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3D-structured electrocatalysts for improved mass-transfer in proton-exchange membrane fuel cell cathodes

Matthieu Tempelaere ^{1,2}, Marc Zimmermann ¹ and Marian Chatenet ^{2, †}

¹ NAWA Technologies, 190, Avenue Célestin Coq, 13106 Rousset Cedex – FRANCE

² Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, Grenoble INP (Institute of Engineering and Management), LEPMI, 38000 Grenoble, France

†Corresponding author:

Tel.: +33 4 76 82 65 88; E-mail address: marian.chatenet@grenoble-inp.fr

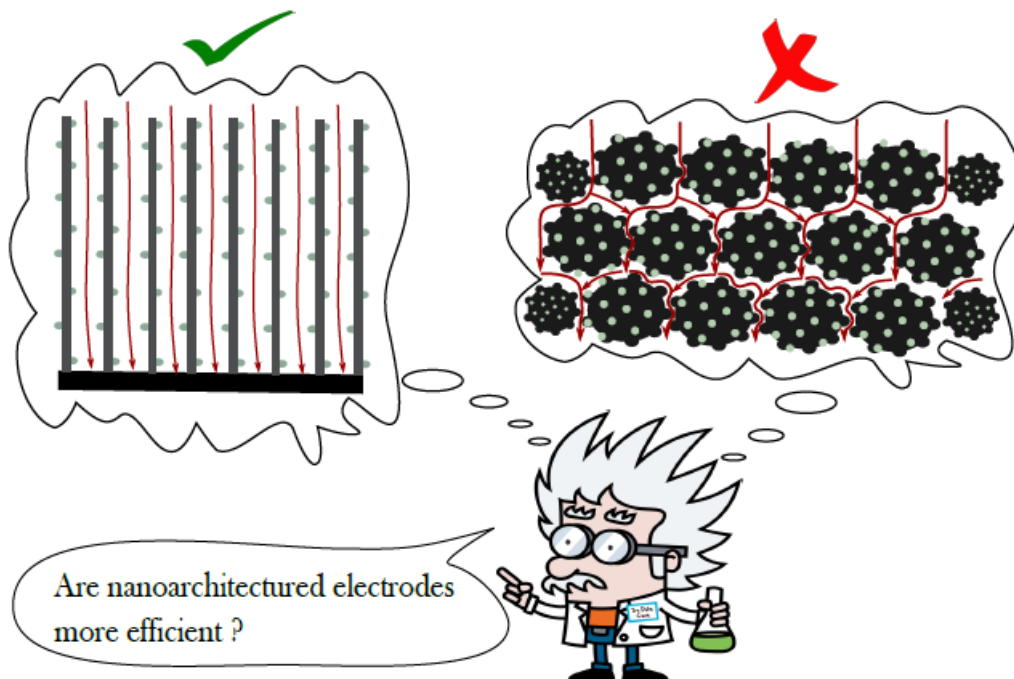
Abstract

High-performance proton-exchange membrane fuel cells (PEMFCs) are required to decarbonize the industry and transportation sectors. Implementing new technologies in PEMFCs may enable to overcome their technological barriers, notably their short lifespan and insufficient specific power per mass of costly and poorly-available platinum-based electrocatalysts. Pt-based electrocatalysts, the present state-of-the-art, must be more efficiently utilized in the PEMFC electrodes and in particular the cathode. This review presents that, despite recent successes, conventional randomly-organized Pt/carbon-black plus ionomer active layers cannot optimize the complex interplay between Pt electrocatalytic activity and proton/oxygen gas/liquid water mass-transfer within their structure. Numeric models clearly show that oriented electrodes or 3D-structured electrodes should better utilize the Pt electrocatalyst, thanks to more efficient mass-transfer to/from the catalytic sites in operation. The recent achievements in these exciting technologies will be recalled, and their advantages and drawbacks summarized, so to propose a strategy for future developments towards their implementation in practical PEMFCs.

Keywords

Proton exchange membrane fuel cell (PEMFC), oxygen reduction reaction (ORR), platinum-based electrocatalysts, mass-transfer, 3-dimensional electrode (3D-structured electrode), catalyst layers (CLs)

Graphical abstract



Highlights

- Classical PEMFC catalyst layers (CL) are not optimized for efficient mass-transfer
- 3D-structured CLs enable better mass-transfer
- Carbon-free 3D-structured CLs fail to properly manage water
- Vertically-aligned carbon nanotubes (VACNT) are promising Pt supports

Glossary

ALD: Atomic Layer Deposition

AST: Accelerated stress test

CL: Catalyst layer

CNT: Carbon nanotubes

DOE (or US DOE): (United states) Department of Energy

ECSA: Electrochemical surface area

FCCJ: Fuel Cell Commercialization Conference of Japan

FE-SEM: Field-emission gun scanning electron microscope

GCNT: Pt/graphene CNT composites

GDL: Gas diffusion layer

GDP: Gross Domestic Product

HOR: Hydrogen oxidation reaction

J-PtNWs/C: Jagged platinum nanowires

KB: Ketjen black (carbon)

MA: Mass activity

MEA: Membrane electrode assembly

MPL: Microporous layer

NCNT: N-doped carbon nanotubes

NP: Nanoparticles

NSTF: Nanostructured thin films

NT: Nanotubes

NW: Nanowires

ORR: Oxygen reduction reaction

PEM: Proton exchange membrane

PEMFC: Proton exchange membrane fuel cells

PGM: Platinum group metal

Pt/C: Carbon-supported platinum nanoparticles

PtM/C: Carbon-supported platinum alloys nanoparticles

PTFE: Polytetrafluoroethylene

RDE: Rotating disk electrode

RH: Relative humidity

RHE: Reversible hydrogen electrode

R-PtNWs/C: Rhombus platinum nanowire

SEM: Scanning electron microscope

UHT: Ultrathin holey nanotube

VACNT: Vertically-aligned carbon nanotubes

XC72: Vulcan XC72 carbon black

1- Introduction

Climate change and related challenges motivated 136 countries, accounting for 90% of global Gross Domestic Product (GDP) and 85% of the population, to set net-zero targets [1]. This requires considerable efforts to decarbonize all sectors of the economy; green-hydrogen produced from renewable energies participates to the strategy and must be significantly increased [2]. Fuel cells that convert hydrogen into electricity are considered for mobility applications, e.g. proton exchange membrane systems (PEMFCs), where oxygen reduction reaction (ORR) and hydrogen oxidation reaction (HOR) take place [3]. The high cost of PEMFCs stems from their core materials (carbon-supported platinum (Pt/C) or Pt-alloy (PtM/C) electrocatalysts, perfluorosulfonated membranes – typically Nafion®, bipolar plates, gas diffusion media, etc.), which impedes their commercial development. In addition, PEMFC operating conditions are demanding to these materials (carbon substrate and platinum-based nanoparticles (NPs) corrosion, essentially at the cathode); this affects their lifespan, which remains insufficient for transport applications [4].

Researchers presently strive to discover more active PtM/C ORR electrocatalysts; while the last decade enabled significant improvements of their intrinsic activity, that improved significantly ($\times 5-10$) beyond classical Pt/C, advanced PtM/C electrocatalysts still fail to validate their promises in real PEMFCs [5]. Being usually tested in lab scale using the rotating disk electrode (RDE), which is limited by O_2 mass-transfer in liquid electrolyte, hence not capable to measure directly the ORR activity at PEMFC cathode relevant potential/current density, some suggested that the technique cannot forecast real PEMFC operation for such materials. However, recent measurements in gas diffusion electrode or differential cell showed that advanced electrocatalysts do maintain their promises at larger current density/lower potential [6][7], which means that it is the PEMFC cathode catalyst layer (CL) that cannot - to date - efficiently use them owing to severe O_2 and/or H^+ mass-transfer limitation to the catalytic sites. Indeed, Pt utilization (how well the Pt catalysts is in condition of “triple contact” with the gas, ionomer – H^+ - phase and electron-conducting phases, the required conditions to render the sites electrochemically active) and effectiveness (how well Pt sites are accessible at the “proper rate” to the reactants) are important parameters of PEMFC cathode CLs [8]. So, tailoring PEMFC electrodes to enhance their operational performance/durability is mandatory.

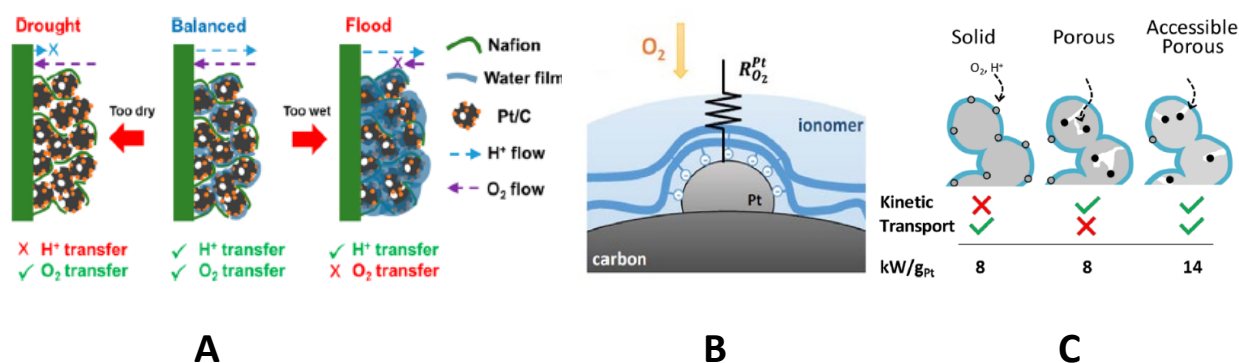
2- Classical PEMFC CLs

Present PEMFC CLs are built by randomly mixing PtM/C nanoparticles (NPs) with the ionomer in appropriate solvents; once formulated, this ink is deposited on the PEM or the gas diffusion layer, GDL. In that methodology, one hopes that the CL structure will enable fast mass-transfer of the protons in the ionomer/water phase and of the gaseous reactants in open pores between the PtM/C-ionomer agglomerates [9] (**Figure 1A, 1B**). Because PEMFCs operate below 100°C (typically $60-80^\circ\text{C}$), the main product of the H_2/O_2 (air) conversion is liquid water, and its efficient removal from the cathode is pivotal. Using a properly-designed and partially hydrophobic (PTFE treatment) porous gas diffusion medium, usually bearing a carbon-fiber-based GDL added to a carbon-black-based microporous layer (MPL) enables to efficiently manage liquid water [10]. Appropriate pore structure and composition (hydrophobicity) in the GDL (and CL) are mandatory [11][12][13]. Since the 2000s, numerous groups optimized the elaboration of PEMFC CLs, to tune Pt(M)/C integration [14][15][16][17]. Other strategies to better manage water in the CL were developed [18], like to include hydrophobic binder in the CL (operation at high relative humidity (RH) conditions) [19], or hydrophilic ones (operation at low RH conditions) [20][21]. Although this worked out until the 2010s using classical Pt/C electrocatalysts, the advanced electrocatalysts presently available render this strategy insufficient, especially for low-loading CLs. These suffer additional mass-transfer resistance and should be further optimized, so to accelerate the fluxes of protons and molecular oxygen to the Pt(M) sites and that of liquid water from the sites [22]. The intimate contact between the perfluorosulfonated ionomer and the Pt(M) NPs was

recognized limiting, owing to (i) Pt(M)-sites poisoning by $-\text{SO}_3^-$ moieties and (ii) non-negligible O_2 mass-transfer resistance through the 2-5 nm-thick ionomer film covering the NPs [23][24]: ionomer-covered Pt(M) is less active [25] and less accessible to O_2 [25][26] (**Figure 1B, 1C**). Models of the Pt|ionomer interface show that the ionomer orientation depends on the hydrophilicity/hydrophobicity of the electrocatalyst surface: the ionomer adsorbs through the $-\text{SO}_3^-$ groups on hydrophilic surfaces, leaving the hydrophobic PTFE backbone facing the pore (yielding more hydrophobic CLs), and by the PTFE backbone on hydrophobic surfaces, leaving the hydrophilic $-\text{SO}_3^-$ groups facing the pore (yielding more hydrophilic CLs). This has major consequences in the water management of the CL [27][28] and on its structure: improper interaction between the ionomer and the Pt(M)/C electrocatalyst in the ink leads to inappropriate (too big) ionomer/electrocatalyst agglomerates, that adversely affect mass-transfer in the CL [17][29].

The O_2 transport resistance to the Pt(M) NPs can be enhanced using short-side chain ionomers [30] or highly-oxygen permeable ionomers (HOPI) [31], in which the larger strain in the polymer backbone weakens the $-\text{SO}_3^-$ adsorption at the Pt(M) sites (hence lowers poisoning), and enables larger proton conductivity at small RH and smaller O_2 transport resistance. Modifying the Pt(M)/C electrocatalyst is also possible, e.g. by increasing the electrochemical surface area (ECSA), hence multiplying the number of active sites, which mechanically reduces the required fluxes to each site [5,32]. Employing mesoporous carbon supports, in which there is no (or less) direct ionomer contact with the Pt(M) NPs “buried” in the mesopores (hence no (less) poisoning or major O_2 transport resistance) [25][33][34] leads to the same result (**Figure 1C**). Lazaridis et al. [34], Kodama et al. [25] and Gottesfeld [24] rationalized the interest of such materials as Pt(M) NPs support, provided the mesopores are neither too small (microporous constriction would prevent fast O_2 transport) nor too big (ionomer could intrude the pores and/or flooding would hinder O_2 transport).

The importance of the cathode CL structure was illustrated by Garsany et al. [35]: dual-layer cathode CLs, based on commercial carbon-supported platinum electrocatalysts of high microporosity (Ketjen Black EC-300J) or low porosity (Vulcan XC-72) show 20%-improved performance at low RH (25%), conditions that generally inhibit PEMFC performance. Electrochemical impedance spectroscopy indicates that dual-layer cathodes ease water management, leading to lower kinetic losses and improved ionomer/membrane hydration. Also, Lee et al. textured the interface between the CL and the membrane, which enabled larger ECSA and performance (by 70-90% for wrinkled versus flat interfaces) [36]. Other methods are based on this “classical PEMFC CL” structure; modern processes such as a movable type printing method can for example enable to synthesize promising single atoms catalysts [37], but it must be stated that this type of multi-element non-PGM material have still not been demonstrated in real applications.



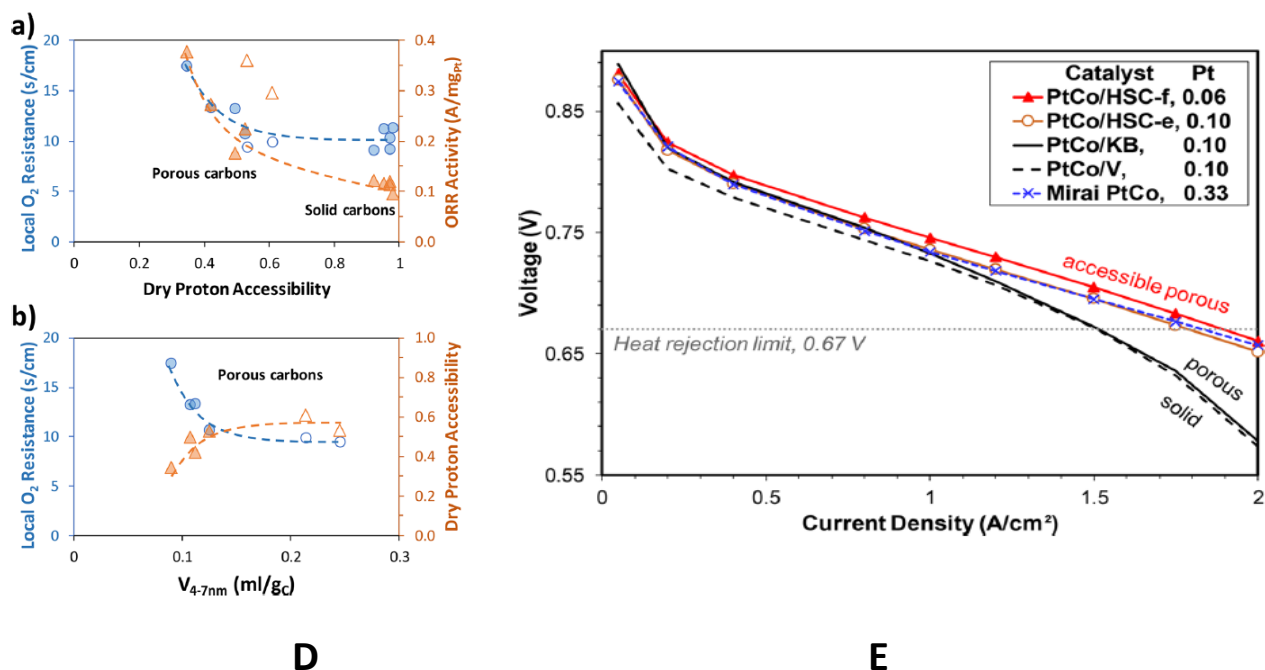


Figure 1: **A.** Tuning the CL water content for ideal performance [38]. **B.** Adsorption and diffusion resistance of O₂ to the Pt/C nanoparticle through an ionomer film [31]. **C.** ORR kinetic and transport (O₂ and proton) characteristics of CL structures made from three types of carbon (gray). Small black and gray circles represent relatively high and low activity Pt particles, respectively, due to ionomer (blue) adsorption [32]. **D.** (a) Local-O₂-transport resistances and ORR mass activities of Pt electrocatalysts on several carbon supports as a function of dry proton accessibility (determined from CO-stripping voltammetry). (b) O₂ and proton accessibility versus the volume of carbon mesopores (4–7 nm) for porous carbons. Open symbols represent electrocatalysts with accessible porous carbons [32]. **E.** Fuel cell performance comparison of PtCo electrocatalysts on different carbons. Anode Pt loadings: 0.025 mg_{Pt}/cm², cathode Pt loadings (mg_{Pt}/cm²) indicated in legend. Operating conditions: anode/cathode: H₂/air, 94°C, 65/65% RH, 250/250 kPa abs,outlet, stoichiometries of 1.5/2, 50 cm² active area [32].

3- Towards organized CLs

The previous section made clear that present CLs are very complex, and still require major optimization to reach the targeted performance. Models of water transport in PEMFCs highlight the benefits of organizing the electrode, and notably to align “the catalyst intrusions, MPL fractures, GDL weave holes, and gas channel to enhance water management” [39]. Modelling ideal CLs, Barreiros Salgado confirmed that reduced mass-transport limitation is possible using straight tubes or wires oriented in a through-thickness direction (perpendicular to the MEA plane) [40] (**Figure 2A**). This conclusion was reached by combined experimental and modeling studies by Bonnefont et al. [41], where ordered CLs (possible for a variety of materials, **Figure 2B**) proved effective to enhance mass-transport and increase the Pt effectiveness factor, thereby enabling high power density with ultralow Pt loading [42][43]. Organized structures also ease water transport within the CL, which positively influences PEMFC performance at high current density, where ions, gas and liquid flows, and water phase change occur concomitantly [38][44]. The idea of better organizing the complex interplay of complementary materials (catalysts, ionomer, porosity, etc.) in 3D-structured electrodes has been emphasized recently. The next two sections will summarize some striking recent achievements in the field, both for carbon-containing CLs and for carbon-free CLs.

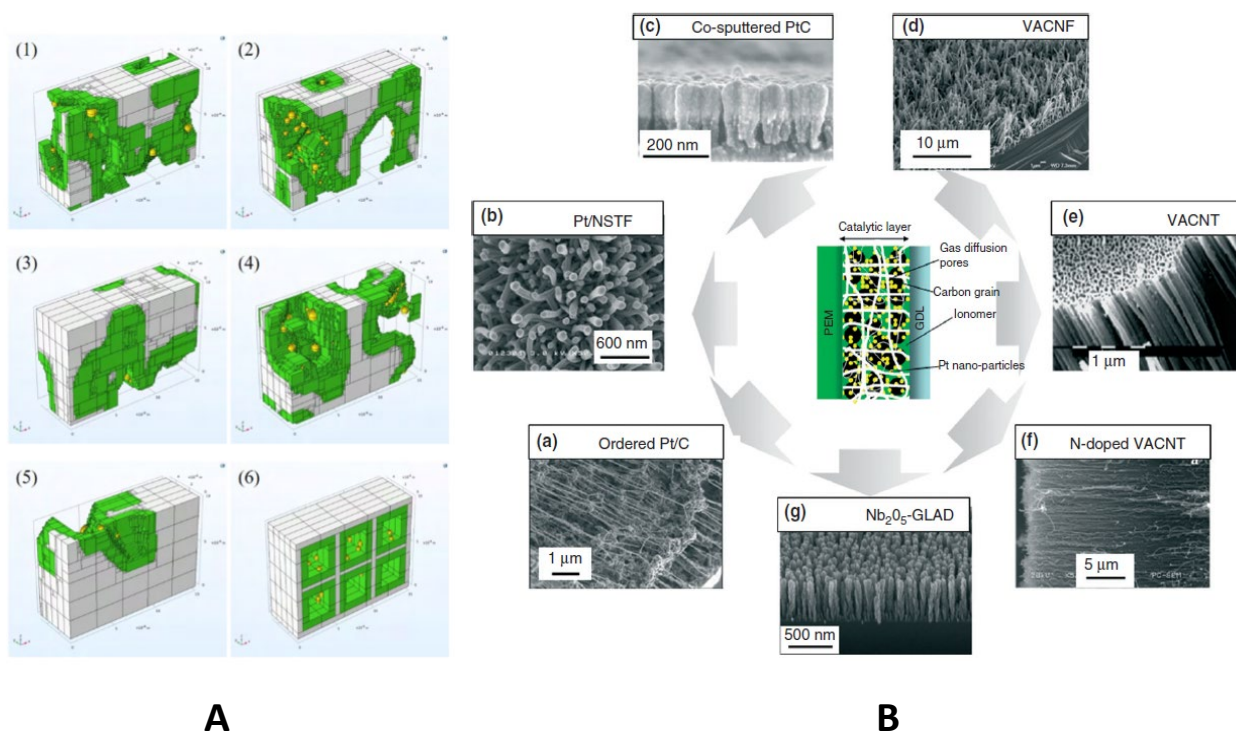


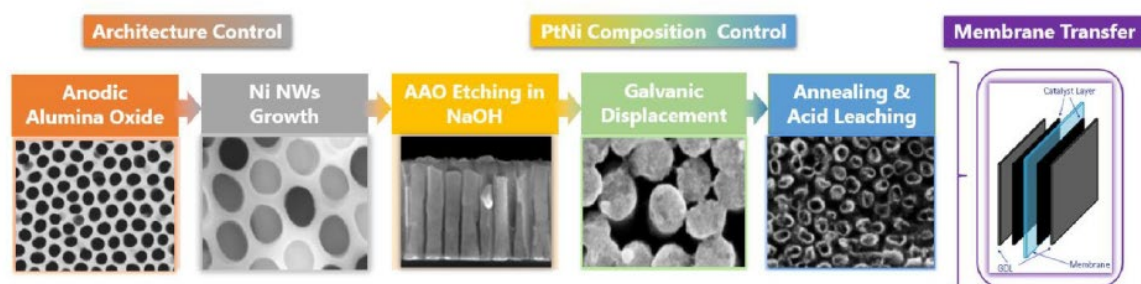
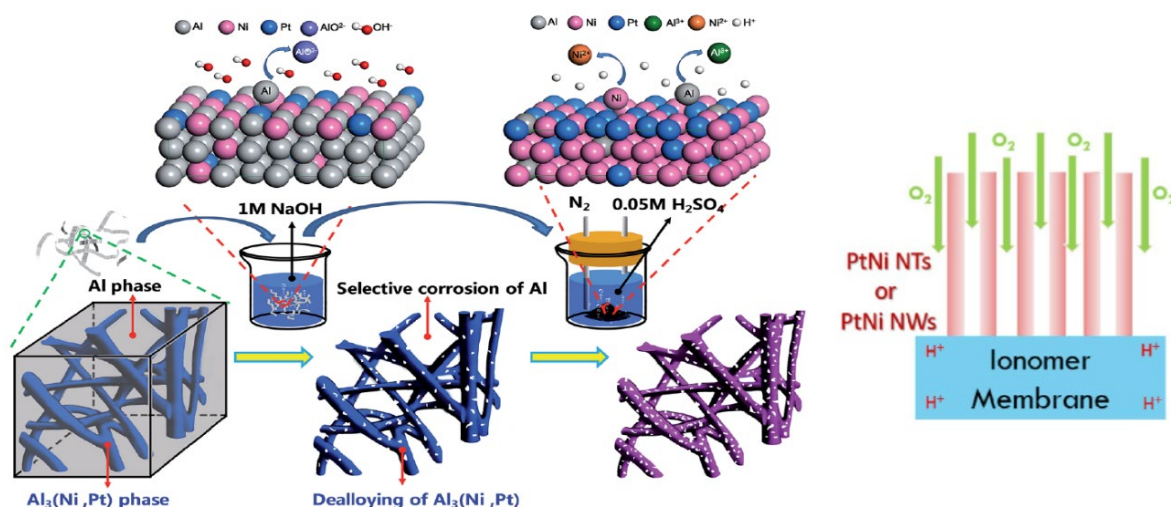
Figure 2: A. Agglomerate geometries analyzed at the cathode CL scale. (1–5) 3D structure models based on Electron Microscopy images and (6) ideal structure [38]. **B.** Principal directions for the development of ordered nanostructured catalytic layers for PEMFCs, with representative SEM micrographs [39].

3.1- Carbon-free CLs

The seminal and pivotal studies of 3M with the “nanostructured thin films” (NSTF) is a first example of carbon-free 3D-structured electrode [45]. Pt/NSTF electrodes consisted of core-shell structures (non-conducting whiskers covered by percolating Pt aggregates ensuring the catalytic function and electron-conductivity), and offered a revolutionary manner to improve performance and reduce Pt cost in PEMFCs [46]: at high-humidity and 80°C, 0.15 mg_{Pt}/cm² Pt/NSTF performed similarly to traditional 0.4 mg_{Pt}/cm² Pt/Ketjen Black electrodes, outperforming them in durability (electrochemical surface area (ECSA) loss upon high voltage cycling): while Pt/KB lost 90% of ECSA in 2000 cycles of base-load accelerated stress test (0.6-1 V AST), Pt/NSTF only lost 33% of ECSA in 9000 cycles [47]. Despite these apparent promises, reality was more complex: Pt/NSTF led to insufficient Pt dispersion and performed badly in dry conditions. A single-phase model identified that low proton conductivity caused the poor Pt/NSTF performance upon dry operation [45], the rate of water formation at the cathode being 20 to 30 times higher than for a commercial electrode (proportional to the thickness) at a given current density [48]. The number of papers published on Pt/NSTFs for PEMFC applications significantly decayed recently, showing that these difficulties of water management were not overcome in practice. However, NSTF supports are extremely promising for electrolysis [49], where (i) water management is less complex, (ii) gases evacuation is facilitated by the organized electrode structure, and (iii) the risk of corrosion are reduced with this carbon-free material.

Unsupported metal nanowire (NW) or nanotubes (NT), e.g. Pt, PtNi, PtFe structures (**Figure 3A,3B**), have been developed following the NSTF studies. As platinum and other PGM metals are the most active catalysts for ORR, such materials display good performances in terms of initial properties [22],

while the absence of corrodible carbon support in principle enhances their durability [51] compared to Pt/C benchmarks (Figure 3D,3E).



	ECSA (m ² /g _{Pt})	Specific activity (mA/cm ²) at 0.90 V	Half-wave potential (V)	Mass activity at 0.90 V (A/mg _{Pt})	(A/mg _{Pt}) at 0.935 V
J-PtNWs/C	118	11.5	0.935	136	2.87
R-PtNWs/C	110	1.59	0.899	1.76	0.5
Pt/C	74	0.35	0.860	0.26	0.06
Octahedron Pt _{2.5} Ni/C (17)	21	NA	NA	3.3	NA
Nanoframe Pt ₃ Ni/C (23)	67.2	NA	NA	5.7	NA
Mo-Pt ₃ Ni/C (19)	67.7	10.3	NA	6.98	NA
DOE 2017 target	NA	NA	NA	0.44	NA

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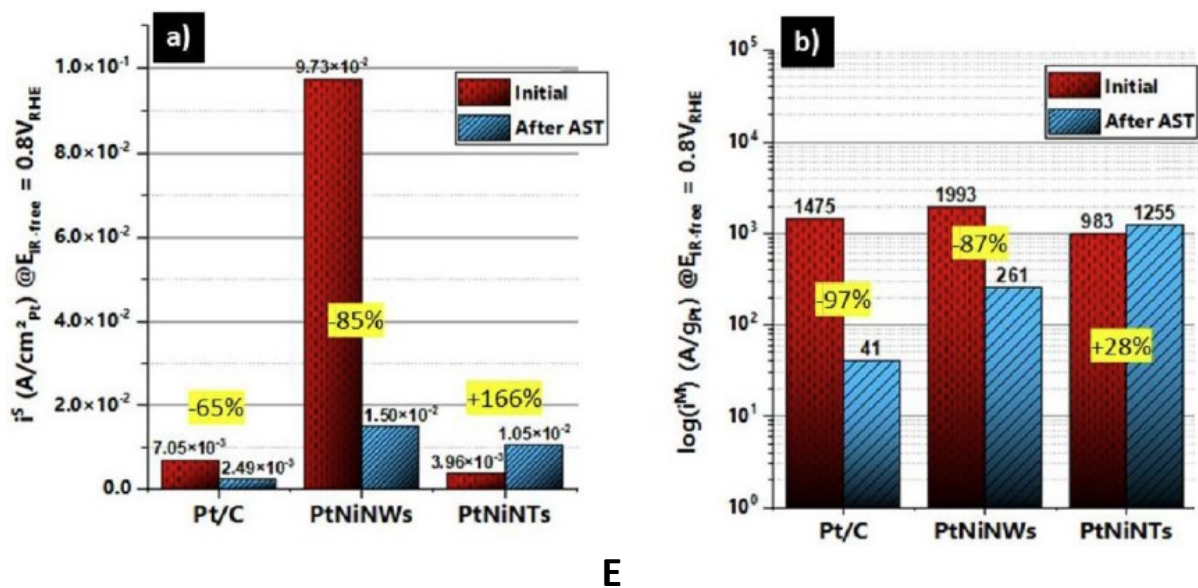


Figure 3: A. Fabrication process and formation mechanism of the PtNiNP/NWs [55]. B. Scheme of the cross-section of oriented carbon-free PtNi nanotubes (PtNiNTs) arrays transferred onto a proton-exchange membrane [51]. C. Methodology of the elaboration process of PtNi nanowires and nanotubes [51]. D. Electrochemically active surface area (ECSA), specific activity, half-wave potential, and mass activity of J-PtNWs/C, R-PtNWs/C, and Pt/C electrocatalysts, in comparison to those in several representative recent studies [56]. E. Comparison of the tested MEAs composed of Pt/C, PtNiNWs, and PtNiNTs as cathodes, before degradation and after 50 K potential cycles in H₂/O₂. Data recorded at $E_{IR-free} = 0.8 V$ vs RHE: (a) Specific activity before and after degradation, (b) mass activity before and after degradation [51].

PtNi nanotubes (PtNiNTs) is an example of such carbon-free organized structures: PtNiNT electrodes enable very large specific activity (0.97 A/cm^2_{Pt} at $0.8 V$ vs RHE), roughly 6-fold larger than Pt/NSTF and 13-fold more than conventional Pt/C [49]. This suggests that the oriented nanotube architecture, which displays straight and short routes across the electrode thickness, eases mass-transfer and enables better reactant distribution and accessibility to the active sites (no nonconductive material hinder Pt-utilization, as in NSTF). As opposed to the nanowire or nanowhiskers architecture, nanotube-based electrodes are said to allow improved O₂ accessibility and to limit the flooding in the nanostructured electrode, which was the main weakness of NSTF.

Supported PtNW on N-doped CNTs (PtNW/NCNT) is a mixed structure that was shown more ORR efficient compared to commercial Pt/C [52]. They take advantage of the defective structure of PtNW (large extent of grain boundaries and microstrain [53] that enhance the ORR), and of the strong interaction between the N-doped CNT and PtNW, which strengthens the resistance to Pt degradation/reorganization. Hence, PtNW/NCNTs electrodes exhibit high performance in single PEMFC and proved more durable than Pt/C electrodes, with an average voltage loss after 500-hour dynamic cycle durability test of 3.6% versus 7.2% for Pt/C. While Pt/C suffered significant Pt NPs growth [54] and aggregation, PtNW only exhibited minor alterations. PtNW/NCNTs illustrate the benefit of combining carbon/non-carbon ordered structures as electrocatalyst for PEMFC cathodes [52].

However, alike Pt/NSTFs which have been disqualified from being viable alternatives for mobility applications, Pt-based NT/NW structures will likely not be transferred industrially. Indeed, as for Pt/NSTF, metal NT/NW structures are very sensitive to RH variations [51]. In addition, their manufacturing complexity prevents large-scale deployment: fabricating PtNiNTs and PtNW/NCNTs involves very complicated protocols [51][52], with numerous different (electro)chemical/thermal steps, organic solvents/strong acids/bases, and precise thermal and mechanical operations, the overall yield being not given (Figure 3C). The protocol of [55] is even more complex, with 9 steps: high-

frequency vacuum induction heating, tempered-cooling, roller melt spinning by high-frequency induction heating in a quartz tube, melt-spinning under controlled argon atmosphere, dealloying in 1 M NaOH solution for 6 h and then in N₂-saturated 0.05 M H₂SO₄ solution for 12 h and several final washing with ultra-pure water followed by vacuum drying (**Figure 3A**).

Whatever these experimental difficulties, it is essential to see how materials behave electrochemically. In their work, Li et al. compared different materials including J-PtNWs/C, Pt/C and other state of the art materials (**Figure 3D**). Whatever the indicator chosen, J-PtNWs/C outperform Pt/C. Lagrichi et al. carried out 50k cycles of ageing (**Figure 3E**) and obtained a 166% increase in current density for PtNiNTs compared with a 65% loss for Pt/C. The same trend was observed for mass activity: +28% for PtNiNTs and -97% for Pt/C [51], showing that such materials could meet the DOE durability targets.

3.2- Organized CNT-based CLs

The recent literature revisited the use of CNTs, using them as “simple” supports of Pt-based electrocatalysts for ORR in acid media [57], though CNTs were employed as 3D-organized mats (typically, vertically-oriented CNTs, VACNTs). CNTs take advantage of combined high-surface area (enabling Pt dispersion), large electronic conductivity [58] (**Figure 4A**), good mechanical properties and high resistance to electrochemical oxidation (thanks to their high level of crystallinity) [59].

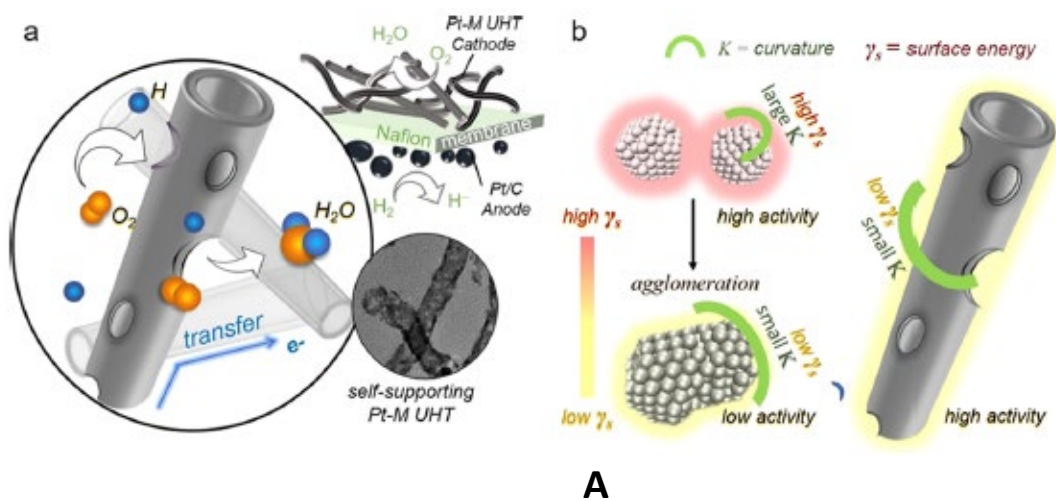
Murata et al [60] successfully developed PEMFC cathodes that enable high current density operation by incorporating VACNTs as electrocatalyst support. The current density at 0.6 V vs RHE was 2.6 A cm⁻² (0.1 mg_{Pt}/cm² loaded cathode). This value was achieved owing to the improved mass-transfer within the electrode structure: pore continuity, non-agglomerating electrocatalyst supports and good electrical contact between the CL and MPL.

More recently, ultrathin electrospun PtNi/ultrathin holey nanotube (UHT) CLs were found to meet the DOE requirements of initial performance and durability for automotive applications. The ultra-thin CLs (66 μg_{Pt}/cm², 10 wt% Nafion® – the optimal ionomer content being very small for such thin CLs) exhibited 1430 mW/cm², compared to 908 mW/cm² for classical Pt/C CLs [61], though in conditions that are not fully representative of the application. PtNi/UHT (**Figure 4B**) displayed impressive durability in base-load (0.6-1 V, 30000 cycles) and start-stop (1-1.5 V, 5000 cycles) ASTs: PtNi/UHT maintained 62% of the initial mass activity measured at 0.9 V (MA) after the base-load AST, exceeding the DOE durability target, while Pt/C severely degraded (no detectable MA at 0.9 V) after the AST. Likewise, after the start-stop AST, the ECSA retention of Pt/C was 39%, with no current measured at 0.9 V, when PtNi/UHT kept 79% of ECSA and 86% of MA. The study also underlined that classical RDE characterizations could not demonstrate the benefit of these structures, and that single PEMFC tests (in conditions of high current density) were mandatory, as concluded in [6,7].

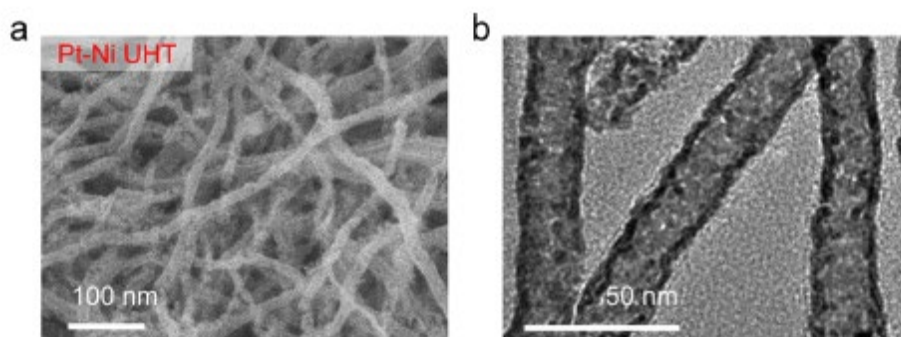
Liang et al. [62] reached similar performance with Pt/VACNT CLs loaded at 0.1 mg_{Pt}/cm². They highlighted the importance of optimizing such structures to prevent or at least retard flooding at large current density: the best compromise was obtained for 26 nm spacing between VACNTs and 300 nm length of VACNT, with an average ionomer film thickness of 2 nm covering the Pt/VACNT structures. These optima shall however depend on the operating conditions.

Pt/graphene CNT composites (GCNT) [59] proved more durable (graphitic carbon) and more active (numerous graphitic edges for Pt NPs anchoring, leading to high Pt dispersion and activity) than classical Pt/XC72 catalysts (**Figure 4C**). However, these results were obtained in unrealistic experimental conditions (pure H₂/O₂, high stoichiometries and back pressure, 100% RH).

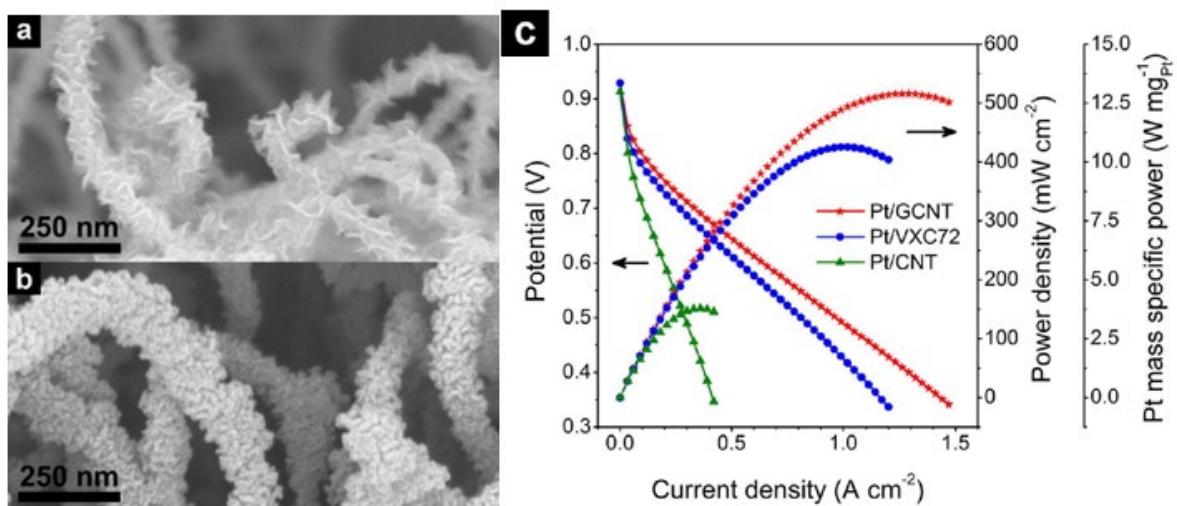
Issues of water management were also highlight by Mensharapov et al. [63], when modelling Pt/VACNT CLs: hydrophilic CNT likely flood at high current density and high RH, but seem adequate for use at low RH. This complexity of water management was also discussed previously for Pt/NSTFs and metal NTs or NWs.



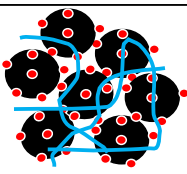
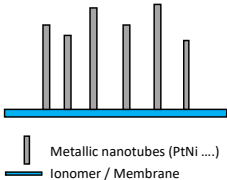
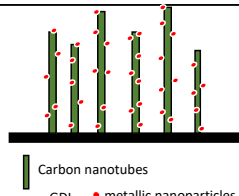
A



B



C

	Classical CLs	Carbon-free CLs	Organized CNT-based CLs
Schematic diagram	 <ul style="list-style-type: none"> ● Carbon particles ● Platinum nanoparticles — Ionomer 	 <ul style="list-style-type: none"> ▭ Metallic nanotubes (PtNi ...) — Ionomer / Membrane 	 <ul style="list-style-type: none"> ▭ Carbon nanotubes ▭ GDL ● metallic nanoparticles
Disadvantages	<ul style="list-style-type: none"> ○ Mass transport limitation ○ Low Pt utilization/effectiveness ○ Low durability 	<ul style="list-style-type: none"> ○ Hard to manufacture ○ Method at its infancy ○ Issue with water management 	<ul style="list-style-type: none"> ○ Method at its infancy ○ Assembly in MEA to be demonstrated
Advantages	<ul style="list-style-type: none"> ✓ Easy to produce ✓ Cheap to produce ✓ Great know-how in industry 	<ul style="list-style-type: none"> ✓ High Pt utilization/effectiveness ✓ Durable ✓ Optimal structure from theory 	<ul style="list-style-type: none"> ✓ High Pt utilization/effectiveness ✓ Easier to make than carbon-free CLs ✓ Good electron conductivity ✓ Optimal structure from theory

D

Figure 4: A. (a) Efficient mass transports in the self-supporting UHT catalyst layer, ensuring full utilization of the tube surface. (b) Relatively low surface energy (γ_s) of the nanotube due to the low curvature, K , of the tube wall compared with small nanoparticles [58]. **B.** Morphology, structure, and composition of Pt–Ni UHT. (a) SEM image, (b) TEM image [58]. **C.** Physical characterization of the GCNT and Pt/GCNT hybrids. Morphological characterization with FE-SEM of (a) the GCNT hybrids and (b) the Pt/GCNT hybrids. (c) Polarization curves of the Pt/GCNT, Pt/VXC72 and Pt/CNT cathodes [59]. **D.** Advantages and drawbacks of the 3 methodologies presented herein to prepare PEMFC CLs.

Figure 4D summarizes the main the 3 paths discussed in this article, providing their main advantages and drawbacks. Compared to the classical methodology to build PEMFC CLs, the selected examples cited above reveal that there is no perfect solution, yet, to build a PEMFC CL based on 3D-structures and in particular VACNTs. However, many technical possibilities exist to improve these materials, that have numerous assets.

Sahoo et al. exfoliated CNT (creating defects) to maximize the Pt NPs dispersion; combined with the intrinsic high electron conductivity of CNTs, this enables to outperform classical Pt/C cathodes in PEMFC operation [64]. Chi et al., by controlling and modifying PEMFC CL via texturation (pore structure) and chemical modifications (hydrophobicity), using 3D-structured CNTs and PTFE composites [10], obtained improved water management and significantly-improved PEMFC power density. Lastly, Atomic Layer Deposition (ALD) [65][66] enables to deposit highly dispersed Pt NPs at 3D-structured carbon supports with a high degree of conformity. This technique, by the precise control of the Pt morphology/loading is particularly adapted for 3D-structured supports for cathode CLs, like VACNTs.

4- Conclusion

The results obtained recently make it clear that future electrodes for PEMFC applications should be 3D-structured. This particular architecture, made possible by the latest technological advances, enables a better use of active materials, good water management and reactant mass-transfer, and high durability. This emphasizes the interest of materials sciences and electrochemical engineering to meet the expectations and constraints set by governmental agencies like the US DOE, Hydrogen Roadmap Europe or the FCCJ. The term 3D-structured architecture covers a wide range of materials, but given the potential of carbon-based materials, we posit they are the most suitable candidates, in particular CLs based on VACNTs, for which tailored electrocatalyst materials could be deposited in roll-to-roll using techniques like ALD.

In recent years, many research groups have started to look at this type of materials, but the authors think that too many people are still looking at classical CL materials, no doubt because of the (apparent) complexity of manufacturing 3D-nanoarchitected structures at the laboratory scale. Industrially speaking, though, roll-to-roll processes are already feasible at the industrial scale (notably at NawaTechnologies).

So, research needs to focus on these structures, which are believed to be the future of (electro)catalysis for PEMFCs. The authors are convinced that roll-to-roll techniques compatible with large-scale industrialization, particularly with the development of ALD, are within our grasp.

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Author contributions

All authors have contributed equally.

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Papers of particular interest, published within the period of review, have been highlighted as:

- * Paper of special interest
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