Mw of 455000 Sigma-Aldrich) was dissolved in 5.0 ml of Dimethylformamide (DMF, anhydrous, 99.8%, Sigma-Aldrich). The mixture was magnetically stirred at room temperature until complete dissolution of the polymer was achieved. Separately 100 mg of CD-NS were dissolved in 2.0 ml of DMF. The two solutions were mixed together and stirred at room temperature. The film was casted with a film applicator, Elcometer 4340. The film was immersed for 2.0 s in methanol and then in water for 24 h and then left to dry in ambient air, at room temperature for 48h.

The membranes surface morphologies were examined using field-emission scanning electron microscopy (FESEM, JEOL-JSM-6700F). Thermogravimetric analyses (TGA) were performed in the temperature range of 25 to 800 °C at a heating rate of 10 °C/min under N₂ (60 mL/min) with a TGA/SDTA 851 instrument from Mettler (Switzerland). Contact angles measurements on each membrane were performed at room temperature using a Drop Shape Analyzer DSA 100 Krüss. Initially, water drops of about 10 µl were deposited on the membrane surface with a tight syringe. Five consecutive measurements were obtained for each membrane and both the mean value and standard deviation were calculated. Both oxygen and water permeability values of the membranes were measured by an Extrasolution MultiPerm instrument. The membranes were mounted on the instrument with a surface reducing frame in order to realize an exposed surface of 2.27 cm². Analyses were performed using a pressure of 1.0 atm, at the temperature of 25 °C, and a humidity level of 85 %.

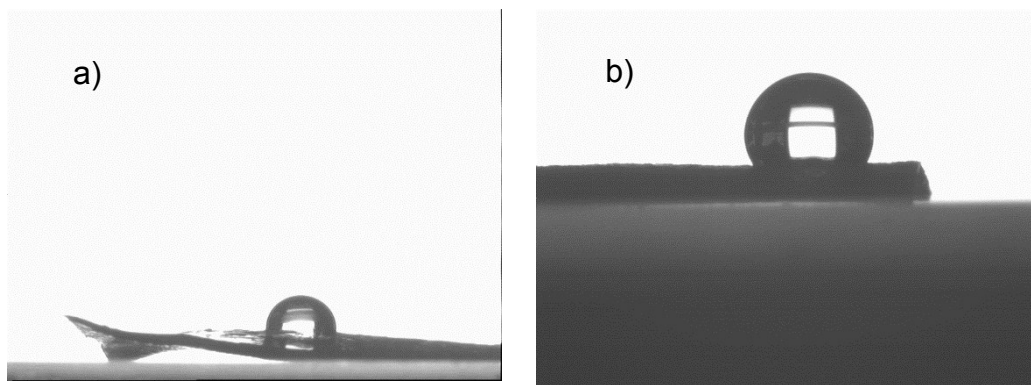


Fig.S1 Images of the water droplets for contact angle measurements. (a) PVDF-HFP loaded Si oil membrane, (b) PVDF-HFP-NS membrane. The values of the contact angles are reported in Table 1.

2. Pd CNF synthesis, description of the cathode preparation and cell assembly.

Mesoporous carbon nanofibers doped with Palladium nanoparticles (Pd CNFs) have been synthesized by electrospinning with subsequent thermal treatment processes. The solutions for the

electrospinning were based on a 10 wt. % PAN polyacrylonitrile (PAN, 150.000 mol/g, Sigma-Aldrich) in Dimethylformamide (DMF, Sigma-Aldrich). 2.5mmol of $\text{Pd}(\text{CH}_3\text{COO})_2$ (Sigma-Aldrich). An amount equal to 7.5 mmol of [3-(2-aminoethylamino)propyl]trimethoxysilane (AEAPTS, Sigma Aldrich) were added to the 10 wt. % PAN solution before the electrospinning process. The electrospinning process was performed using a multispinneret with 3 syringes at a flow of 2-3 ml/h, moving at 120 m/s, with a distance of 15 cm, a $V = 29.9\text{KV}$ and a collector rod rotating at 300 rpm. The thermal treatment was carried out in a multistage process based on a first step of heating at $1^\circ\text{C}/\text{min}$ up to 280°C , dwelling time of 1h at 280°C under air and then a second heating step at $5^\circ\text{C}/\text{min}$ up to 1000°C with a dwelling time of 1h under N_2 .

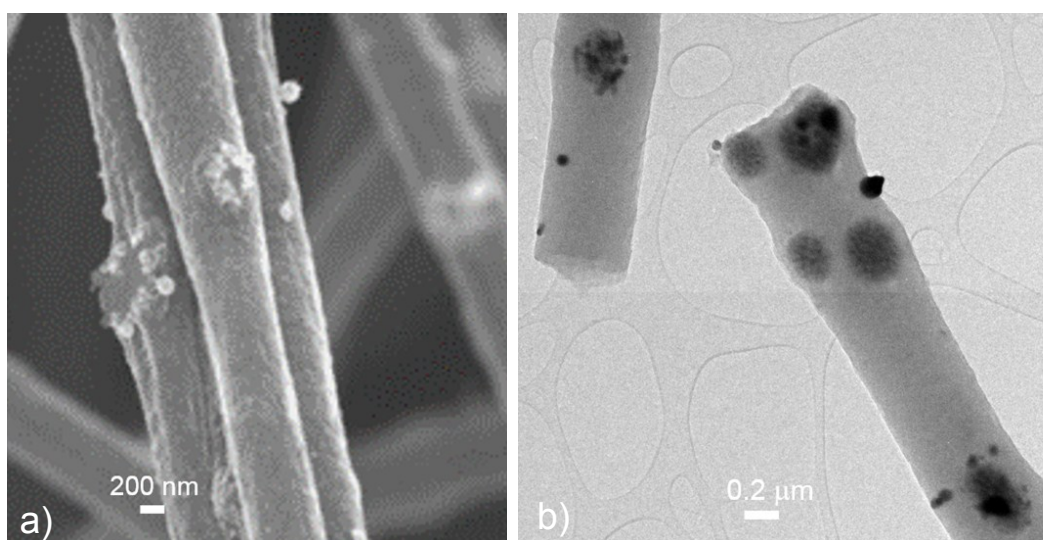


Fig.S2 FESEM image of the Pd CNF (a) cathode material and HRTEM image (b).

The CNFs are decorated by homogeneously distributed $\text{Pd}(0)$ nanoparticles, the Pd aggregates were formed by loosely packed metal nanoparticles.

In order to characterize the Pd CNF material used at the air cathode, the metal content analysis was performed by ICP-MS (Agilent 7500, Agilent Technologies). Nitrogen adsorption isotherms at 77 K were recorded with aNova 2200e equipment (Quantachrome Instruments). The specific surface

area of the samples was obtained by BET method within the relative pressure range of 0.05 to 0.2. The pore size distributions (PSDs) were determined by the BJH method calibrated for cylindrical pores according to the improved KJS method. The detailed description along with the experimental results are reported in ref [18].

The Pd CNF based air-cathodes were prepared as coating layers over the carbon paper gas-diffusion layers (GDL, SIGRACET GDL-24BA, SGL Technologies). Pd/CNFs and Poly-vinylidene Fluoride binder (Kynar® 761 Units Arkema - referred as PVdF, in the weight ratio of 90:10) were mixed using a mixer mill (Retsch, MM 400). N-methyl-2-pyrrolidone (NMP) solvent was then added to the solid mixture in order to obtain a uniform slurry, which was further stirred at room temperature. The top of the GDL was coated with the slurry using doctor blade technique, the thickness of the deposited slurry was set at 300 μm . The coating was dried at 60 °C overnight to evaporate the NMP solvent. The cathodes were further dried in vacuum at 120 °C overnight, by a Buchi Glass Oven B-585 dryer vacuum system. The pouch cells were then assembled in the dry room (Soimar), with a thermo-sealer with magnets and cutting blade MOD 7914.245, using coffee bag envelopes. For the cathodes, discs of geometric area of the 2.54 cm² were cut with an El-Cell puncher. Lithium discs (18 x 0.2 mm, Chemetall s.r.l.) were used as anodes. A glass fibre separators (18 x 0.65 mm, ECC1-01-0012-A/L) were saturated in the electrolyte, which was a solution of 0.5 M LiClO₄ (Aldrich) in tetra (ethylene glycol) dimethyl ether (TEGDME, Solvoionic). The current collectors for the anode and cathode were the copper and aluminium meshes (kindly supplied by Dexmet Corporation), respectively. For the pouch cell with the membrane, the membrane was located behind Al mesh current collector. Its size was 2.5 cm x 2.5 cm; being a square sheet. The geometrical area exposed to air was 0.785 cm².



Fig.S3 Image of the pouch Li-air cell configuration. The geometrical area exposed to air is 0.785 cm².

3. Electrochemical testing procedure

The cells (with and without the membrane) were discharged and charged in galvanostatic mode by an Arbin BT-2000 battery tester at room temperature, at the gravimetric current density of 20 mA g⁻¹ referred to the total material coated on the GDL (0.8 mg cm⁻², also considering the amount binder) and to the exposed geometrical area of the cell. Galvanostatic cycling tests were carried out by time-voltage controlled mode between 2.25 V and 4.35 V vs. Li⁺/Li with a time limit of 5 h for both the discharge and charge processes, curtailing the capacity at 100 mA h g⁻¹. Ambient air (17 % RH) continuously fed the pouch cells. Prior to each test, the Li-air cell rested 6 h at OCV under air 17 % RH.

As the main purpose of the work was to verify the behavior of the membrane as a moisture barrier, we assembled a cell with a cathode (Pd/CNF) with known electrochemical performance in dry oxygen feeding and we followed almost the same capacity-limited protocol we previously used, ref [18] in this manuscript. At high depth of discharge, in fact, Li₂O is formed in larger amounts and its insulating nature explains the irreversibility of the Li-O₂ system in full discharge conditions [1].

Furthermore, the resistance of the Li_2O_2 layer increases with the depth of discharge [2]. It follows that the reversible formation/decomposition of Li_2O_2 can be achieved by limiting the depth of discharge of the cell [3]. It has been demonstrated, that both phase and morphology of Li_2O_2 are dependent to the discharge current density applied to the cell: at a low discharge rate, large Li_2O_2 crystals are formed whereas at a high discharge rate, a film-like less crystalline product is more likely to be formed [4]. It follows that we selected the same discharge current in all the experiments. As for the time duration of the discharge/charge cycles, due to the high value of the full discharge capacity of the cell comprising the Pd/CNF fed by oxygen [18], the pouch cells tested in air were discharged at less than 6% of the total achievable capacity.

A summary of the cycling conditions along with the number of cycles obtained is reported in Table S1.

membrane	cathode	material load (mg/cm ²)	electrolyte	gas	gravimetric current & time (mA/g; h)	curtailed capacity (mAh/g)	cycles	ref
-	Pd/CNF	0.72	TEGDME/ LiClO_4	Dry O_2 flow	20 mA/g ; 10h discharge/ 10h charge	200	85-90	[18]
-	Pd/CNF	0.72	TEGDME/ LiClO_4	Air 17%RH	20 mA/g; 5h discharge/ 5h charge	100	37	this work
PVDF-HFP_NS	Pd/CNF	0.72	TEGDME/ LiClO_4	Air 17%RH	20 mA/g; 5h discharge/ 5h charge	100	145	this work

Table. S4 Galvanostatic discharge and charge cycles conditions of the Li-air cells.

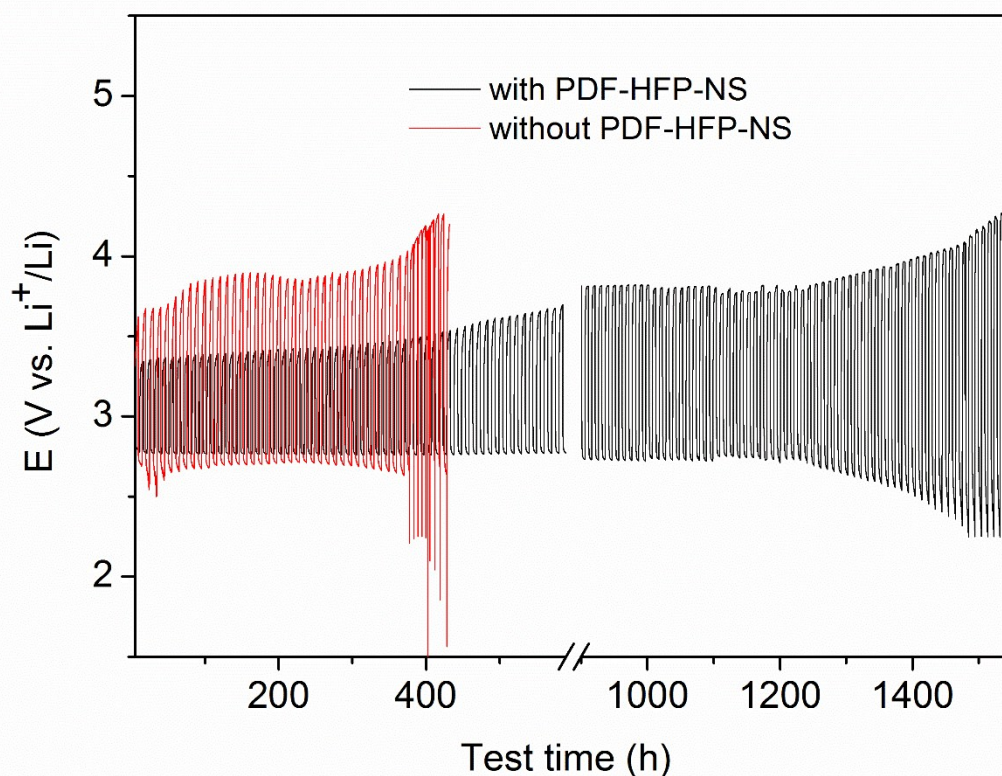


Fig. S4 Voltage vs. time profiles of the two pouch cells assembled with (black line) and without (red line) the PVDF-HFP-NS membrane, at the curtailed capacity of 100 mA h g^{-1} and at the applied gravimetric current of 20 mA g^{-1} . Cut-off voltages of 2.25 V and 4.35 V vs. Li^+/Li , time limit: 5h of discharge, 5h of charge. Ambient air feeding 17 % RH.

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