

Origins, Developments, and Perspectives of Carbon Nitride-Based Electrocatalysts for Application in Low-Temperature FCs

by *Vito Di Noto, Enrico Negro, Ketì Vezzù, Federico Bertasi, and Graeme Nawn*

Fuel cells (FCs) operating at low temperatures ($T < 200$ °C) show several very attractive features, including: (a) relatively simple assembly; (b) good compatibility with the environment; and (c) very high efficiency with respect to internal combustion engines. However, the full potential of low-temperature FCs can only be achieved by addressing a number of crucial issues involved in their operation. One of the most important bottlenecks is represented by the slow kinetics of the oxygen reduction reaction (ORR).¹ Typical examples of low-temperature fuel cells include proton exchange membrane fuel cells (PEMFCs) and anion-exchange membrane fuel cells (AEMFCs).¹ To achieve energy conversion efficiencies and power densities compatible with applications, all these devices require suitable ORR electrocatalysts (ECs) to minimize cathode polarization losses.

Ideally, ORR ECs should possess the following features:

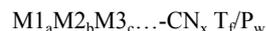
- Active sites capable of the highest turnover frequency at the lowest overpotentials;
- A large active surface area, maximizing the number of active sites;
- A morphology that facilitates the efficient transport of reactants and products to and from the active sites;
- High electron conductivity, to minimize ohmic losses;
- A high dielectric environment to aid the ion exchange processes between the active sites and the ion-conducting membrane;
- High stability under operating conditions, to achieve high durability.

To comply with these requirements, state-of-the-art ORR ECs consist of Pt-nanocrystals supported on conductive carbon nanoparticles (NPs) that possess a spherical morphology and a large surface area² (indicated as “Pt/C ref. ECs”). These systems are characterized by a high dispersion of the ORR active sites, which are easily accessible by the reactants. Their performance is comparable to that of pristine “Pt-black” ECs, but with a reduced loading of precious metal. However, the large-scale rollout of FC technology employing Pt/C ref. ECs is hindered by their insufficient durability and very high costs.

“Carbon nitride-based electrocatalysts” (CN-based ECs) have shown great promise to address the issues outlined above. CN-based ECs are composed of a carbon-based matrix embedding nitrogen atoms. The matrix coordinates metal-based species, including: (a) NPs of metals (*e.g.*, Pt, Pd), metal alloys (*e.g.*, PtNi_x, PdCo_yNi_z), oxides (*e.g.*, Fe₃O₄) or carbides (*e.g.*, FeC_x); or (b) coordination complexes of single metal atoms (*e.g.*, Fe, Co).³ There are two main driving forces behind the development of CN-based ECs. CN-based ECs including Pt-group elements (PGMs) show very high ORR activity and a remarkable tolerance towards the oxidizing conditions typical at the cathodes of low-temperature FCs.⁴ The carbon nitride (CN) matrix embeds the various inorganic NPs in “nitrogen coordination nests”.⁵ These strong interactions inhibit the main mechanisms involved in the long-term degradation of typical Pt/C ref. ECs, especially

particle agglomeration and particle detachment from the support.⁶ Furthermore, the presence of N atoms promotes ORR kinetics by means of bifunctional and electronic mechanisms,⁵ thus promoting the ORR in the absence of PGMs.^{7,8}

The nomenclature of CN-based ECs is a subject of considerable confusion. Today: (1) no widely accepted family name exists, resulting in the use of a variety of labels in the literature, including “nitrogen-doped carbons”,⁹ “M-N/C electrocatalysts”⁷ among many others; (2) a consistent labeling of the materials is uncommon. Therefore, a correct nomenclature is required, which takes into consideration the following general features. ECs: (a) are inorganic systems; (b) include a carbon-based matrix; (c) present N atoms, which are vicarious with carbon in the carbon-based matrix; and (d) exhibit a negligible concentration of hydrogen and oxygen heteroatoms. For the sake of clarity, it is crucial to adopt a nomenclature in accordance with the widely accepted regulations set out by IUPAC.¹⁰ Now, the matrix of these materials is an “inorganic binary” system, whose “electropositive constituent” is carbon and its “electronegative constituent” is nitrogen. “The name of the electronegative constituent is constructed by modifying the element name with the ending ‘-ide’”, hence “nitride”. Taken all together, in terms of IUPAC rules, the systems discussed here must be correctly indicated as “carbon nitride-based electrocatalysts”.¹⁰ As for consistent labeling, one rational label of CN-based ECs is:



M1, which is typically a PGM such as Pt or Pd, is the “active metal”; M1 can be Fe or Co in “Pt-free” CN-based ECs. M2, M3... are the “co-catalyst” metals, which facilitate the performance of the “active metal”; $i = n(\text{Mn})/n(\text{M1})$ with $i = a, b, c, \dots$ is the molar ratio between Mn ($n = 2, 3, \dots$ N) and the M1 metal; $-CN_x$ is the carbon nitride matrix with x the weight percentage of nitrogen in the matrix. If $x = l$ N-concentration is lower than 5 wt%; if $x = h$ it is higher than 5 wt%. T_f is the main pyrolysis temperature in the preparation of the CN-based ECs; P indicates the conductive “core” used as support for the CN matrix, and w is the weight ratio between “core” NPs and the CN-based matrix.⁴

Among the large number of different approaches proposed in the literature to synthesize CN-based ECs,³ there are two main steps: (1) the precursor preparation; and (2) the pyrolysis process. The precursors are typically obtained by adsorbing one or more molecules onto carbon black, thus providing the desired chemical species (*e.g.*, metal atoms, nitrogen, carbon) to be introduced in the EC. The vast majority of these precursors are based on low-molecular weight adsorbates. However, as early as 1989, it was shown that macromolecules can be used to synthesize CN-based EC precursors.¹¹ Until the late 1990s, most of the research was focused on precursors obtained by adsorbing onto the support only one chemical specie, comprising both N, C and the metal atoms.¹² In the late 1980s, precursors were prepared by adsorbing more than one molecule on the support.¹¹ In general, iron acetate and

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other complexes were added to introduce metal atoms¹³ while urea, perylenetetracarboxylic anhydride and others were added to introduce N and C into the ECs.^{13,14} In the last 50 years, a number of metal ion complexes based on ligands containing C and N were prepared for use as ORR ECs without resorting to any pyrolysis process.^{15,16} These ECs, which consist mainly of inorganic coordination complexes with macrocycles, polypyrrole-like macromolecules and other ligands, cannot be confused with “CN-based ECs”. Indeed, the pyrolysis process plays a crucial role in the synthesis of CN-based ECs since it: (a) integrates all the elements of the precursors into the final 3D solid-state EC; (b) triggers the synthesis of the ORR active sites; and (c) fine-tunes the spongy-like morphology of CN-based ECs. In general, the pyrolysis process adopted for the preparation of CN-based ECs consists of only one step.¹⁷ A variety of methods and techniques were used to optimize the parameters of this single pyrolysis step and, consequently, the ORR performance of the CN-based ECs. The most widely adopted “*ex situ*” technique used to study the ORR performance of such ECs is cyclic voltammetry using a rotating (ring) disk electrode.^{18,19} Since 1994 some authors have also succeeded in testing CN-based ECs in single fuel cell configuration.²⁰

Despite these efforts, until 2006, the progress on CN-based ECs was slow and results were modest. Indeed, the precise nature of the ORR active sites remained very controversial.³ No consensus emerged on the role played by the different metal atoms in the ORR active sites in terms of: (a) coordination geometry; (b) electrochemical activity; and (c) morphology. These studies point out that the activity of the CN-based ECs was not directly correlated to the concentration of metal or N atoms. Indeed, the best ORR performance was achieved in ECs at a specific composition;³ when a critical metal concentration in ECs was reached, the metals coalesced in carbide/oxide/metal NPs,

compromising their performance. The best results were obtained with a very low (≈ 0.01) M/N atomic ratios ($M = \text{Fe}, \text{Co}, \dots$), suggesting that it was better to devise ECs with the concentration of N being as large as possible.³ At this stage it was impossible to pursue a rational synthesis approach to obtain active sites with well-defined ORR performance. In general, the morphology of these CN-based ECs was very complex and a wide variety of highly heterogeneous and different nanostructures were reported. Optimization efforts strongly relied on “trial-and-error” approaches, without a solid grasp of the fundamental interplay between the preparation parameters and the properties of the final CN-based ECs. The room for this large dispersion of results likely originated from the adoption of small molecules as precursors and the use of a single pyrolysis step. As expected the thermal decomposition of the precursor, which takes place tumultuously, made it difficult to control the morphology and of the reproducibility of the final products; thus, several “post-pyrolysis steps” were required. For instance, to modulate the content of N in the CN matrix it was necessary to add a second pyrolysis step conducted under Ar and ammonia or acetonitrile,^{12,21} likewise, to remove selectively the inert metal species¹² it was necessary to employ an etching process with acid or alkaline solutions. The second pyrolysis step consolidated the ECs, improving the “*ex situ*” ORR performance. Nevertheless, their electrochemical performance in single FCs operating in “practical” conditions was very poor. Taking all together, the development of a rational synthetic approach able to yield ECs with desired performance in FCs was elusive.

The shortcomings of the “classical” preparation protocols for CN-based ECs were addressed by proposing two types of 3D-crosslinked hybrid macromolecular precursors with a well-controlled stoichiometry. These precursors were obtained by two different simple synthetic routes (see Fig. 1a).²²⁻²⁵ The first, which was originally proposed in 1997,²⁶ includes “Zeolitic Inorganic-

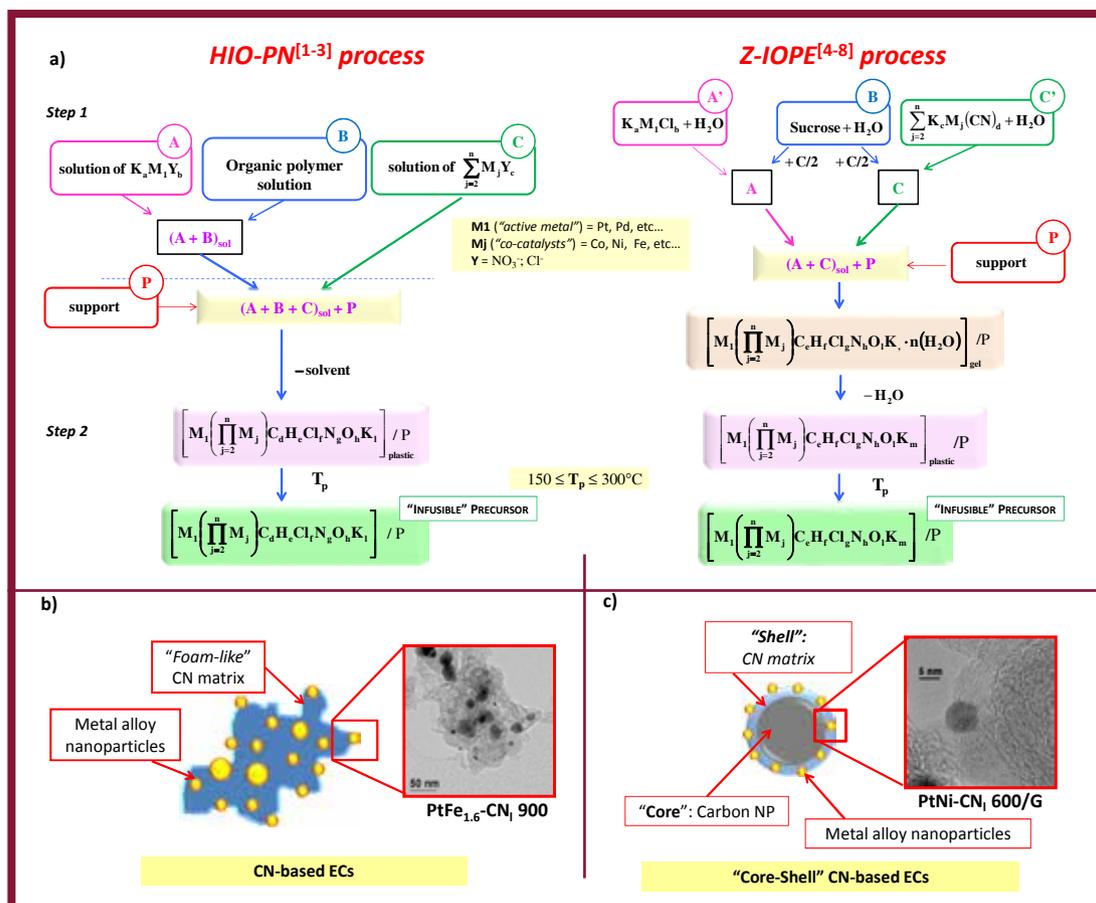


Fig. 1. (a) Schematic representation of HIO-PN and Z-IOPE processes for the synthesis of CN-based electrocatalysts (ECs). M_1 ("active metal") = Pt, Pd, Fe, etc.; M_j ("co-catalysts") = Co, Ni, Fe, etc.; $Y = \text{NO}_3^-$, Cl^- ; $n = 2, 3$ for bimetal and trimetal systems, respectively. T_p is the processing temperature required to obtain the infusible precursor ($150 \leq T_p \leq 300$ °C). Selected high-resolution TEM images of: (b) CN-based ECs; and (c) "core-shell" CN-based ECs.

Organic Polymer Electrolyte” (Z-IOPE) precursors. Z-IOPEs consist of mono-plurimetallic clusters networked by suitable molecular or macromolecular ligands with a high –OH concentration. The second, which was first reported in 2007,²⁷ comprises “Hybrid inorganic-organic polymer network” (HIO-PN) materials. These are three-dimensional crosslinked systems obtained by coordinating metal ions with macromolecular ligands bearing nitrogen functional groups. Both Z-IOPE and HIO-PN precursors are very stable 3D hybrid inorganic-organic macromolecular systems where “soft” atoms such as Pd or Pt or “hard” elements such as Fe, Ni and others are coordinated by C and/or O and/or the N functional groups to form the desired crosslinks of the precursor.

A crucial improvement in performance and reproducibility of synthetic protocols arose from the adoption of a two-step pyrolysis process. The first step is carried out at a T_p (processing temperature) in the range $150 < T_p < 300$ °C (see Fig. 1a). At T_p , a controlled, gradual expulsion of low-molecular weight species occurs, yielding a stable, “infusible” 3D crosslinked material. In this “soft” pyrolysis process, the metal atoms interdiffuse into the bulk system, yielding a very

homogeneous matrix with a well-controlled stoichiometry in terms of N and the desired metal atoms.²⁸ The second high-temperature pyrolysis step (T_f) accomplishes the following targets:

- It promotes the diffusion of the metals in the bulk “infusible precursor”. Nucleation of metals into alloy NPs bearing the ORR active sites is obtained. These exhibit a well-controlled stoichiometry and a high turnover frequency in the ORR process. In general, the size of the alloy NPs is smaller than 10 nm.
- It improves graphitization of the 3D “infusible precursor”, yielding a highly conducting CN matrix. Thus, a good electrical contact between the ORR active sites and the external circuit is guaranteed.
- It provides “nitrogen-carbon coordination nests”, which act to stabilize the metal alloy NPs in the CN matrix (see Fig. 2).

The requirements for the synthesis of CN-based ECs from HIO-PN and Z-IOPE precursors (see Fig. 1a) are summarized in Fig. 3.

In general, in ECs, the “active metals” are chosen from Pt, Pd, Ir, Fe and others, while Fe, Co, Ni, Rh and Au are used as “co-catalysts”.^{4,29} The activity of Pd towards the ORR is only slightly lower than that of Pt. The best “co-catalysts” are first-row transition elements such as Fe, Co and Ni, which behave as strong Lewis acids and, owing to a bifunctional mechanism, promote the desorption of the ORR reaction products (see Fig. 2).^{4,30} The matrix of CN-based ECs, which shows an extremely porous “foam-like” morphology (see Fig. 1b),³¹ stabilizes the alloy NPs with “nitrogen coordination nests” through strong metal-ligand coordination interactions.³² The best ECs are obtained when T_f ranges from 600 to 900 °C. If $T_f < 600$ °C, the graphitization of the CN matrix is not complete, resulting in matrices with a high content of O and H and poor conductivity. At $T_f > 900$ °C, N atoms involved in the coordination of metal alloy NPs are expelled, facilitating the coalescence and growth of NPs. In the range $500 \leq T_f \leq 900$ °C, N atom concentration in the CN matrix is mostly modulated by the chemical composition of the “infusible precursor”. Typically, the CN matrix obtained with Z-IOPE precursors includes an amount of $N \leq 5$ wt%.²⁹ In this case N, which is introduced by the metal complexes, is present in the matrix only in “coordination

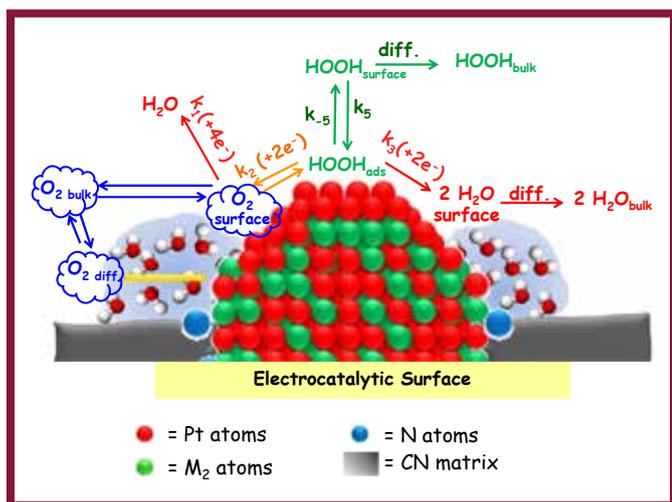


FIG. 2. Bifunctional mechanisms for CN-based ECs.

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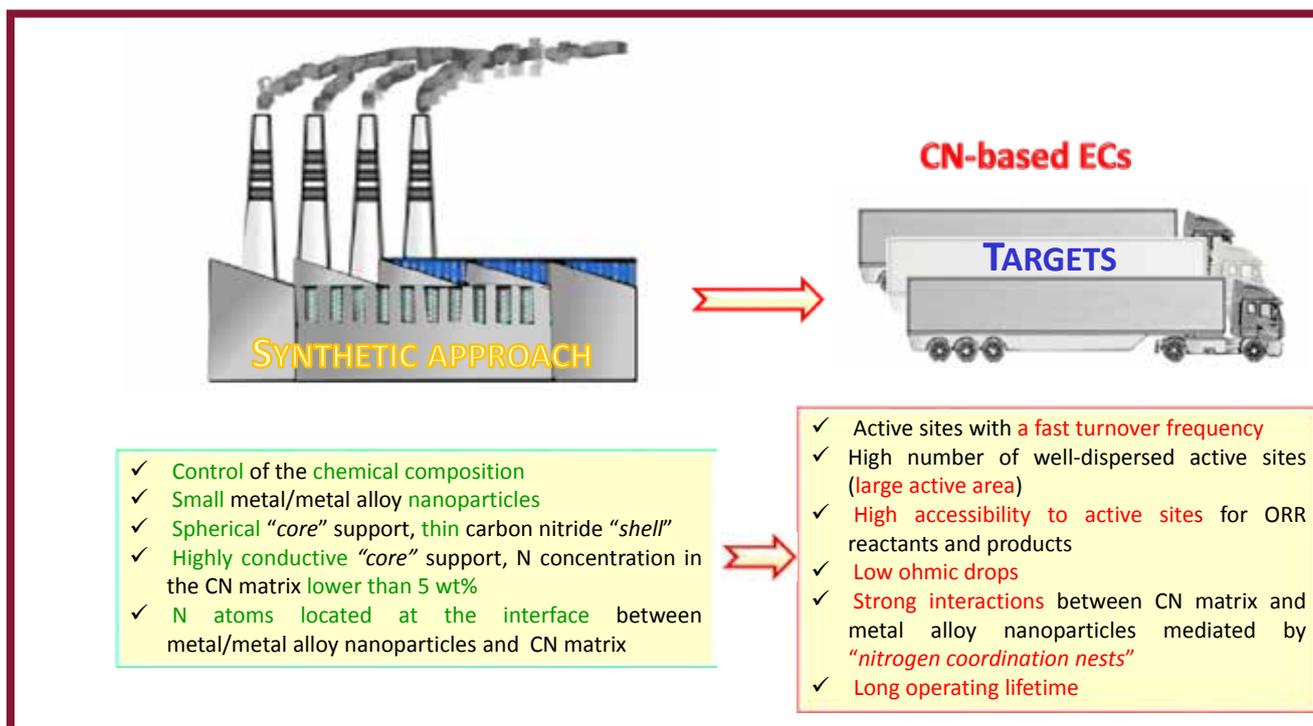


FIG. 3. Requirements for the synthesis of CN-based ECs.

“nests” of alloy NPs. The CN matrix prepared from HIO-PN precursors shows a much higher N concentration, which is distributed throughout the entire CN matrix. The electrical conductivity of the CN matrix is shown to decrease with N.³³

The amount of N in the CN matrix plays a crucial role. Indeed, at N > 5 wt%, the ECs exhibit an improved tolerance towards halides or methanol contaminants. However, they exhibit a lower ORR performance with respect to CN-based ECs where the N atoms are located only in alloy NP “coordination nests” (lower N content).³³ Taken all together, the best results are obtained when N is introduced into the CN matrix by the metal complexes and not by the macromolecular or organic ligands used to prepare the precursor. This goal is easily achieved by using Z-IOPE precursors, that provide ECs with: (a) N < 5 wt%, and located only around the metal alloy NPs; (b) efficient electronic and bifunctional effects; and (c) high conductivity of the whole CN matrix.

A crucial advancement in CN-based ECs was achieved with the introduction of the “core-shell” approach^{24,25} (see Fig. 1c). This has shown to improve the reagents accessibility to the metal active sites. “Core-shell” CN-based ECs are obtained with the same two-step pyrolysis process (T_p and T_f) and comprise a conductive “core” support covered by a CN matrix “shell” which embeds the metal alloy NPs. The first stage in the preparation of a “core-shell” CN-based EC consists of the impregnation of a “core” support with a Z-IOPE or HIO-PN precursor,^{5,34} in order to modulate carefully (see Fig. 1): (a) the chemical composition; and (b) the stoichiometry of alloy NPs. In ECs

obtained from HIO-PN precursors, N is homogeneously distributed within the bulk “shell” of CN matrix, while in ECs prepared using Z-IOPE systems, N is found only in “coordination nests” of alloy NPs.

The conductive “core” support, which acts as a template in the coverage of the support with the precursor, enhances the electrical conductivity of the material.^{30,35,36} Several studies were carried out to investigate the interplay between the morphology of the “core” support, the chemical composition of the precursor, and the ORR performance of the ECs both in “*ex situ*” electrochemical experiments and in “*in situ*” single fuel cell tests under operating conditions. The best results were obtained with conductive C “core” NPs covered by a thin layer (a few nm) of Z-IOPE precursor (see Fig. 1c).^{5,30,34} In the supported CN matrix, small metal alloy NPs ($d < 10$ nm) are formed, which: (a) provide a very large active area; (b) are chemically stable; (c) benefit from both electronic and bifunctional effects of “nitrogen coordination nests;” and (d) facilitate access of reagents and products to and from the active sites. In these ECs, no post-pyrolysis steps are required to achieve an outstanding performance in the ORR. Both pristine and “core-shell” CN-based ECs comprising Pt-X active sites (X = Fe, Co and Ni) show ORR overpotentials up to ca. 10-30 mV lower than that of Pt/C ref. ECs. Pd-trimetallic “core-shell” ECs show an ORR performance which increases as: (a) T_f is raised; and (b) the N concentration in the “shell” decreases^{5,35,36} (see Fig. 4). The “*ex situ*” electrochemical performance of CN-based ECs is successfully transferred into membrane-electrode assemblies (MEAs) of a single PEMFC working under operative conditions.³⁷ The best “core-shell” CN-based ECs allow fabrication of MEAs which, with respect to a reference Pt/C MEA, use 1/3 of Pt to achieve the same performance (see Fig. 4).³⁴ When the CN matrix is supported on highly nanoporous conductive supports, the “core-shell” CN-based ECs show a lower performance, both “*ex situ*” in RRDE and in single FC also in the kinetic region.^{35,36}

To complete the study of the interplay between chemical composition, morphology and performance of “core-shell” CN-based ECs in single PEMFCs it is necessary to analyze some suitable parameters which account for the accessibility of reagents to the active sites (Ψ) and for the transferability of the catalytic yield from “kinetic” to “mass-controlled” conditions (Φ). Ψ is (Eq. 1):

$$\Psi = \frac{MMP \text{ in } O_2}{MMP \text{ in air}} \quad (1)$$

where “MMP in O_2 ” and “MMP in air” are the values of the maximum specific power per mass of active M1 metal measured when the PEMFC is fed with pure O_2 and air, respectively. Φ is (Eq. 2):

$$\Phi = \frac{MMP \text{ in } O_2}{MP @ 50 A \cdot g_{M1}^{-1} \text{ in } O_2} \quad (2)$$

where “MP @ 50 $A \cdot g_{M1}^{-1}$ in O_2 ” is the specific power measured at 50 $A \cdot g_{M1}^{-1}$ in oxygen. Φ , which describes the ability to transfer the catalytic yield observed in the kinetic regime in mass transport-limited operating conditions, is a parameter which is very sensitive to the morphology of the electrocatalyst (see Fig. 5). It expresses the ability of a catalytic site to operate at a high turnover frequency in a complex matrix.

The Ψ vs. Φ correlation of Fig. 5 shows that CN-based ECs, on their morphology and N concentration, can be distinguished into two main groups (I and II). Group I ECs, which show values comparable to those of the Pt/C ref., are endowed with high Φ and low Ψ values, while group II ECs, which includes ECs with complex microporous morphologies, presents low Φ and high Ψ values. Ψ increases with the wt% of N and with the porosity of CN-based “shells”.

Figure 5 demonstrates that: (a) the morphology and the concentration of N in the CN matrix significantly affects the site accessibility of reactants and the transferability of catalytic yield of ECs from the kinetic regime to the operating conditions typical of MEAs; and (b) the best CN-based ECs are endowed with the highest Φ and the lowest Ψ values, a low Ψ corresponds to ECs with both a low porosity and tortuosity.

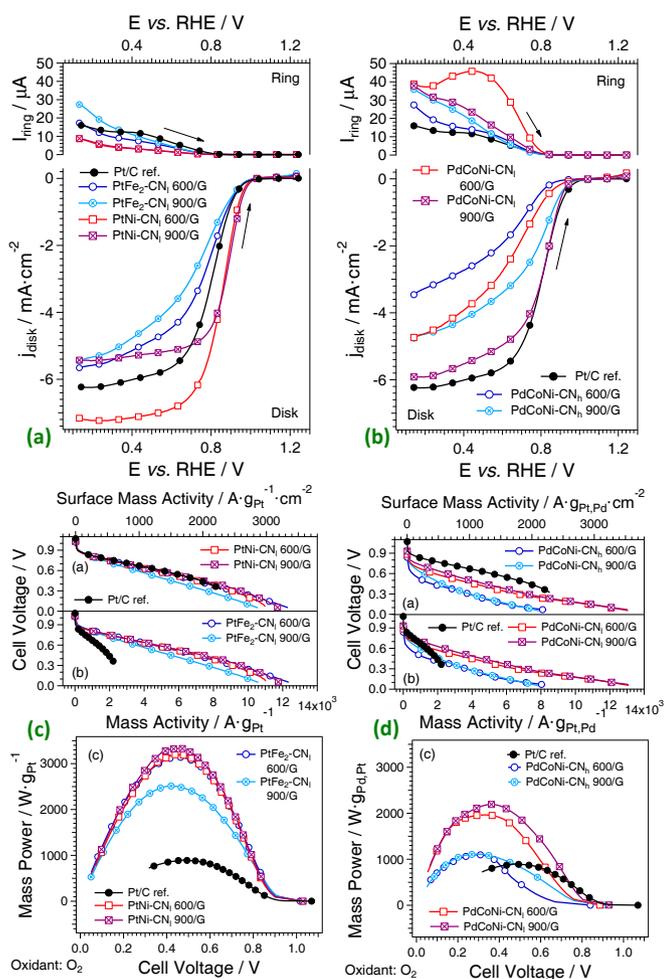


Fig. 4. Selected “core-shell” CN-based ECs; Pt- (a, c) and Pd- (b, d) based systems. (a, b) “*Ex situ*” ORR performance determined with cyclic voltammetry and rotating ring-disk electrode (CV-TF-RRDE); (c, d) tests in single fuel cell.^{4,5,34}

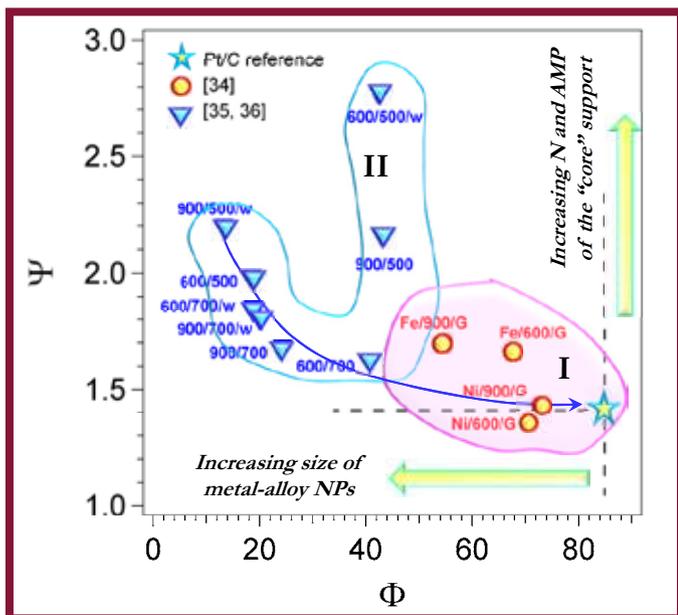


Fig. 5. O_2 site accessibility (Ψ) vs. transferability of catalytic yield (Φ) of CN-based ECs; (★) Pt/C ref.; (●) PtX-CN₁T_j/G, with X = Fe or Ni and (▼) PtNi-CN₁T_j/PY/W; Y is the “core” support pyrolysis temperature; and W is the fraction of P support to CN matrix. AMP is the average area of the micropores.

CN-based ECs comprising PGMs are able to achieve an outstanding ORR performance. They exhibit an improved tolerance to the harsh environments present at the cathode of low-temperature FCs; “Pt-free” ECs are approaching an acceptable level of performance and durability at low costs.³⁸⁻⁴⁰

In summary, results point out that:

- the best protocol for the preparation of CN-based ECs consists of the pyrolysis of Z-IOPE precursors. In this case, N is introduced in the CN matrix by the transition metal complexes, thus forming “coordination nests” for alloy NPs;
- the concentration of nitrogen influences:
 - the conductivity of the CN matrix, which decreases as the N wt% is raised;
 - the coordination of alloy NPs; the higher the concentration of N in the CN matrix, the more the alloy NPs are stabilized, thus improving the tolerance toward oxidizing conditions;
 - the bifunctional and electronic effects on the active sites located on the surface of alloy NPs.
- the complexity of morphology, which increases with N, hinders the performance of the CN-based ECs in the kinetic regime of MEAs;
- the high-performing CN-based ECs are those having N only in “nitrogen coordination nests” of alloy NPs. N is required to stabilize the NPs and improve the catalytic performance through bifunctional and electronic effects.
- the alloy NPs should be easily accessed by the reactants (corresponding to low Ψ values) and should maintain a high turnover frequency in the ORR process in the mass-transfer limited regime found in single FC (high Φ). ■

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About the Authors



VITO DI NOTO is a full Professor of Chemistry for Energy and Solid State Chemistry at the Department of Chemical Sciences of the University of Padova, Italy. He is an electrochemist with over 25 years of experience. Since 1992 he is the founder and the team leader of the “Chemistry of Materials for the Metamorphosis and the Storage of Energy” (CheMaMSE) group in Padova (URL: http://www.chimica.unipd.it/lab_DiNoto/index.html). His research activity is focused on the synthesis and studies on ion-conducting, and electrode materials for the development of: (a) batteries (Li, Mg, Na, Al and others); (b) fuel cells (PEMFCs and AEMFCs); (c) electrolyzers; and (d) redox flow batteries. Prof. Di Noto is author and co-author of over 220 publications, including papers in international “peer reviewed” journals and 20 patents. He may be reached at vito.dinoto@unipd.it.



ENRICO NEGRO graduated in Materials Science in 2001 at the University of Padova, Italy and was awarded his PhD in Materials Engineering in 2005 by the University of Trento. In the same year he joined the research group “CheMaMSE” at the Department of Chemical Sciences of the University of Padova, where he is currently a research associate. His main research interests comprise the synthesis and characterization of advanced electrocatalysts, and their implementation in operating fuel cells. To date he is co-author of 64 peer-reviewed articles published in high-impact journals, 3 book chapters and 14 patents. He may be reached at enrico.negro@unipd.it.



KETI VEZZU graduated in Chemical Engineering in 2002 at the University of Padova, Italy, where she also received her PhD in the same discipline in 2006. Since 2013 she is researcher at Veneto Nanotech S.C.p.a. Her research is focused on the development and study of electrocatalysts for applications in PEMFCs and AEMFCs. She is co-author of 30 publications in international journals and 1 book chapter. She may be reached at keti.vezzu@gmail.com.



FEDERICO BERTASI was awarded a degree in Materials Science by the University of Padova in 2010. He obtained his PhD in Materials Science and Engineering at the University of Padova in April 2014 discussing a dissertation entitled “Advanced Materials for High Performance Secondary Lithium and Magnesium Batteries.” He is a postdoctoral fellow in the “CheMaMSE” group at the Department of Chemical Sciences of the University of Padova, and his activity is focused on the development of new materials for application in high-temperature polymer electrolyte fuel cells. He is co-author of 11 papers in international journals and 4 patents. He may be reached at federico.bertasi@unipd.it.



GRAEME NAWN attended the University of Bath from 2002-2008, where he obtained both MChem and MPhil degrees. In 2013 he completed his PhD in Chemistry at the University of Victoria, Canada, where he primarily investigated and developed a new redox-active ligand family. In 2014 he joined the “CheMaMSE” group at the Department of Chemical Sciences of the University of Padova, under the supervision of Prof. Vito Di Noto; he is now carrying out postdoctoral research activity mainly focused on the preparation and study of ion-exchange materials for applications in fuel cells. To date he is co-author on 8 peer-reviewed articles published in high-impact journals. He may be reached at nawn@unipd.it.

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