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# Impact of ionomer structuration on the performance of bio-inspired noble-metal-free fuel cell anodes

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## Summary

Molecular-engineered bio-inspired catalysts hold promise for the next generation of proton-exchange membrane fuel cells (PEMFCs). Yet, their implementation in catalytic layers with Nafion ionomer faces nanocomposite formulation issues. Here, we use various DuBois nickel

catalysts immobilized on carbon nanotubes to exemplify how self-assembly at the mesoscale affects H<sub>2</sub> oxidation anode performances. We exploited the reversible activity of these catalysts together with potential-step chronoamperometry to locally produce H<sub>2</sub> and probe mass transport within the catalytic layer. Small-angle neutron scattering studies serve to build a model, describing how the surface functionalization drives the structuration of the ionomer and impacts the diffusion of protons and gas from and to catalytic centres. This study thus demonstrates that implementation of unconventional catalysts in catalytic layers requires the redesign of the whole system of materials. Based on such information, catalytic layer formulation was optimized, allowing order of magnitude performance enhancement of noble-metal free PEMFCs.

## **Introduction**

Hydrogen gas is a promising storage framework for renewable energies through the combination of water-splitting, in electrolyzers or photoelectrochemical cells,<sup>1</sup> with fuel cells (FC), releasing energy from hydrogen as supply/demand dictates.<sup>2</sup> Proton exchange membrane (PEM) devices are an attractive technology, but they rely on the powerful catalytic properties of platinum, the replacement of which by lower cost and more abundant materials is a requisite for economic viability.<sup>3-4</sup> Noble metal-free hydrogen FC are classically based on the alkaline technology<sup>5</sup> or exploit hydrogenase enzymes in homemade laboratory experimental setups.<sup>6-8</sup> However, none of them allow taking advantage of the low internal resistance, compactness and high stability of PEMFCs optimized over the last decades.<sup>5</sup> The combination of a bio-inspired molecular approach<sup>9</sup> with nanochemical tools, through the attachment of mimics<sup>10-11</sup> of the active sites of hydrogenases (Fig. 1b) on multi-wall carbon nanotubes (MWNTs) has allowed to prepare nickel-based nanomaterials with unique properties for bidirectional catalysis

(hydrogen evolution and oxidation) under conditions compatible with PEM technology.<sup>12-17</sup> Their active sites are nickel(II) bisdiphosphine complexes<sup>10-11</sup> bearing amine pendant bases directly inspired from the structure of the dithiomethylamine cofactor found at the active site of [FeFe]-hydrogenases (Fig. 1a).<sup>18-20</sup> During H<sub>2</sub> oxidation, these amine groups polarize the H-H bond to facilitate its heterolytic cleavage into proton and hydride. Reversely, they serve as proton relays to promote protonation of metal-hydride intermediate towards H<sub>2</sub> evolution.<sup>11</sup> In this study, we focus on three previously described catalysts immobilized on MWNTs represented in Fig. 1. They are named **1<sup>Arg</sup>** ([Ni(P<sub>2</sub><sup>Cy</sup>N<sub>2</sub><sup>Arg</sup>)<sub>2</sub>]<sup>6+</sup>), **1<sup>Ester</sup>** ([Ni(P<sub>2</sub><sup>Cy</sup>N<sub>2</sub><sup>Ester</sup>)<sub>2</sub>]<sup>2+</sup>) and **1<sup>Py</sup>** ([Ni(P<sub>2</sub><sup>Cy</sup>N<sub>2</sub><sup>Py</sup>)<sub>2</sub>]<sup>2+</sup>) after their anchoring groups, an arginine,<sup>21</sup> an activated ester<sup>22</sup> and a pyrene.<sup>14</sup> The anchoring group are designed for stable grafting on appropriately functionalized MWNTs (Fig. 1b) through polycationic/polyanionic electrostatic or  $\pi$ -cation interactions,<sup>15</sup> covalent amide linkage<sup>22</sup> and  $\pi$ -stacking of the pyrene moiety on MWNT,<sup>14</sup> respectively. While optimisation of the three-dimensional structure of the electrodes yielded current densities up to 40 mA·cm<sup>-2</sup> in the case of MWNT-NH<sub>3</sub><sup>+</sup>/**1<sup>Ester</sup>**,<sup>16</sup> power densities in technologically relevant setups remain below expectations. Indeed, when formulated with Nafion ionomer in a catalytic layer assembled with a NRE 212 Nafion membrane and assessed in a compact PEMFC, **1<sup>Py</sup>** yielded only 23  $\mu$ W·cm<sup>-2</sup> power output.<sup>23</sup> Further optimization is therefore clearly required to find alternative formulations of the catalytic layers that account for the specificity of these innovative catalytic hybrid materials.<sup>9, 24</sup>

The use of Nafion is widely adopted in the formulation of Pt/C-based catalytic inks as it both enhances proton transport throughout the thickness of the electrode and provides good contact with the PEM in a compact fuel cell.<sup>25</sup> However, while perfluorinated sulfonic acid membranes have been thoroughly investigated,<sup>26-27</sup> less information is available for Nafion-containing catalytic layers.<sup>28-31</sup> The Nafion covering of the carbon support is often heterogeneous, composed of clusters that fail to impregnate the support smaller porosities, hence greatly

hindering the proton conductivity in the latter.<sup>32-33</sup> The morphology of the clusters might be tuned through the degree of graphitization or the functionalization of carbon black,<sup>34-35</sup> which in turn impacts direct access of catalytic active sites to the electrolyte. To the best of our knowledge, no such information is currently available for carbon nanotubes-based catalytic layers, although the latter hold promises to reach technological PEMFC benchmarks.<sup>12-13, 36</sup> In addition, Nafion was originally selected for being the best compromise as ionomer in the very case of Pt/C catalysts.<sup>5</sup> The whole system of materials within the catalytic layer may have to be redesigned for implementing alternative catalysts as even fewer data is available regarding the interaction of Nafion with alternative noble-metal free catalysts.<sup>13, 30, 36-40</sup>

## **Results and discussion**

### *Overview of catalytic systems*

Surface concentrations of the three catalysts immobilized on MWNTs (Fig 1) have been determined by cyclic voltammetry (CV) in CH<sub>3</sub>CN through integration of the Ni<sup>II</sup>/Ni<sup>I</sup> signal and found similar in all three cases (Table 1). All three systems were already demonstrated to reversibly catalyse H<sub>2</sub> evolution and oxidation when drop-cast on one side of a gas diffusion layers (GDL) fed with H<sub>2</sub> from the back and immersed in 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte in three-electrode half-cell configuration.<sup>14-15, 22</sup> Structural differences in the outer sphere of nickel entail distinct catalytic behaviours, as previously reported: linear sweep voltammetry (LSV) measurements (Fig. S1) indeed show that MWNT-NH<sub>3</sub><sup>+</sup>/**1**<sup>Ester</sup> and MWNT/**1**<sup>Py</sup> are biased towards H<sup>+</sup> reduction<sup>14, 22</sup> while MWNT-COO<sup>-</sup>/**1**<sup>Arg</sup> is biased towards H<sub>2</sub> oxidation.<sup>15, 21, 41</sup> Chronoamperometry (CA) measurements showed that the catalytic activity of all three systems is sustained for hours under such conditions,<sup>14-15, 22</sup> supporting stability of both molecular catalyst structure and surface grafting.

**Table 1:** Electrode composition (Ni/C ratio from energy-dispersive X-ray spectroscopy (EDX) measurements and site loading from CV measurements) and H<sub>2</sub> oxidation current densities of the three systems. Site loading is measured in the absence of Nafion and Ni/C ratio is given in the Nafion-containing electrodes (1:1 Nafion/MWNT dry mass ratio).  $j_{ox}$  is given at 300 mV vs. the reversible hydrogen electrode (RHE), after stabilization of the current.

Electrode	MWNT-NH <sub>3</sub> <sup>+</sup> /1 <sup>Ester</sup>	MWNT-COO <sup>-</sup> /1 <sup>Arg</sup>	MWNT /1 <sup>Py</sup>
Ni/C atomic ratio (%)	0.3	0.3	0.6
Catalytic sites loading (nmol·cm <sup>-2</sup> )	2.7 ± 0.5	2.5 ± 0.5	3.1 ± 0.5
MWNTs loading (mg·cm <sup>-2</sup> )	0.50 ± 0.01	0.36 ± 0.05	0.36 ± 0.05
$j_{ox}$ w/o Nafion (mA·cm <sup>-2</sup> )	2.1 ± 0.3	20 ± 3	2.3 ± 0.3
$j_{ox}$ w/ Nafion (mA·cm <sup>-2</sup> )	0.5 ± 0.1	17 ± 3	0.0 ± 0.1

#### *Catalytic behaviour in presence of Nafion*

For MWNT/1<sup>Py</sup>/Nafion or MWNT-NH<sub>3</sub><sup>+</sup>/1<sup>Ester</sup>/Nafion anodes integrated in a compact PEMFC, the low activation energies measured in a previous work for H<sub>2</sub> oxidation<sup>23</sup> suggested that the current density is limited by mass transport in the bulk of the electrode. To gain more insight into the effect of Nafion on the performances of the Ni-based catalysts, we first studied inks formulated with a Nafion to MWNT dry mass ratio of 1, *i.e.* with a composition similar to that used in the above mentioned study,<sup>23</sup> co-dispersed via sonication in ethanol and drop-cast onto

GDL used as a conductive support. Note that the catalyst content represents 40-45% of the dry mass of these inks. Confirming our previous observations, the addition of Nafion to MWNT/**1**<sup>Py</sup> turns off almost all activity (Table 1 and Fig. S2). When mixed with MWNT-NH<sub>3</sub><sup>+</sup>/**1**<sup>Ester</sup>, Nafion triggers a fourfold drop in oxidation current (Table 1 and Fig. S3). However the presence of Nafion impacts H<sup>+</sup> reduction or H<sub>2</sub> oxidation currents measured at MWNT-COO<sup>-</sup>/**1**<sup>Arg</sup> anodes to a lesser extent (Table 1 and Fig. S4), mirroring the situation observed for ultra-low loaded MWNT/Pt systems fabricated using a polyol method (Fig S5).<sup>42</sup>

Several scenarios can lead to a drop of activity when adding Nafion to the MWNT-catalyst composite ink: i) the catalyst might be chemically inactivated by Nafion through interactions affecting the amine positioning in the second coordination sphere of nickel; ii) the catalyst might electrically disconnect from the MWNT; iii) the catalyst might lose access to its substrates, H<sup>+</sup> or H<sub>2</sub>; iv) the catalyst might be unable to release the product H<sub>2</sub> or H<sup>+</sup>.

The lack of detrimental effect of CF<sub>3</sub>SO<sub>3</sub>H, mimicking perfluorosulfonic chains of Nafion, on the catalytic activity of DuBois's catalysts immobilized onto MWNTs (Fig. S6) does not indicate that Nafion's sulfonate groups strongly interact with amine groups in the second coordination sphere of nickel. In addition, data shown in Figure S2-4 show that the catalytic bias (i.e. the ratio between oxidation and reduction currents) is only marginally affected by the presence of Nafion in the case of MWNT-COO<sup>-</sup>/**1**<sup>Arg</sup> and MWNT-NH<sub>3</sub><sup>+</sup>/**1**<sup>Ester</sup>: For MWNT NH<sub>3</sub><sup>+</sup>/**1**<sup>Ester</sup> (Fig S3), there is a two-fold effect on the catalytic bias induced by the presence of Nafion that may be accounted for to such Nafion-catalyst interactions. While the same effect may be valid for MWNT/**1**<sup>Py</sup>, a complete loss of current at all potentials is observed (Fig. 3a), again indicating detachment of the catalyst from the MWNTs or complete mass transport inhibition as discussed below. The catalytic bias of MWNT-COO<sup>-</sup>/**1**<sup>Arg</sup> is almost unchanged, although addition of Nafion (Fig S4) induces a change of the shape of the linear scan voltammograms.

To account for such changes, we then hypothesized that while Nafion plays its expected proton-transport role for MWNT-COO<sup>-</sup>/1<sup>Arg</sup>/Nafion, it might prevent H<sub>2</sub> access to the catalytic sites in MWNT-NH<sub>3</sub><sup>+</sup>/1<sup>Ester</sup>/Nafion and in MWCNT/1<sup>Py</sup>/Nafion. Recent literature has shown that H<sub>2</sub> mass transport can use different channels than H<sup>+</sup> in hydrated Nafion.<sup>43-45</sup> Scanning electron microscopy (SEM) images recorded for the three systems (Fig. 2) revealed that, for the same loading in catalytic ink, MWNT-COO<sup>-</sup>/1<sup>Arg</sup> displays a thickness (~ 10 μm) five times greater than that of the other systems (~ 2 μm). Looking more closely at individual nanotubes in the composites (Fig. 2), differences are observed in the association of the MWNTs and Nafion: in MWNT-NH<sub>3</sub><sup>+</sup>/1<sup>Ester</sup>/Nafion and MWNT/1<sup>Py</sup>/Nafion, MWNTs are wrapped in a Nafion matrix to form a packed layer, while the MWNT-COO<sup>-</sup>/1<sup>Arg</sup>/Nafion composite appears loosely arranged in balls of entangled MWNTs and Nafion. Such a porous structure being more suitable for gas and electrolyte diffusion, we concluded that mesoscale morphology is the major driver for catalytic performances in such hybrid materials.

To inquire about the effect of Nafion wrapping, we took advantage of the reversible catalytic activity of this family of catalysts and designed a potential-step chronoamperometric measurement. By first probing the electrodes under nitrogen flow at -100 mV *vs.* RHE for 60 seconds to accumulate hydrogen locally, then suddenly switching the potential to +300 mV *vs.* RHE, H<sub>2</sub> was produced at the catalytic site just before probing its oxidation.

These measurements were performed on MWNT/1<sup>Py</sup>, MWNT-NH<sub>3</sub><sup>+</sup>/1<sup>Ester</sup> and MWNT-COO<sup>-</sup>/1<sup>Arg</sup> with and without Nafion (Fig. 3). In all cases, the measurements allow to warrant that the catalysts are electrochemically accessible and capable of bidirectional reversible catalysis in the absence of Nafion (dotted lines). Despite the difference in catalytic bias among the catalysts, they are all able to produce hydrogen continuously during the reduction phase and to



oxidize the available hydrogen after the potential step. Only a very small part of the hydrogen produced during the reduction phase is oxidized after the step and the current drops within 2 seconds, because of the hydrogen fast diffusing away.

The picture is different in the presence of Nafion (continuous lines). First the MWNT/**1**<sup>Py</sup>/Nafion catalytic layer shows a complete loss of current at all potentials (Fig. 3a), again indicating either detachment of the catalyst from the MWNTs or complete mass transport inhibition. Additional control measurements performed with other combinations between nickel catalysts and functionalized MWNTs (Fig. S9) also show that the catalytic activity is almost completely inhibited by Nafion in all the cases where the catalyst is not strongly attached to the MWNTs. This is an indication for a strong affinity of Nafion for MWNT and/or DuBois catalyst that will destabilize the catalyst-MWNT contact required in supported catalysis.

As a contrary, the catalytic H<sub>2</sub> evolution activity of MWNT-COO<sup>-</sup>/**1**<sup>Arg</sup>/Nafion increases in the presence of Nafion (Fig. 3c), showing that **1**<sup>Arg</sup> stays active and electrically connected to MWNTs. At the potential step, the oxidation current produces a peak and then falls to zero within 2 seconds, as in the absence of Nafion. The electrochemical behaviour of **1**<sup>Arg</sup> in the presence of Nafion is thus essentially similar to that without Nafion. It shows that the overall catalytic behavior of the DuBois catalyst (substrate capture and release, pendant amine movements to the active site) is not affected by the polyanionic ionomer and rules out the possibility that Nafion inactivates the catalyst via strong interactions with the positively charged arginine moieties.

Finally, the MWNT-NH<sub>3</sub><sup>+</sup>/**1**<sup>Ester</sup>/Nafion electrode also shows an increase in proton reduction current (Fig. 3b), and then features a transient oxidation current over more than 30s. Integrating the current indicates that a huge part (>50%) of the hydrogen produced in the 30s before the

potential step is oxidized in the 30s after. This transient signal drops significantly with a lower amount of Nafion (Fig. S7). Taken together, these data indicate a singular behaviour for MWNT-NH<sub>3</sub><sup>+</sup>/1<sup>Ester</sup>/Nafion: H<sub>2</sub> produced locally at the 1<sup>Ester</sup> site accumulates in its vicinity when Nafion is present and remains temporarily trapped, available for local oxidation, highlighting limited mass transport from the catalyst in the composite. Furthermore, in potential-step chronoamperometry tests under H<sub>2</sub> flow (Fig. S8), under conditions where MWNT-COO<sup>-</sup>/1<sup>Arg</sup>/Nafion delivers 22 mA·cm<sup>-2</sup> steadily,<sup>46</sup> the oxidation current from MWNT-NH<sub>3</sub><sup>+</sup>/1<sup>Ester</sup>/Nafion is slightly enhanced compared to tests under N<sub>2</sub> flow, showing that H<sub>2</sub> hardly permeates towards the catalyst. As a consequence of local H<sub>2</sub> accumulation, the proton reduction current is slightly inhibited at equilibrium (i.e. in the presence of H<sub>2</sub>, Fig. S3), a typical behaviour for product-hindered catalytic kinetics which has been reported for such reversible catalysts<sup>11</sup> and hydrogenase enzymes.<sup>18</sup>

To gain further structural insight, we recorded small angle neutron scattering (SANS) data for the three systems (Fig. 4). Samples of MWNT/catalyst/Nafion (MWNT/Nafion mass ratio 1/1) were drop-casted on quartz glass as a dry layer, and then equilibrated for 3 days in a chamber at 98 % relative humidity (RH) at room temperature. A sample of dry MWNT-COOH served as a reference. All SANS 1D profiles (Fig. 4a) show a decaying intensity characterized by oscillatory features and a local minimum around values of the scattering vector  $Q \sim 0.06 \text{ \AA}^{-1}$ , corresponding to a characteristic distance  $d \sim 10 \text{ nm}$ . These profiles are typical of the form factor  $P(Q)$  of relatively monodisperse, infinite cylindrical particles such as carbon nanotubes (see supporting information for details). All catalyst SANS profiles have a lower intensity in the region of the form factor oscillation due to a loss of contrast between the cylinder and the solvent, indicating that a different material has been added on the cylinder. In the dry material,

the high- $Q$  intensity decays as  $Q^{-4}$  (so-called Porod's behaviour) indicating sharp interfaces between the scattering particles and the surrounding medium. By contrast, a flat signal is observed in the hydrated samples due to incoherent scattering from hydrogen atoms, *e.g.* water captured during the hydration step. Sample MWNT-COO<sup>-</sup>/1<sup>Arg</sup>/Nafion shows a 10 times higher flat signal, proving a much higher hydrophilicity. This enhanced ability to bind water might constitute a significant advantage for 1<sup>Arg</sup> as compared with the other DuBois catalysts in the catalytic process, as water is required for substrate entry/product release paths. Thus, these SANS data picture our samples as a brightly scattering network of MWNTs surrounded by an organic material with different degrees of water uptake.

For closer analysis, the profiles were fitted with a core-shell cylinder model (see supplementary information for details), taking the core diameter, the shell thickness, the scattering length density of the shell ( $SLD_{\text{shell}}$ ) and of the medium ( $SLD_{\text{medium}}$ ) as adjustable parameters (Fig. 4b). Note that in case of hydrated materials a constant background is added to account for the high- $Q$  plateau. The MWNT-COOH reference SANS profile fits very well to a model with an empty core of  $4.2 \pm 0.1$  nm diameter and a  $2.4 \pm 0.1$  nm thick carbon shell (see model in supplementary information and fitted SLD profiles in Fig. S10), as expected from TEM images of MWNT (Fig. 4a inset). Deviation from the cylinder form factor at low  $Q$  values ( $<0.02 \text{ \AA}^{-1}$ ) is due to scattering by the MWNT entangled network at the micron-scale, but the mesh size could not be investigated because of the limited range at low  $Q$ .

The MWNT/1<sup>Py</sup>/Nafion and MWNT-NH<sub>3</sub><sup>+</sup>/1<sup>Ester</sup>/Nafion profiles show a very good fit with a carbon shell of larger thickness ( $2.7 \pm 0.1$  and  $2.9 \pm 0.1$  nm respectively) and lower shell scattering length density ( $SLD_{\text{shell}} = 6.5 \pm 0.5 \cdot 10^{-6} \text{ \AA}^{-2}$  instead of  $10 \pm 1 \cdot 10^{-6} \text{ \AA}^{-2}$ ) than control. These results are congruent with the observation of MWNTs surrounded by organic material. Interestingly, the MWNT-NH<sub>3</sub><sup>+</sup>/1<sup>Ester</sup>/Nafion data shows a significant excess intensity in the range  $Q \sim 0.1\text{-}0.3 \text{ \AA}^{-1}$ , that is not accounted for by the core-shell model but can be understood

as an additional scattering peak (see below). The MWNT-COO<sup>-</sup>/1<sup>Arg</sup>/Nafion profile is different: the fitted shell has the same characteristics as for MWNT-COOH, but the scattering length density of the medium rises up to  $1.8 \pm 0.5 \cdot 10^{-6} \text{ \AA}^{-2}$  (instead of  $0 \pm 0.2 \text{ \AA}^{-2}$  in the previous cases), a value that approaches that of a matrix of hydrated Nafion and/or 1<sup>Arg</sup>. Besides, the SANS profile shows a strong additional signal at  $Q \sim 0.1-0.3 \text{ \AA}^{-1}$ , a region where the peak of hydrated Nafion is usually reported in the literature (yellow crosses).<sup>47</sup> The excess of signal around  $Q \sim 0.1-0.3 \text{ \AA}^{-1}$  reads better after subtraction of the MWNT-COOH reference SANS profile (Fig. 4c). Then an intense, well-defined correlation peak appears, centered at  $Q_{\text{peak}} = 0.12 \text{ \AA}^{-1}$ , *i.e.* corresponding to mean separation distances of  $\sim 5 \text{ nm}$ . Note that this peak appears identical in the catalyst-free MWNT-COOH/Nafion control sample (black line) and can be safely assigned to the nanoscale structure of hydrated Nafion. Indeed, the so-called ionomer peak due to hydrophilic/hydrophobic phase segregation was reported at position  $Q = 0.12 \text{ \AA}^{-1}$  in bulk Nafion membranes equilibrated at 98% RH.<sup>48</sup> Moreover, we notice that this ionomer peak is also present in the MWNT-NH<sub>3</sub><sup>+</sup>/1<sup>Ester</sup>/Nafion sample, although much less pronounced. The same features and difference of behaviour among the three catalytic systems was observed on samples in contact with excess water, therefore indicating that hydration in liquid water does not modify the nature of the interactions found between Nafion and the various MWNTs.

The present MWNT/catalyst/Nafion systems thus appear to adopt two types of nanoscale structural organization depending on the nature of catalyst and distinct catalyst-Nafion interactions. In the case of MWNT-COO<sup>-</sup>/1<sup>Arg</sup>/Nafion, the ionomer forms bulk-like domains composed of hydrophobic polymer fibers and aqueous channels as reported for pure Nafion.<sup>47</sup> This structure interacts poorly with MWNT-COO<sup>-</sup>/1<sup>Arg</sup>, just providing a water-rich matrix as described in Scheme 3d. By contrast, in the MWNT/1<sup>Py</sup>/Nafion, Nafion hydrophobic chains stick at the MWNT surface as a polymer surfactant, so that no ionomer is available to form a developed fibre/channel structure, as described in Scheme 3e. Indeed, the 1:1 Nafion to MWNT

dry mass ratio implies that Nafion would wrap as a 1.4 nm thick shell if covering the MWNT evenly, which more or less corresponds to a monolayer. This Nafion/MWNT interaction then competes with the  $\pi$ -stacking of  $\mathbf{1}^{\text{Py}}$  onto MWNT and probably leads to displacement of the catalyst from their surface. Finally, the MWNT-NH<sub>3</sub><sup>+</sup>/ $\mathbf{1}^{\text{Ester}}$ /Nafion system has an intermediate behaviour, though closer to the inefficient structure of MWNT/ $\mathbf{1}^{\text{Py}}$ /Nafion.

#### *Meso-scale structuration of the MWNT/catalyst/Nafion catalytic layer*

A contrasted picture of their meso-scale arrangement, depicted in Fig. 5, arises from the combined analysis of the electrochemical behaviour and SANS profiles of our series of MWNT/catalyst/Nafion composites. Although the three grafting methods attain approximately the same loading of catalyst on MWNT (Table 1) in the absence of Nafion, the bond type has a significant impact on the physicochemical behaviour of the MWNT network, and consequently on the structuration of the MWNT/Nafion composite. The very efficient  $\pi$ - $\pi$  interaction used in MWNT/ $\mathbf{1}^{\text{Py}}$  construct relies on the hydrophobic nature of the MWNT surface, but the very same mechanism happens to disturb Nafion self-organization, as was previously observed with other hydrophobic substrates.<sup>49-51</sup> Measurement of active site loading under aqueous conditions (Fig. S11) revealed that competition of  $\mathbf{1}^{\text{Py}}$  and Nafion backbone for the hydrophobic surface of MWNTs induces a massive (> 85%) desorption of the catalyst (Scheme 4a),<sup>39, 52</sup> which is the likely cause for the complete loss of electrocatalytic activity for both H<sub>2</sub> production and oxidation. We cannot however exclude that some catalyst remain trapped between MWNTs and Nafion, with mass transport from and to the electrolyte being fully stopped. It thus proves impossible to use hydrophobic interactions both for grafting the catalyst on the MWNT support, and for making ionomer ion-conducting paths in the same active layer. The covalent binding strategy used in MWNT-NH<sub>3</sub><sup>+</sup>/ $\mathbf{1}^{\text{Ester}}$  avoids this competition pitfall (Scheme 4b). Nevertheless, the required functionalization of the MWNTs by amine

moieties turns them into MWNT-NH<sub>3</sub><sup>+</sup> polycations, and thus induces a strong affinity for the Nafion as a polyanion. This leads to a tight wrapping of most of the Nafion around the MWNT-NH<sub>3</sub><sup>+</sup> as observed in similar systems.<sup>52 53</sup> This Nafion shell reduces H<sub>2</sub> diffusion to and from the MWNT surface, explaining the observed transient currents. However, part of the MWNT-NH<sub>3</sub><sup>+</sup>/1<sup>Ester</sup> material remains uncovered with Nafion and connected to few ionomer bulk-like domains (Fig. 4c), therefore able to achieve bidirectional electrocatalysis. Finally, the ionic interaction between anionic MWNT-COO<sup>-</sup> and cationic 1<sup>Arg</sup> proves much more favourable (Scheme 4c). First, although not covalently bound, 1<sup>Arg</sup> does not significantly desorb from MWNT-COO<sup>-</sup> by competition with the anionic moieties of Nafion. Indeed, CV measurements performed in aqueous potassium phosphate electrolyte at a pH value corresponding to negligible H<sub>2</sub> evolution catalysis indicate that 70-85% of the active sites remain electrochemically connected to MWNTs after Nafion addition (Fig. S12). Second, the MWNT-COO<sup>-</sup>/1<sup>Arg</sup> and Nafion have no strong affinity, so that both can independently organize into the desired electron- and ion-conductive networks respectively. The MWNT-COO<sup>-</sup>/1<sup>Arg</sup>/Nafion composite thus provides the best mesostructure for electrocatalysis in the series.

#### *Optimization of performance and implementation in PEMFC*

From these data, the MWNT-COO<sup>-</sup>/1<sup>Arg</sup>/Nafion composite proves the best choice for implementation in a PEMFC. Membrane-electrode assemblies (MEAs) were fabricated by drop-casting MWNT-COO<sup>-</sup>/1<sup>Arg</sup> /Nafion on a GDL and subsequent hot-pressing of the electrode against a side of an activated Nafion NRE-212 membrane. MEAs fabrication was first optimized for H<sub>2</sub> oxidation currents (Table S1) and electrode homogeneity. The best currents (28 mA·cm<sup>-2</sup> current at 300 mV overpotential in half-cell configuration) arise for a Nafion to MWNT (0.36 mg<sub>MWNT</sub>·cm<sup>-2</sup>) dry weight ratio of 1, catalytic loading in 1<sup>Arg</sup> of 0.2 μmol·cm<sup>-2</sup> (125 μg·cm<sup>-2</sup>) and MEA prepared by hot-pressing for 60 s at 80 °C and 1000 kg·cm<sup>-2</sup>

<sup>2</sup>. This yields a flat catalytic layer with quite homogeneous thickness of 20  $\mu\text{m}$ , with very few MWNTs intruding into the GDL pores (SEM images in Fig. S13). The MEA was completed with a cathode consisting of Co/N/MWNT catalyst<sup>54</sup> and Nafion, drop-cast on a GDL and hot-pressed under the same conditions. Mounted in a 0.126  $\text{cm}^2$  fuel cell setup, this noble-metal free PEMFC displayed an open circuit voltage of  $820\pm 5$  mV and a maximum power output of  $325\pm 2$   $\mu\text{W}\cdot\text{cm}^{-2}$  at 415 mV (Fig. 6), resulting in a 15-fold improvement compared to the performance of the previously reported MEA based on MWNT/**1<sup>Py</sup>**/Nafion ( $23$   $\mu\text{W}\cdot\text{cm}^{-2}$  at 500 mV).<sup>23</sup> Although MWNT-COO<sup>-</sup>/**1<sup>Arg</sup>** possesses a  $\sim 3$ -fold higher H<sub>2</sub> oxidation activity than MWNT/**1<sup>Py</sup>** (Fig. S1), the difference in the intrinsic activity between the distinct active sites cannot alone explain the observed improvement observed here, which again points to the better compatibility of MWNT-COO<sup>-</sup>/**1<sup>Arg</sup>** with Nafion (Fig. S4) as compared to MWNT/**1<sup>Py</sup>** (Fig.S2).

## Conclusion

In this study, we have designed an effective approach to efficiently integrate molecular-engineered bio-inspired catalysts with Nafion ionomer in a membrane electrode assembly. While Nafion may slightly affect the subtle positioning of amine groups in the second coordination sphere of nickel and the intrinsic catalytic bias of the catalysts, the major issue relies in the control of both the electronic connection of the catalysts with the carbon-based support and the mass transport within the catalytic layer. Combining SANS, SEM and electrochemical measurements, we have shown that the structuration of Nafion ionomer in a catalytic ink is deeply influenced by the surface functionalization of MWNTs. Mixing MWNTs functionalized with hydrophilic carboxylate functions and Nafion yields a porous catalytic layer promoting mass transport of protons and gas, therefore with the desired functionality for integration in PEMFC. By contrast, unfavourable interactions take place when the carbon

nanotubes are either functionalized with ammonium sites or left unfunctionalized, leading to a detrimental effect of Nafion addition on mass transport of product and substrate within the catalytic layer. As a consequence, the catalytic performance of the electrode does not always reflect the intrinsic properties of the catalysts. Our results show that, even within the same family of catalysts, the grafting strategy appears crucial as it not only influences the catalyst reactivity at the molecular scale but also the nanocomposite self-assembly at the mesoscale. This finding led to a 15-fold improvement of the performance of platinum-group metal-free membrane electrode assemblies and opens novel perspective regarding the optimization of active layers for operating electrocatalytic devices. More generally, our findings imply that implementing novel catalysts including ultra-small Pt particles,<sup>4, 39</sup> transition metal nitrogen-doped carbon (TM/N/C) ORR catalysts<sup>55-56</sup> and bio-inspired catalysts<sup>40</sup> may require reengineering the electrode composite,<sup>24</sup> with special attention to intermolecular interactions. A favourable impact of positive charges on carbon black was recently reported in the case of low Pt-loaded electrodes, favouring triple-point boundaries.<sup>35</sup> The cationic functionalization of the support studied here with bio-inspired Ni catalysts shows an opposite effect, suggesting that surface functionalisation of the electrode is certainly instrumental to control the microstructure of the active layer and enhance global catalytic performances. A thorough investigation including all components of the catalytic layer should be undertaken when using unconventional catalysts in H<sub>2</sub> technologies, or in emerging electrocatalytic processes such as CO<sub>2</sub> valorization<sup>57</sup> and N<sub>2</sub> reduction to NH<sub>3</sub>.<sup>58</sup> Finally, we note that the pyrene-based grafting method has gained a great popularity in molecular science for the oxygen reduction reaction as well as other multi-electron multi proton catalysis such as water splitting (hydrogen evolution<sup>59</sup> and water oxidation<sup>60</sup>) or CO<sub>2</sub> reduction.<sup>61-63</sup> In these fast growing domains, the fatal effect of Nafion competition on catalysts immobilized by  $\pi$ -stacking should be considered as a serious Achilles' heel of the pyrene functionalization.



## Experimental Procedures

### *Resource Availability*

Lead contact: Pascale Chenevier ([pascale.chenevier@cea.fr](mailto:pascale.chenevier@cea.fr))

Materials Availability : this study did not generate new unique reagent or material

Data and Code Availability: this study does not use unpublished codes, software and algorithm

### *Materials*

All chemicals and solvents, including the Nafion perfluorinated resin solution (5 wt. % in lower aliphatic alcohols and water), were purchased from Sigma-Aldrich and used without further purification unless otherwise stated. UP-NC7000WT MWNTs (purity >90% in carbon) were obtained from Nanocyl (Belgium) and used as received. The gas diffusion layers (GDL w/o MPL) were purchased from Paxitech (Grenoble, France). (4-aminoethyl)benzene diazonium tetrafluoroborate,<sup>22, 64</sup>  $[\text{Ni}(\text{MeCN})_6](\text{BF}_4)_2$ ,<sup>65</sup>  $[\text{Ni}(\text{P}^{\text{Cy}}_2\text{N}^{\text{CH}_2\text{Pyrene}_2})_2](\text{BF}_4)_2$  (**1<sup>Py</sup>**)<sup>23</sup> and  $[\text{Ni}(\text{P}^{\text{Cy}}_2\text{N}^{\text{Arginine}_2})_2](\text{BF}_4)_2$  (**1<sup>Arg</sup>**)<sup>21</sup> were synthesized according to published procedures. For the Pt/MWNT electrocatalysts, the platinum salt ( $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ , 99.9% metal basis) was purchased from Alfa Aesar, the ethylene glycol from Roth (Rotipuran > 99.9 %) and the NaOH from Sigma-Aldrich 99.99 %, Merck. MilliQ water was systematically used.

### *Instrumentation*

NMR spectra were recorded at room temperature in 5 mm tubes on a Bruker AC 300 spectrometer equipped with a QNP probe head, operating at 300.0 MHz for  $^1\text{H}$ , and 121.5 MHz for  $^{31}\text{P}$ . Solvent peaks were used as internal references relative to  $\text{Me}_4\text{Si}$  for  $^1\text{H}$

chemical shifts; H<sub>3</sub>PO<sub>4</sub> (85%) was used as external reference for <sup>31</sup>P NMR spectra. All <sup>31</sup>P NMR spectra were proton decoupled. Electrospray ionization mass spectrometry (ESI-MS) spectra were recorded with a Bruker Daltonics Esquire 3000 Plus device. The elemental analyses were carried out on a C, H, N analyser (SCA, CNRS). Scanning Electron Microscopy (SEM) images and Energy Dispersive X-ray spectroscopy (EDX) were acquired with a ZEISS Ultra 55+ Electron Microscope, using an electron beam at 5.0 kV. Transmission Electron Microscopy (TEM) images were acquired with a Cs-probe corrected FEI Titan Themis microscope at 80 kV.

#### *Electrochemical measurements*

Electrochemical experiments were carried out using a Bio-Logic SP300 potentiostat and a three-electrode electrochemical cell. For aqueous electrochemical measurements, the working electrode was the GDL-MWNT assembly, the counter-electrode was either titanium or platinum wire and the RE-2CP (Hg/Hg<sub>2</sub>SO<sub>4</sub>/sat. K<sub>2</sub>SO<sub>4</sub>; calibrated versus RHE in 0.5 M H<sub>2</sub>SO<sub>4</sub>) was used as reference electrode. Non-aqueous voltammograms were measured against an Ag/AgCl/3M KCl reference electrode and referenced to the Fc<sup>+0</sup> couple by the addition of an internal standard after the final experiment. Cyclic voltammetry and chronoamperometry experiments were recorded in a homemade miniaturized half-cell setup,<sup>22, 66</sup> in aqueous 0.5 M H<sub>2</sub>SO<sub>4</sub> purged with argon. Gases were provided in the back of the GDL at atmospheric pressure (P<sub>atm</sub>) and 20 mL·min<sup>-1</sup> and atmospheric pressure with the use of Bronkhorst Mass-Flows through Swagelok fittings.

#### *Small Angle Neutron Scattering*

SANS measurements were performed on the D22 spectrometer at the Institut Laue Langevin (ILL, Grenoble, France) and on the PAXY spectrometer at the Laboratoire Léon Brillouin

(LLB, Paris, France). Two configurations were used to cover an extended  $Q$ -range, from  $4 \times 10^{-3}$  to  $0.6 \text{ \AA}^{-1}$  and  $7 \times 10^{-3}$  to  $0.6 \text{ \AA}^{-1}$  (ILL and LLB experiments, respectively),  $Q$  being the scattering vector defined as  $Q = (4\pi/\lambda)\sin(\theta/2)$  where  $\lambda$  is the wavelength of the incident neutron beam, and  $\theta$  the total scattering angle. The isotropic 2D patterns recorded in the two configurations were radially averaged to obtain the 1D scattered intensities  $I(Q)$ , and further corrected using standard procedures (detector efficiency, background, and empty cell subtraction) using PASINET and GRASP data reduction in-house softwares. As data taken in the two configurations were perfectly overlapping in the intermediate  $Q$ -region, the  $I(Q)$  were merged to obtain a single profile for each sample. Prior to the SANS experiment, the hydrated materials deposited on quartz window were inserted in round cells and maintained at 98% RH by equilibrating them in a fixed vapor pressure environment. Absolute intensities were obtained by normalized  $I(Q)$  by the mass of MWNTs in each sample. Fitted data are shifted for clarity and therefore plotted in arbitrary units. Spectra fitting was performed using SASView software. The best fits were obtained with the core-shell cylinder form factor and the hard-sphere structure factor, with a size dispersity of 40% in core radius, shell thickness and length.

### *SANS 1D profile fitting*

SANS profiles were fitted using the SASView software, with the core-shell cylinder model. This corresponds to the following model:

$$I(q, \alpha) = \frac{1}{V_s} F^2(q, \alpha) \cdot \sin(\alpha) + \text{background}$$

where

$$F(q, \alpha) = (\rho_c - \rho_s) V_c \frac{\sin(q \frac{1}{2} L \cos \alpha)}{q \frac{1}{2} L \cos \alpha} \frac{2J_1(q R \sin \alpha)}{q R \sin \alpha} \\ + (\rho_s - \rho_{\text{solv}}) V_s \frac{\sin(q (\frac{1}{2} L + T) \cos \alpha)}{q (\frac{1}{2} L + T) \cos \alpha} \frac{2J_1(q (R + T) \sin \alpha)}{q (R + T) \sin \alpha}$$

and

$$V_s = \pi (R + T)^2 (L + 2T)$$

and  $\alpha$  is the angle between cylinder axis and  $q$ ,  $V_s$  is the total volume,  $V_c$  is the volume of the core,  $L$  is the length of the core,  $R$  is the radius of the core,  $T$  is the thickness of the shell,  $\rho_c$  is the scattering length density of the core,  $\rho_s$  is the scattering length density of shell,  $\rho_{solv}$  is the scattering length density of the solvent, and *background* is the background level.  $J_1$  is the first order Bessel function.

### Synthesis

#### **P<sub>Cy</sub><sub>2</sub>N<sup>Ph</sup>CH<sub>2</sub>CH<sub>2</sub>COOH<sub>2</sub>**

To a suspension of paraformaldehyde (408 mg, 13.6 mmol) in degassed, dry ethanol (60 mL) cyclohexylphosphine (0.88 mL, 6.68 mmol) was added drop-wise. The suspension was heated at 78 °C overnight under argon, after which 3-(4-aminophenyl)propionic acid (1.1 g, 6.65 mmol) was added, and the solution stirred at 78 °C for an additional night. After cooling in the freezer at -18 °C for several hours, the voluminous white precipitate was filtered with cannula and washed several times with ethanol. The precipitate was then recrystallized from DMF and water, filtered and dried to give 1.63 g of a white powder (2.67 mmol, 80%); <sup>1</sup>H NMR (DMSO-d<sub>6</sub>):  $\delta$  11.97 (s, 2H, COOH), 6.95 (d, <sup>2</sup>J = 7.4 Hz, 4 H, NC<sub>6</sub>H<sub>4</sub>), 6.46 (d, <sup>2</sup>J = 7.6 Hz, 4 H, NC<sub>6</sub>H<sub>4</sub>), 4.13 (d, <sup>2</sup>J = 13.7 Hz, 4 H, PCH<sub>2</sub>N), 3.89 (d, <sup>2</sup>J = 13.3 Hz, 4 H, PCH<sub>2</sub>N), 3.31 (s, 8 H, CH<sub>2</sub>CH<sub>2</sub>COO), 1.07 – 2.90 ppm (m, 22 H, C<sub>6</sub>H<sub>11</sub>); <sup>31</sup>P NMR (DMSO-d<sub>6</sub>):  $\delta$  -42.22 ppm.

#### **P<sub>Cy</sub><sub>2</sub>N<sup>Ph</sup>CH<sub>2</sub>CH<sub>2</sub>COOPht<sub>2</sub>**

To a solution of P<sub>Cy</sub><sub>2</sub>N<sup>Ph</sup>CH<sub>2</sub>CH<sub>2</sub>COOH<sub>2</sub> (459 mg, 0.75 mmol) in 15 mL DMF was added *N*-hydroxyphthalimide (489 mg, 3 mmol) and *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (577 mg, 3 mmol) and the mixture stirred overnight. The yellow suspension was added drop-wise to rapidly stirred water to precipitate the product, which was collected by filtration and recrystallized from chloroform and diethyl ether, then

washed copiously with water, ethanol and ether to give 595 mg of a light yellow product (0.66 mmol, 88%);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.81 – 7.91 (m, 8 H, pht), 7.08 (d,  $^2J = 8$  Hz, 4 H,  $\text{NC}_6\text{H}_4$ ), 6.66 (d,  $^2J = 8$  Hz, 4 H,  $\text{NC}_6\text{H}_4$ ), 4.31 (t,  $^3J = 13.5$  Hz, 4 H,  $\text{PCH}_2\text{N}$ ), 3.57 (d,  $^2J = 15$  Hz, 4 H,  $\text{PCH}_2\text{N}$ ), 2.93 (m, 8 H,  $\text{CH}_2\text{CH}_2\text{COO}$ ), 1.35 – 1.99 ppm (m, 22 H,  $\text{C}_6\text{H}_{11}$ );  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  –39.64 ppm.

### **1<sup>Ester</sup>**

In an argon-purged Schlenck flask, 130 mg  $\text{P}^{\text{Cy}_2\text{N}}^{\text{PhCH}_2\text{CH}_2\text{COOPht}_2}$  (0.144 mmol) and 26.7 mg  $[\text{Ni}(\text{MeCN})_6](\text{BF}_4)_2$  (0.057 mmol) were dissolved in ~5 mL dry, degassed acetonitrile and stirred overnight at room temperature under argon. The purple solution was filtered and the solvent removed to give 102 mg of  $[\text{Ni}(\text{P}^{\text{Cy}_2\text{N}}^{\text{PhCH}_2\text{CH}_2\text{COOPht}_2})_2](\text{BF}_4)_2$  (**1<sup>Ester</sup>**) as a purple powder (0.05 mmol, 88%);  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  7.88 (s, 16 H, pht), 7.27 (d,  $^2J = 8.3$  Hz, 8 H,  $\text{NC}_6\text{H}_4$ ), 7.04 (d,  $^2J = 8.3$  Hz, 8 H,  $\text{NC}_6\text{H}_4$ ), 4.09 (d,  $^2J = 14.1$  Hz, 4 H,  $\text{PCH}_2\text{N}$ ), 3.83 (d,  $^2J = 14.2$  Hz, 4 H,  $\text{PCH}_2\text{N}$ ), 3.75 (d,  $^2J = 14.5$  Hz, 4 H,  $\text{PCH}_2\text{N}$ ), 3.56 (d,  $2J = 13.9$  Hz, 4 H,  $\text{PCH}_2\text{N}$ ), 3.02 (s, 16 H,  $\text{CH}_2\text{CH}_2\text{COO}$ ), 1.39 – 2.22 ppm (m, 44 H,  $\text{C}_6\text{H}_{11}$ );  $^{31}\text{P}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  6.34 ppm; mass spectrometry (ESI<sup>+</sup>):  $m/z$  929.7  $[\text{M}-2\text{BF}_4^-]^{2+}$ ; cyclic voltammetry:  $\frac{1}{2}(\text{Epa} + \text{Epc}) = -0.65$  and  $-1.11$  V vs.  $\text{Fc}^{+/0}$  (Fig. S14); elemental analysis (%) calculated for  $\text{C}_{100}\text{H}_{108}\text{B}_2\text{F}_8\text{N}_8\text{NiO}_{16}\text{P}_4$ : C, 59.05; H, 5.35; N, 5.51; found: C, 56.95; H, 5.33; N, 5.52.

### *Grafting and ink preparation*

#### **MWNT-COO<sup>-</sup>/1<sup>Arg</sup>**

Adapting from a recently developed procedure,<sup>15</sup> MWNTs (50 mg) are sonicated in 150 mL of argon-degassed DMF for 45 minutes. 1.5 g of 6-amino-2-naphtoic acid and 1.1 mL of isoamyl nitrite are added, to trigger the *in situ* formation of 2-naphthoic acid 6-diazonium and

its subsequent reduction onto the MWNTs. The reaction vessel is purged with argon, closed then heated under stirring at 80 °C for 12 hours. After cooling, the MWNTs are filtered on a 0.45 µm Teflon filter, sonicated overnight in 150 mL of DMF then filtered again. They are rinsed thoroughly with hot DMF and EtOH and dried under vacuum to yield around 50 mg of MWNT-COOH. 6 mg of MWNT-COOH are then dispersed by sonication in 1 mL of abs. EtOH. The suspension was diluted with abs. EtOH, either without or with Nafion (1:1 Nafion:MWNTs dry mass ratio, 150 µL of a 5% solution) to reach a final volume of 2 mL. This suspension (200 µL) was mixed in a 3:1 ratio with a 3 mg·mL<sup>-1</sup> solution (67 µL) of **1**<sup>Arg</sup> in pH 6, aqueous, 0.1 M MES:HEPES (1:1 v/v) buffer. 20 µL of this suspension were then drop cast directly onto a 0.126 cm<sup>2</sup> circular area of GDL and air-dried.

#### **MWNT-NH<sub>3</sub><sup>+</sup>/1<sup>Ester</sup>**

As described in our early work for similar complexes bearing activated ester function,<sup>16-17</sup> MWNTs (2.5 mg) are dispersed by sonication in 25 mL abs. EtOH, and filtered onto a 5 cm<sup>2</sup> circular piece of GDL. 4-aminoethyl)benzene diazonium tetrafluoroborate (25 mg in 50 mL degassed MeCN / 0.1 M nBu<sub>4</sub>NBF<sub>4</sub>) was electrochemically reduced onto the MWNT layer through cyclic voltammetry by recording 2 cycles at 20 mV·s<sup>-1</sup> between 0.5 V and -0.8 V vs. Ag/AgCl, yielding MWNT-NH<sub>3</sub><sup>+</sup>. Amine coverage before grafting has been estimated around 2 % (N/C ratio) corresponding to about one atom of nitrogen per 40 MWNT surface carbon atoms.<sup>67</sup> The electrode was then soaked in a 1 mmol·L<sup>-1</sup> solution of **1**<sup>Ester</sup> in DMF in the presence of 10 eq. of 2,6-lutidine overnight, then rinsed with DMF, MeCN and air-dried. Fig. S15 presents the cyclic voltammetry characterization of the MWNT-NH<sub>3</sub><sup>+</sup>/**1**<sup>Ester</sup>. Fig. S16 shows the stability of a MWNT-NH<sub>3</sub><sup>+</sup>/**1**<sup>Ester</sup> electrode during both H<sub>2</sub> production and oxidation at 300 mV overpotential.

Alternative strategies for modification of the MWNTs were employed to ensure that the behaviour of the MWNT-NH<sub>3</sub><sup>+</sup>/**1**<sup>Ester</sup> system did not arise from the electrodeposition of the diazonium salt. Following the protocol for the synthesis of MWNT-COOH, replacing the 6-amino-2-naphtoic acid by 4-(2-aminoethyl)aniline yielded MWNT-NH<sub>3</sub><sup>+</sup>. Although the overall areal current densities were lower with this functionalization mode, no qualitative difference was observed when compared to the MWNT-NH<sub>3</sub><sup>+</sup> made by electrodeposition of the diazonium salt. Even more interestingly, the order of the addition of Nafion for the Nafion-containing electrodes, whether it was added as described above or deposited on top of the electrodes (200 μL·cm<sup>-2</sup>) after electroreduction of diazonium, was proven to have no qualitative effect on either electrochemistry results or the aspect of individual MWNTs in SEM images. Addition of Nafion was done by dropcasting a 5 wt. % in lower aliphatic alcohols and water onto the electrode to reach a 1:1 Nafion:MWNTs dry mass ratio (typically 125 μL per cm<sup>2</sup>).

### **MWNT/**1**<sup>Py</sup>**

This grafting method was also described in our previous work.<sup>23</sup> No prior modification of the MWNTs was required, and they were simply dispersed in abs. EtOH by sonication (6 mg·mL<sup>-1</sup>) and diluted to 2 mL with abs. EtOH either without or with Nafion (1:1 Nafion:MWNTs dry mass ratio). This MWNT suspension was mixed in a 3:1 ratio with a 1 mmol·L<sup>-1</sup> solution of **1**<sup>Py</sup> in DCM and 20 μL of this mixture were drop-casted onto a 0.126 cm<sup>2</sup> circular area of a GDL and air-dried.

### **MWNT/Pt (ULL Pt)**

The deposition of the Pt nanoparticles onto the various MWNT was performed through the following process:<sup>42</sup> a given amount of Pt salt was dissolved in a 2:1 ethylene glycol:deionized water (18.2 MΩ cm) solution (for a typical synthesis, 88 mg of Pt salt in 100

mL of solution). Then, the solution was brought to pH 12.5, using a deionized water solution saturated in NaOH and vigorously stirred under argon atmosphere for 1 h. The temperature was then increased to 120 °C and maintained for 3 h. Meanwhile, MWNTs were dispersed in a 1:1 ethylene glycol:deionized water solution, aiming a 1 % theoretical weight fraction of Pt onto the carbon support (wt. %). The solution containing the Pt colloidal solution and the dispersed carbon support were mixed and the pH of the solution was decreased down to 2.5 to allow the nanoparticles deposition onto the carbon support. After  $t = 22$  h, the solution was filtered, washed and dried for  $t = 45$  min at  $T = 110$  °C.

The obtained dry powder was then dispersed in EtOH at  $3 \text{ mg}\cdot\text{mL}^{-1}$ , with or without Nafion solution (1:1 Nafion:MWNTs dry mass ratio) and deposited onto a GDL in order to obtain a final surface loading of 7 or  $14 \text{ }\mu\text{g}\cdot\text{cm}^{-2}$  of Pt.

### **Membrane-electrode assembly**

The anode was a MWNT-COO<sup>-</sup>/ $\mathbf{1}^{\text{Arg}}$  electrode with Nafion to MWNT-COOH dry mass ratio of 1, prepared as follows: 3 mg of MWNT-COOH were dispersed by sonication in 1 mL of absolute EtOH in the presence of 5 wt. % Nafion solution (75  $\mu\text{L}$ ). This suspension (200  $\mu\text{L}$ ) was mixed in a 3:1 ratio with a  $3 \text{ mg}\cdot\text{mL}^{-1}$  solution (67  $\mu\text{L}$ ) of  $\mathbf{1}^{\text{Arg}}$  in pH 6 aqueous 0.1 M MES:HEPES (1:1) buffer. This ink was deposited on GDL at a loading of  $160 \text{ }\mu\text{L}\cdot\text{cm}^{-2}$  (corresponding to  $125 \text{ }\mu\text{g}\cdot\text{cm}^{-2} \mathbf{1}^{\text{Arg}}$ ) and air-dried.  $0.126 \text{ cm}^2$  anodes were then punched out. A Nafion membrane sheet (NRE-212, 50  $\mu\text{m}$  thick, Alfa Aesar) was activated prior to use following a standard procedure<sup>68</sup> in 4 steps at 80 °C: 30 min in 3 wt. % H<sub>2</sub>O<sub>2</sub> aqueous solution, 30 min in deionized water, 30 min in H<sub>2</sub>SO<sub>4</sub> (0.5 M) and then 30 min in deionized water. The activated membrane was stored in distilled water and superficially dried before use.



The Co/N/MWNT oxygen-reduction cathode was prepared as described in previous work. [ENREF 54](#)<sup>54</sup> 20 mg of this Co/N/CNT catalyst was dispersed under sonication in a 3:1 (v/v) mixture of EtOH and H<sub>2</sub>O (1.04 mL) in the presence of 5 wt. % Nafion solution (160 μL). The ink was sonicated for 60 minutes. 400 μl of this ink were deposited on the GDL (5 cm<sup>2</sup>) substrate and dried at 80 °C under ambient atmosphere leading to a final catalyst loading of around 1333 μg·cm<sup>-2</sup>. The drop-casting was repeated twice to get a final loading of 4 mg·cm<sup>-2</sup>. 0.126 cm<sup>2</sup> cathodes were then punched out.

Half-MEA measured in Table S1 were prepared by pressing 0.126 cm<sup>2</sup> anodes with a conditioned Nafion NRE-212 membrane at various temperatures and pressures for 1 min.

Full MEA were prepared by pressing 0.126 cm<sup>2</sup> anode and cathode against either side of a Nafion NRE-212 membrane at 80°C and 1000 kg·cm<sup>-2</sup> for 1 min. The as-prepared MEA was further assembled in the single-cell PEMFC. Polytetrafluoroethylene (PTFE) gaskets (FuelCellStore) with ~5 mm diameter holes were used at both anode and cathode side. The gasket thickness were chosen to achieve ca. 15 % compression of the electrodes.

### *Fuel cell measurements*

Testing PEMFC tests were performed with a single-cell fuel cell (5 cm<sup>2</sup> active area, Paxitech) with serpentine flow field using an in-house fuel cell bench and a Bio-Logic potentiostat with a 10 A load. Stainless steel gas tubing (Swagelock) was connected to BronkHorst mass flow controllers providing the flow rates for humidified H<sub>2</sub> and O<sub>2</sub> of 80 mL·min<sup>-1</sup>, downstream of the fuel cell. For the tests, humidifier's temperatures were 80 °C. The gas outlets were let at atmospheric pressure. Heating cartridges (PID, RS Components) were connected to the fuel cell and allowed fine control (2 °C) over the temperature of the cell as a whole. Before measurement with a Bio-Logic SP-300 potentiostat, the fuel cell was degassed with N<sub>2</sub> for 20 minutes prior to purging the anode and cathode with H<sub>2</sub> and O<sub>2</sub> respectively. Polarization

curves were recorded by scanning the cell voltage from open circuit voltage (OCV) down to 0.3 V at a scan rate of 2 mV·s<sup>-1</sup>.

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## **Author Contributions**

Conceptualization : P. C and V.A.; Funding acquisition : P.C. and V.A.; Investigation: N. C. B. R., T. N. H., F. V. R.T. J., S. G., E.S.A, T.A., A. M., P.C and S. L.; Methodology: P.C., S. L. and V.A.; Resources: B. J., A. L-G.; Supervision: F. M., P. C. and V.A.; Writing – original draft: T.N. H, R. T. J, N. C.; Writing – review & editing: N.C., P.C and V.A.

## **Declaration of Interests**

The authors declare no conflict of interest.

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## Figures titles and Legends

**Fig. 1.** Molecular-engineered catalytic materials: a: Three molecular complexes for H<sub>2</sub> oxidation and evolution with anchoring groups, inspired from the active sites of [FeFe]-hydrogenases. Here, the active site of *C. reinhardtii* HydA (bottom left) is represented in its native state and a H<sub>2</sub> molecule can coordinate where the red arrow points. b: Three bio-inspired molecular engineered nanomaterials for H<sub>2</sub> oxidation: MWNT-COO<sup>-</sup>/1<sup>Arg</sup>, MWNT-NH<sub>3</sub><sup>+</sup>/1<sup>Ester</sup> and MWCNT/1<sup>Py</sup>.

**Fig.2:** Scanning electron microscopy images of catalytic layers (CL) based on the three systems (top:  $\mathbf{1}^{\text{Arg}}$ , middle:  $\mathbf{1}^{\text{Ester}}$ , bottom:  $\mathbf{1}^{\text{Cy}}$ ) mixed with Nafion (MWNT/Nafion 1:1 dry mass ratio) deposited on GDL. In all images, the catalytic layer is face up.

**Fig. 3:** (a, b, c) Potential-step chronoamperometry measured for the MWNT/catalyst electrodes (see table 1 for catalytic loading) with (continuous line) and without Nafion (MWNT to Nafion ratio of 1, dotted line). Half-cell setup,  $S = 0.063 \text{ cm}^2_{\text{geom}}$ , electrolyte is aqueous 0.5 M  $\text{H}_2\text{SO}_4$ ,  $T = 25 \text{ }^\circ\text{C}$  and  $P_{\text{N}_2} = 1 \text{ atm}$ . (d) corresponding potential vs. time profile.

**Fig. 4:** SANS data and models for the self-organization of MWNTs and ionomer in the samples. (a) Neutron scattering 1D profiles of MWNT-COOH (black circles) as a reference compared to hydrated samples of MWNT-COO<sup>-</sup>/ $\mathbf{1}^{\text{Arg}}$ /Nafion (red squares), MWNT-NH<sub>3</sub><sup>+</sup>/ $\mathbf{1}^{\text{Ester}}$ /Nafion (blue up triangles), MWNT/ $\mathbf{1}^{\text{Py}}$ /Nafion (green down triangles). MWNT to Nafion weight ratio was set to 1. Inset: TEM image of a MWNT-COOH. (b) Best fits of the SANS data with a core-shell cylinder model. The hydrated Nafion profile (yellow crosses) is reproduced from ref. <sup>47</sup>. (c) Background-subtracted SANS 1D profiles of MWNT-COO<sup>-</sup>/ $\mathbf{1}^{\text{Arg}}$ /Nafion (red squares), MWNT-NH<sub>3</sub><sup>+</sup>/ $\mathbf{1}^{\text{Ester}}$ /Nafion (blue up triangles), MWNT/ $\mathbf{1}^{\text{Py}}$ /Nafion (green down triangles) and MWNT-COOH/Nafion (black dots) showing the ionomer peak. The background was obtained as a sum of the MWNT-COOH profile normalized at  $Q=0.06 \text{ \AA}^{-1}$  and a flat high-Q incoherent background fitted at  $Q=0.4 \text{ \AA}^{-1}$ . (d, e) Model schemes for the MWNT/Nafion ionomer structure in the hydrated samples: (d) independent MWNT network and ionomer structure producing aqueous channels,<sup>47</sup> (e) tight adhesion of ionomer as a shell around MWNT, preventing ionomer self-organization.

**Fig. 5:** Schemes representing the ionomer and catalyst arrangement in the MWNT network in the MWNT/**1**<sup>Py</sup>/Nafion (a), MWNT-NH<sub>3</sub><sup>+</sup>/**1**<sup>Ester</sup>/Nafion (b) and MWNT-COO<sup>-</sup>/**1**<sup>Arg</sup>/Nafion (c) composites at the mesoscale.

**Fig. 6.:** Power curve of a MWNT-COOH/**1**<sup>Arg</sup>/Nafion | Nafion NRE-212 membrane | Co/N/MWNT fuel cell under humidified pure H<sub>2</sub> (anode) and O<sub>2</sub> (cathode) feeds at 20 mL·min<sup>-1</sup>,  $S = 0.126 \text{ cm}^2$ , room temperature,  $P_{\text{atm}}$ .