ONE-POT SINTHESYS OF LIGNIN-BASED ELECTROSPUN OXYGEN REDUCTION REACTION ELECTROCATALYSTS

Francisco José García-Mateos[1], Ramiro Ruiz-Rosas[1*], Alejandro Ortega[2], Diego Cazorla-Amorós[2], Emilia Morallón[2], José Rodríguez-Mirasol[1], Tomás Cordero[1]

[1] *Universidad de Málaga, Departamento de Ingeniería Química, Andalucía Tech, Facultad de Ciencias, Campus de Teatinos s/n, 29010 Málaga - Spain*

[2] *Instituto Universitario de Materiales. Universidad de Alicante, 03690 San Vicente del Raspeig, Alicante – Spain*

*ramiro@uma.es

Introduction

The use of high amounts of platinum in the cathode due to the sluggish kinetic rate of the oxygen reduction reaction (ORR) is hampering the commercial utilization of fuel cells. There exists a great interest to prepare advanced electrocatalysts that would not only reduce the Pt loading amount by increasing their activity and stability but could also allow its replacement by other precious and non-precious metal catalysts.

Carbon fibers have been used for a long time as a catalyst supports and gas diffusion layers in the electrodes of fuel cells thanks to their adequate combination of high surface area, enhanced mass transport, electrical conductivity and electrochemical resistance. Carbon electrodes are usually coated with the metal catalysts in an impregnation step. Achieving homogeneous surface loading and a strong anchorage of the active phase during this step is mandatory for avoiding leaching, sintering and loss of activity of the catalyst. One pot synthesis strategies are envisaged in order to ease the fabrication of electrodes and solve these problems.

We have recently demonstrated that the electrospinning of lignin, a widely available and non-expensive biopolymer, allows the production of porous carbon cloths, which have been already utilized as electrodes for supercapacitors[1]. Moreover, metals nanoparticles can be easily casted in the carbon fibers by the simple addition of a metal precursor in the electrospun solution. Following this premise, we have prepared carbon fibers loaded with platinum nanoparticles[2]. Owing to the high platinum dispersion, electrical conductivity and electrochemical resistance, the resulting Pt-loaded carbon fibers were found to show high activity for the electrochemical methanol oxidation[3].

In this work, we propose the electrospinning of lignin and precious/non-precious metal precursors for one-pot production of ORR catalysts. Fe, Co, Pd and Pt salts have been incorporated onto lignin-ethanol solutions and have been electrospun in microsized, metal-decorated lignin fibers.

Materials and Methods

Lignin fibers containing different metal precursors were prepared by electrospinning of 40 wt% Alcell® lignin–ethanol solutions in a co-axial configuration, where additional flow of pure ethanol is added in the outer needle for stabilization purposes. Different amounts of $FeNO_3$, $CoNO_3$, $Pt(AcAc)_2$ and $PdCl_2$ (Sigma Aldrich) were solved in the lignin solution in order to achieve approximately 5 wt.% of the corresponding metal loading in the final carbon fiber. Flow rates were kept at 10:1 ratio between the inner and the outer spinneret. Additional parameters of 30 cm of tip-to-collector distance and 12 kV of electrical field voltage were utilized. Air thermostabilization at 5ºC/h, with a holding temperature of 200 ºC kept for 24 hours was implemented to avoid melting of the fibers during the subsequent carbonization step, which has been performed in a horizontal tubular furnace heated at 10ºC/min up to 900 ºC under N_2 flow rate of 150 cm^3 STP /min.

The morphology and structure of the metal-loaded carbon fibers have been studied using Scanning and Transmission Electron Microscopy (SEM and TEM, respectively) in JEOL JSM-6490LV and Philips CM-200 microscopes. The textural properties have been determined using N_2 adsorption-desorption isotherms at -196 ºC and CO_2 adsorption isotherms at 0 ºC (ASAP 2020, Micrometirics).

Metal loading have been checked using X-Ray Photoelectron Spectroscopy (XPS, 5700C Physical Electronics apparatus). Electrochemical performance in ORR of the samples have been analysed in O_2-saturated acid and alkaline electrolytes using a Metrohm Autolab PSTAT-302 apparatus equipped with a rotating ring disk electrode.

Results and Discussion

The textural properties and metal content of the samples are shown in **Table 1**. It can be seen that the addition of the different salt precursors has rendered different porosity distribution. Thus, the Pt and Pd electrocatalysts have developed similar amounts of micropores and mesopores during carbonization, while the use of nitrate-based salts for the preparation of Co and Fe loaded fibers have generated mesoporous carbon fibers.

Scanning micrographs have confirmed the formation of continuous, unwoven carbon fibers with good ratio aspect and diameters in the range of 1 µm. TEM images have revealed the presence of crystalline nanoparticles homogeneously distributed along the mesoporosity of the carbon fibers in all the cases. In addition, the mean metal particle size is lower and particle size distribution is narrower for the noble metal loaded fibers (2-10 nm vs 5-50 nm for Fe and Co-loaded carbon fibers). **Figure 1** includes SEM and TEM images from Co-loaded carbon fibers in order to illustrate the structure of the samples. ORR measurements have confirmed that high electrocatalytic activity is achieved in both acid and alkaline electrolytes in spite of the use of low metal amounts (**Table 1**).

Table 1. Textural properties and metal content of the electrospun carbon fibers

Sample	S_{BET} m^2/g	V_{DR}^{N2} cm^3/g	V_{DR}^{CO2} cm^3/g	V_{mes} cm^3/g	loading wt.%
Pt	790	0.18	0.25	0.51	7.1
Pd	760	0.23	0.30	0.39	--
Fe	350	0.04	0.07	0.59	4.3
Co	500	0.04	0.09	1.10	3.4

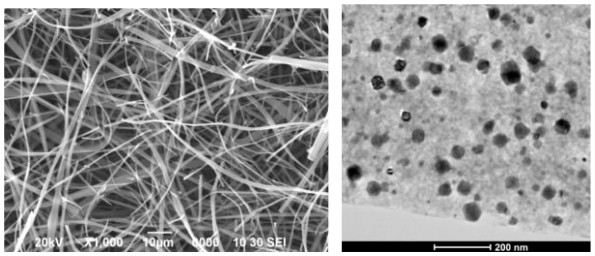

Figure 1. SEM and TEM images of carbon fibers loaded with cobalt nanoparticles

Conclusions

One pot synthesis of carbon fibers with different supported metallic nanoparticles up to 5-7 % wt. loading have been achieved using electrospinning. In addition, the incorporation of metal precursors in the lignin solution enhances the development of mesoporosity in the resulting carbon fibers, a desirable feature for increasing mass transfer rate when used as electrocatalyst, without compromising their electrical conductivity. The electrochemical characterization has confirmed that these carbon cloths are promising ORR catalysts.

Acknowledgment

The authors gratefully acknowledge the financial support by MINECO/FEDER (CTQ2015-68654-R and CTQ2015-66080-R). F.J.G.M acknowledgements the assistance of the MINECO for PTA2015-11464-I

References

1. Berenguer, R., García-Mateos, F.J., Ruiz-Rosas, R., Cazorla-Amorós, D., Morallón, E., Rodríguez-Mirasol, J., Cordero, T. (2016) Biomass-derived binderless fibrous carbon electrodes for ultrafast energy storage, *Green Chem.* 18, 1506–1515

2. Lallave M., Bedia, J., Ruiz-Rosas, R., Rodríguez-Mirasol, J., Cordero, T., Otero, J.C., Marquez, M., Barrero, A., Loscertales, I.G. (2007) Filled and Hollow Carbon Nanofibers by Coaxial Electrospinning of Alcell Lignin without Binder Polymers, *Adv. Mater.* 19, 4292–4296

3. García-Mateos, F.J., Berenguer, R., Valero-Romero, M.J.., Rodríguez-Mirasol, J., Cordero, T. (2018) Phosphorus functionalization for the rapid preparation of highly nanoporous submicron-diameter carbon fibers by electrospinning of lignin solutions, *J. Mater. Chem. A.* 6, 1219–1233