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Hybrid chitosan derivative–carbon support for oxygen reduction reactions†

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New hybrid chitosan derivative–carbon black was prepared and used as a support for Pt nanoparticles. These catalysts showed improved activity toward the oxygen reduction reaction (ORR), compared with a commercial Pt/C catalyst. The biopolymer chitosan provided an efficient and sustainable surface nitrogen source associated with the superior performance of the catalysts.

The oxygen reduction catalysts used in current proton exchange membrane fuel cell (PEMFC) prototypes are carbon supported platinum nanoparticles, but cost and supply constraints for large-scale applications require a factor of >4 increase in catalytic activity per unit mass of precious metal.[1,2] To overcome this barrier, much effort has been made in developing an effective Pt-based alloy with higher precious metal utilization,[3] and even alternative non-precious metal catalysts.[4] Unfortunately, until today, although substantial progress has been achieved, the performance of the best non-precious metal catalysts (generally carbon supported Fe– and/or Co–N catalysts) is still inferior when compared to Pt-based catalysts in terms of both activity and stability.[5]

During the last few years, nitrogen-doped carbon seems to be the most suitable ORR active material to support Pt particles in the cathode catalyst.[6,7] There has been increasing evidence showing that nitrogen dopants have a profound impact on the surface states, electron transfer rates, and adsorption for electrocatalysis processes. Futhermore, it has been shown that the density of states at the Fermi Level and the work function will increase linearly with increasing nitrogen content, creating a metal-like conductivity.[8,9]

In an effort to incorporate N species on the carbon support surface, carbon materials coated with N-containing polymers, such as polypyrrole and polyaniline, and programmable peptides have been investigated.[4,10,11] The polymer, as a nitrogen precursor, promises a more uniform distribution of nitrogen sites on the surface and an increase in the active-site density. Additionally, the presence of a polymer film has been shown to protect otherwise unstable catalysts from degradation in acid media, which is absolutely critical for the low pH environment of PEMFCs.[12] These hybrid materials can possess more suitable properties for their use as catalyst supports than their individual components, which has been ascribed to the higher available surface area and electronic conductivity of the support and easier charge-transfer at the polymer–electrolyte interface allowing a high utilization of deposited metal nanoparticles. This is particularly important for optimizing the synergistic nanoparticle–support interactions and for maximizing the mass activity of expensive Pt catalysts.[13]

Herein, we describe a significant improvement for the ORR by anchoring platinum nanoparticles (PtNPs) onto a new hybrid chitosan derivative–carbon black support. Chitosan is a very abundant, nontoxic and low cost biopolymer, constituted of glucosamine and acetylglucosamine monomers, which has good complexing ability due to the presence of –OH and –NH$_2$ groups on the chain.[14,15] The presence of the amine groups explains its unique properties among biopolymers: (a) its cationic behaviour in acidic solutions, and (b) its affinity for metal ions. However, due to the high viscosity and the limited capacity for incorporation of a high amount of metal, chitosan can easily be modified by chemical or physical processes to prepare chitosan derivatives.[16,17]

To this end, we are conceiving a novel strategy to gain higher nitrogen content and higher affinity for Pt ions on the chitosan biopolymer by incorporation of a new compound with a high atomic N/C ratio. In the approach used, the chitosan derivative was prepared by a Michael reaction with methyl acrylate followed by an amidation reaction with diethylentriamine to obtain chitosan-(*N*-(2-(2-aminoethylamino)ethyl) propanamide) (CSD) (Fig. 1). FTIR and NMR studies confirm the formation of the new chitosan derivative (CSD) (see ESI† for details).

The chitosan derivative obtained was coated on the carbon black (Vulcan XC 72R) with different mass ratios of CSD/carbon (CSD.C) by two different methods to obtain 5 wt% and 10 wt% CSD.C (method 1), and 13 wt% CSD.C (method 2). Method 1

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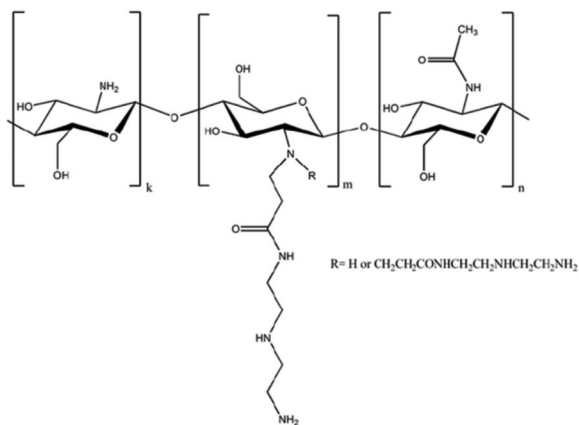† Electronic supplementary information (ESI) available. See DOI: 10.1039/c3ra22416c

Fig. 1 Chitosan (N-(2-(2-aminoethylamino)ethyl) propanamide) (CSD).

Fig. 3 HRTEM images of Pt.5.CSD (A), Pt.10.CSD (B) and Pt.CSD.M2 (C, D).

consisted of mixing the carbon black dispersed in isopropanol with the appropriate amount of chitosan derivative in 2 wt% acetic acid aqueous solution over 2 h, after which the solvent was removed in a rotary evaporator. Method 2 was used to maximized the amount of biopolymer incorporated by mixing the chitosan derivative in 2 wt% acetic acid aqueous solution with carbon black (mass ratio CSD/carbon = 5/1), dispersing with ultrasonic treatment for 30 min, stirring the mixture at room temperature for 24 h and then separating the obtained CSD.C by centrifugation. Finally, Pt nanoparticles (30 wt%) were anchored onto the hybrid CSD.C by impregnation of an appropriate aqueous solution containing chloroplatinic acid, followed by addition of a $NaBH_4$ solution to reduce the metal at room temperature. The electrocatalysts derived from 5 wt% CSD.C, 10 wt% CSD.C and 13 wt% CSD.C are denoted as Pt.5.CSD, Pt.10.CSD and Pt.CSD.M2. A commercial Johnson Matthey Pt/C catalyst with a nominal Pt loading of 40 wt% was employed for a comparison.

An increase of the chitosan loading decreases the BET surface area of the carbon substrate. At the same time, elemental analysis of Pt catalysts showed an increase in the nitrogen content with the content of biopolymer (Fig. 2). This implies that chitosan derivative remains on the carbon surface after incorporation of Pt metal.

High-resolution transmission electron microscopy (HRTEM) images are shown in Fig. 3. Method 1 (Fig. 3A and 3B) produces flower-like Pt nanoparticles with sizes ranging from 10 to 30 nm. However, Pt nanoparticles of the Pt.CSD.M2 catalyst (Fig. 3C and
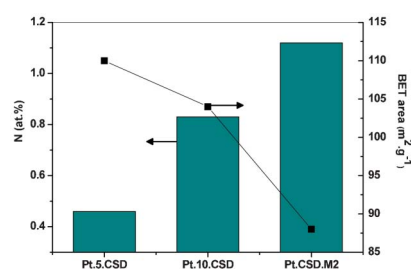
3D) show some areas with a homogeneous distribution centred at 2 nm and other distribution areas with nanoflowers. The high-magnification image (Fig. 3D) displays well oriented 3D flower-like nanoparticles consisting of a core with many small and irregular platinum nanocrystals.

The electrocatalytic activity of the Pt nanoparticles supported on the new hybrid chitosan derivative–carbon black for the ORR was evaluated with a rotating ring disk electrode (RRDE) system in 0.5 M H_2SO_4 at 2 mV s^{-1}. The stability of the hybrid was also checked with cyclic voltammetry, which showed the peak currents remain constant after 100 cycles (Fig. S4†). On the basis of CO-stripping the specific electrochemical active surface areas (ECSAs) of the Pt.5.CSD, Pt.10.CSD, Pt.CSD.M2 catalysts with Pt/C (JM) as a reference, were determined to be 49, 29, 21 and 84 m^2 g$^{-1}_{Pt}$,
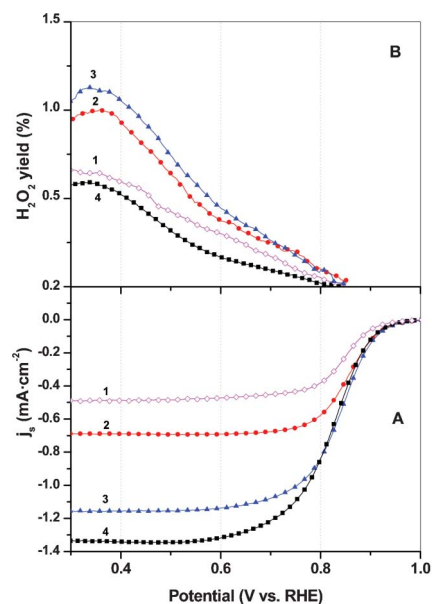

Fig. 2 Nitrogen content and BET surface area of the chitosan-based catalysts.

Fig. 4 Polarization curves on a glassy carbon rotating ring-disk electrode (A) and H_2O_2 yield (B) of Pt/C (JM) (1), Pt.5.CSD (2), Pt.10.CSD (3) and Pt.CSD.M2 (4).

respectively. The lower ECSA of the CSD-based catalysts compared with commercial catalyst was mostly due to the singular nanocrystallites obtained.

The ORR activity and four-electron selectivity (H_2O_2 yield) data for Pt.5.CSD, Pt.10.CSD, Pt.CSD.M2 and Pt/C (JM) are shown in Fig. 4. The kinetic current curves normalized by the ECSA of all catalysts exhibit two distinguishable potential regions, with well-defined diffusion limiting currents (0.2–0.5 V) followed by a mixed kinetic-diffusion control region in the potential window of 0.6–0.9 V with an onset potential of around 1 V. The half-wave potentials of the Pt.5.CSD, Pt.10.CSD, Pt.CSD.M2 and Pt/C (JM) are 0.86, 0.85, 0.84 and 0.85 V, respectively. The specific activity was derived in the mixed-control domain at +0.85 V to be 0.36 mA cm^{-2} for Pt.5.CSD, 0.47 mA cm^{-2} for Pt.10.CSD, 0.42 mA cm^{-2} for Pt.CSD.M2 and 0.22 mA cm^{-2} for the commercial catalyst. The onset potential for the ORR in the chitosan-based catalysts is approximately 20 mV lower than commercial catalyst and does not shift suggesting that the nature of the active site has not changed. The results exhibit that the chitosan-based catalysts posses a better performance than the commercial catalyst.

Based on the ring current generated from the oxidation of H_2O_2, we can see that both the Pt.CSD.M2 and commercial catalyst produced a lower level of H_2O_2 than the Pt.5.CSD and Pt.10.CSD catalysts. Nevertheless, all of them show a H_2O_2 yield below 1.2% over the potential range from 0.2 to 0.8 V *versus* RHE. For instance, at +0.4 V, the yield of H_2O_2 was only 0.52%, 0.59%, 0.93% and 1.05% on the Pt.CSD.M2, Pt/C (JM), Pt.5.CSD and Pt.10.CSD, respectively, corresponding to the numbers of electrons transferred being 3.989, 3.988, 3.981 and 3.979, respectively, signalling virtually complete reduction of O_2 and H_2O in a four-electron process.[18]

Since the nitrogen incorporated in the carbon is considered to be part of the ORR active sites either with or without a bound metal center,[19] the effect of platinum metal on nitrogen speciation in CSD.M2 and Pt.CSD.M2 was studied using XPS as shown in Fig. 5. The component at values close to 400 eV can be assigned to amine groups and to –NH–C=O bonds, while the component at 401.9 eV could correspond to some protonated amines. The peak at low binding energy at 398.7 eV in Pt.CSD.M2 can be assigned to a nitride, therefore indicating the presence of a metal–nitrogen bond.[20]

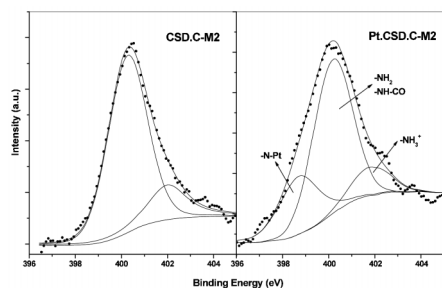The contribution of the chitosan derivative to the electro-catalytic activity is likely to be caused by different cooperative factors: (i) the existence of a good interfacial contact between chitosan molecules, carbon and Pt nanoparticles, which promote the unique nanocrystalite shape; (ii) the ability of the chitosan derivative to produce protonated amine groups, which enable proton transfer on the catalyst surface by performing as an ionomer;[21] (iii) the presence of nitrogen can have an affect on the electron transfer rates and adsorption processes of the ORR.

In summary, a new chitosan derivative was successfully modified and coated on the surface of carbon black, and the hybrids were employed as a catalyst support in this paper. TEM and electrochemical results demonstrate that the hybrid chitosan derivative–carbon is suitable as a support for Pt electrocatalysts. The enhanced catalytic activity toward the ORR may be correlated with the amount of chitosan derivative on the surface. Moreover, given the prevalence of chitosan in many other applications, these hybrid chitosan derivative–carbon supports also have the potential to be generally useful for improving properties and performance in areas beyond catalysts,[22] and in bioelectrochemical systems, such as cathodic catalysts in microbial fuel cells.[23]

Acknowledgements

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Fig. 5 N1s spectra of CSD.M2 and Pt.CSD.M2 samples.

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