Synthesis, studies and fuel cell performance of "core–shell" electrocatalysts for oxygen reduction reaction based on a PtNi$_x$ carbon nitride "shell" and a pyrolyzed polyketone nanoball "core"

V. Di Noto [a,b,*], E. Negro [a,b], S. Polizzi [b,c], K. Vezzù [d], L. Toniolo [b,c], G. Cavinato [a]

[a] Department of Chemical Sciences, University of Padova, Via Marzolo 1, I-35131 Padova (PD), Italy
[b] Consorzio Interuniversitario Nazionale per la Scienza e la Tecnologia dei Materiali, INSTM, Italy
[c] Department of Molecular Sciences and Nanosystems, University of Venice, Calle Larga S. Marta, Dorsoduro, 2137-30123 Venezia (VE), Italy
[d] Veneto Nanotech S.C.p.a., Via San Crispino 106, I-35129 Padova (PD), Italy

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ABSTRACT

This report describes a new class of "core–shell" electrocatalysts for oxygen reduction reaction (ORR) processes for application in Proton Exchange Membrane Fuel Cells (PEMFCs). The electrocatalysts are obtained by supporting a "shell" consisting of PtNi$_x$ alloy nanoparticles embedded into a carbon nitride matrix (indicated as PtNi$_x$-CN) on a "core" of pyrolyzed polyketone nanoballs, labeled 'ST$_p$'. ST$_p$s are obtained by the sulfonation and pyrolysis of a precursor consisting of XC-72R carbon nanoparticles wrapped by polyketone (PK) fibers. The ST$_p$s are extensively characterized in terms of the chemical composition, thermal stability, degree of graphitization and morphology. The "core–shell" ORR electrocatalysts are prepared by the pyrolysis of precursors obtained impregnating the ST$_p$ "cores" with a zeolitic inorganic–organic polymer electrolyte (Z-IOPE) plastic material. The electrochemical performance of the electrocatalysts in the ORR is tested "in situ" by single fuel cell tests. The interplay between the chemical composition, the degree of graphitization of both PtNi$_x$-CN "shell" and ST$_p$s "cores", the morphology of the electrocatalysts and the fuel cell performance is elucidated. The most crucial preparation parameters for the optimization of the various features affecting the fuel cell performance of this promising class of ORR electrocatalysts are identified.

1. Introduction

Fuel cells (FCs) are a family of open electrochemical energy conversion devices operating through the direct electro-oxidation of a fuel (e.g., hydrogen) at the anode and the reduction of an oxidant, usually the oxygen of air, at the cathode [1–3]. Particular attention has been attracted by a family of FCs relying on a proton exchange membrane (PEM) as the electrolyte; these systems are known as proton exchange membrane fuel cells (PEMFCs) [4]. PEMFCs are compact systems characterized by a very high energy conversion efficiency, up to 2–3 times larger in comparison with competing technologies such as internal combustion engines (ICEs) [5]. PEMFCs are particularly suitable to power light-duty electric vehicles and portable electronic devices such as audiovisual players and laptop computers [6,7]. One of the most important bottlenecks in the operation of PEMFCs is the sluggish kinetics of the oxygen reduction reaction (ORR) [8]. Suitable electro-catalysts are required to promote the ORR kinetics in order to achieve an improved performance. As of today, the state of the art in ORR electrocatalysts for PEMFCs consists in nano-composite materials including platinum nanocrystals supported on active carbons characterized by a large surface area and a high electronic conductivity such as XC-72R carbon black [9,10]. These electrocatalysts afford a satisfactory performance; however, they are also very expensive owing to a significant loading of platinum (usually between 10 and 50 wt %) [11]. Furthermore, they suffer from an insufficient long-term durability [12–14]. These drawbacks are still major obstacles towards a widespread diffusion of the promising PEMFC technology. Several approaches are attempted to address the above issues. On one hand, ORR active sites showing an improved turnover frequency were prepared. In general, they include a platinum-group metal (PGM, e.g., Pt, Pd) [10,15] alloyed with one or more first-row transition metals (e.g., Cr, Fe, Co, Ni, Cu) [16–24]. On the other hand, a variety of new supports were investigated, including carbon nano-particles, graphene layers, and carbon nanotubes; some of these systems include suitable heteroatoms (e.g., N or S) to stabilize the active sites and improve the activity and durability of the electrocatalysts [25–27]. In the last decade, our research group proposed an innovative protocol to obtain electrocatalysts for application in fuel cells [28,29]. A suitable hybrid inorganic–organic precursor is prepared, consisting of complexes of the desired metal atoms networked by an organic binder. The precursor undergoes a series of pyrolysis and activation steps, yielding the final electrocatalyst; the latter's stoichiometry is well-controlled and includes the desired concentration of heteroatoms (typically N). The obtained carbon nitride-based electrocatalysts present an improved performance and tolerance to oxidizing conditions [29–31]. The best results are reached in the electrocatalysts with a "core–shell" morphology [30,32,33]. In these systems, the hybrid inorganic–organic precursor is used to impregnate a suitable support before the pyrolysis and activation steps. Highly conductive XC-72R carbon nanoparticles (NPs) were adopted. In such "core–shell" morphology an improved dispersion of the active sites embedded in the carbon nitride "shell" was obtained, which resulted in a better fuel cell performance in comparison with the corresponding bulk electrocatalysts including active sites with the same stoichiometry [32].

In this paper, a new family of supports characterized by an innovative morphology and a large surface area is developed. The supports consist of nanoballs of carbon nanofibers with a diameter on the order of nanometers wrapping "core" carbon nanoparticles of ca. 30–50 nm in size. The supports are obtained in two steps: (1) polyketone (PK) fibers are grown on XC-72R carbon NPs acting as nucleation centers, giving so rise to "balls" showing a nanofibrous morphology; thus, the "support precursor" (SP) is obtained [34]; (2) SP undergoes sulfonation and multi-step pyrolysis procedures. The resulting supports are adopted as the "core" in the preparation of advanced "core–shell" ORR carbon nitride electrocatalysts. In these systems, the "core" is covered by a PtNi$_x$-CN "shell" based on PtNi$_x$ alloy NPs embedded in a carbon nitride (CN) matrix. The "balls" with a nanofibrous morphology of SP are proposed as an innovative template for the modulation of: (a) the morphology and chemical composition of the supports; and (b) the activity and selectivity of the "core–shell" carbon nitride electrocatalysts, which are briefly indicated as PtNi-CN$_l$ T$_f$/ST$_p$ (see the following discussion for more information). PtNi-CN$_l$ T$_f$/ST$_p$ are studied in terms of composition, morphology and single-cell performance under operating conditions in order to obtain information on the most important preparation parameters to design next-generation ORR electrocatalysts characterized by an improved efficiency.

2. Experimental

2.1. Reagents

Potassium tetrachloroplatinate (II), 99.9% and potassium tetracyanonickelate (II), hydrate are supplied by ABCR. D(+)-sucrose, biochemical grade is Acros reagent. EC-20 is received from ElectroChem, Inc. (nominal Pt loading: 20%) and used as the reference. In the following text, EC-20 is labeled "Pt/C reference". Palladium (II) acetate, 98%, p-toluenesulfonic acid monohydrate, 98% and 1,3-bis(diphenylphosphino) propane are obtained from Sigma–Aldrich and in the following are labeled Pd(AcO)$_2$, TsOH, and dppp, respectively. Methanol is purchased by Baker, while sulfuric acid, 98% is obtained from Carlo Erba. All these reagents and solvents are used as received. Carbon monoxide and ethane (C$_2$H$_4$) are supplied by SIAD Company ('research grade', purity > 99.9%). XC-72R carbon black is provided as a courtesy by Carbocrom s.r.l. and washed with H$_2$O$_2$ 10 vol.% prior to use.

2.2. Synthesis of the samples

2.2.1. Preparation of the ST$_p$ "core" supports

The [Pd(dppp)(H$_2$O)(TsOH)](TsOH) and PK are prepared as described in the literature [35,36]. The synthesis of PK is carried out under 45 atm of CO and C$_2$H$_4$ (CO/C$_2$H$_4$ = 1/1) at 85 °C using 0.01 mmol of [Pd(dppp)(H$_2$O)(TsOH)](TsOH), 0.1 mmol of TsOH, 80 mL of MeOH and 1.3 mL of water. After 1 h, the yield is of 6.2 g of PK. The support precursor, labeled "SP", is