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Synthetic Porous Carbon as Support of Platinum Nanoparticles for Fuel Cell Electrodes

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Porous vitreous carbon can be produced by pyrolysis of resorcinol-formaldehyde porous resin. Using surfactants as stabilizers, it is possible to dry the porous resin in air without pore collapse. Having a large surface area (>500 m^2/g) and high electronic conductivity makes the materials suitable as support of electrocatalyst nanoparticles. Pt nanoparticles were prepared by a microemulsion method and impregnated into the carbon pores by adsorption from its suspension. The presence of the Pt nanoparticles is easily detected by the electrochemical reduction of proton and the evolution of H_2, detected by DEMS. The cyclic voltammogram of the modified electrode in presence of CO does not show current due to CO oxidation to CO_2. On the other hand, the differential electrochemical mass spectroscopy (DEMS) signal clearly shows CO_2 production. Methanol can be electroxidized on the electrode containing Pt nanoparticles supported on porous carbon.

Introduction

Fuel cells are an interesting alternative to combustion engines as primary energy source of automobiles [1]. Besides that, the increasing use of portable electronic devices (phones, cameras, computers) gives an ever increasing market for a clean, silent and cold electric energy source [2]. While hydrogen is a very efficient fuel for these devices, the storage remains a problem [3]. Therefore, fuel cells where it is possible to use liquid organic as fuels are of great interest [4]. Among them, methanol is the most thoroughly studied fuel [5]. There is still a need for metal electrocatalysts able to oxidize methanol, with low poisoning, to be used in electrodes of methanol fuel cells [6]. The use of metal nanoparticles is advantageous because the increasing area gives high current density [7]. However, metal nanoparticles have to be supported on a conductive solid which is chemically inert and have large area to allow access of reactants to the electrocatalyst.

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Usually, amorphous carbon (e.g., Vulcan XC72) is used [8]. However, high surface area carbon materials containing tailored pore distribution on porous materials and regularly interconnected mesopores (>2 nm) are particularly desirable for this purpose [9]. One way to fabricate such materials is to produce porous precursor resins, such as resorcinol-formaldehyde (RF), which are then converted into glassy carbon by carbonization. From the methods and processing conditions used on the synthesis, it is possible to affect the final structure of the gel. Ambient air drying of RF gels gives xerogels, without open pores, by the collapse of the gel due to surface tension forces at the water/air interface. To avoid the collapse, the gels could be dried using supercritical liquids (aerogels) [10] or low surface tension solvents (ambigel) [11]. In both cases, the small surface tension forces do not collapse the gel pores. Another way involves sublimation of the solvent from the pores by lyophilization of the gels (cryogels) [12]. Alternatively, mesoporous inorganic matrices could be used to template the pores in the resin [13]. Self-assembled molecular systems can serve as templates in the synthesis of nanostructured materials [14]. Since 1992, a new family of ordered mesoporous inorganic materials has attracted considerable and still growing attention due to their fascinating structures and wide application perspectives [15,16]. These materials with a tailored size pore distribution may be engineered using a variety of micelles of surfactant molecules as templates. They are produced in various compositions, such as oxides (e.g., silica, alumina, titania, zirconia, mixed oxides) by condensation of inorganic species around the arrays of self-assembled aggregates of surfactant molecules in water [17,18]. From the synthesis of RF organic sol-gel according to a hydrolysis condensation reaction mechanism, that is analogous to the synthesis of inorganic oxides, Dietz et al. reported the preparation of porous RF resins using surfactant micelles as templates which are eliminated during carbonization [19]. The material could be air dried without significant contraction. This method is less expensive than the formation of carbon aerogel with the use of supercritical fluids. In the present communication a porous carbon is used as support of metal nanoparticles. Pt nanoparticles were prepared by a microemulsion method and impregnated into the carbon pores by absorption from its suspension.

Experimental

Preparation of Mesoporous Carbons

A precursor solution was prepared from surfactant (S), resorcinol (R), formaldehyde (F), Na_2CO_3 (C) and deionized water (W). Cationic surfactant, Cetyltrimethylammonium bromide (CTAB, BDH), was used in this study. The solution was prepared mixing CTAB, resorcinol (FLUKA), formaldehyde (37 wt%, Cicarelli), and Na_2CO_3 (Cicarelli) from 0.4 M aqueous solution. The molar ratio on the solution was fixed to F/R: 2, C/R: 5×10^{-3} and W/R: 10. The S/R molar ratio was varied in the work. The mixture was stirred and heated over the Kraft temperature of the surfactant. At this moment, the solution became translucent. Then it was heated at 70°C for 24 h at atmospheric pressure. The brown monolithic resorcinol–formaldehyde (RF) polymer was dried at 70°C in air for 6 hours. Finally, it was carbonized under a N_2 atmosphere at 800°C with a heating rate of 40 K h^{-1}.

Synthesis of Pt Nanoparticles

The Pt nanoparticles were obtained by reduction of H_2PtCl_6 with hydrazine. The reaction is carried out in a micellar solution of water in hexane using Brij 30 as

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surfactant. The surfactant concentration was of 16.54% p/p, that is a W/O = 6. The concentration of H2PtCl6 was 0,2 M. The dispersion of Pt ion and hydrazine are prepared separately and then mixed to produce the reaction [20].

Preparation of Carbon Ink

The deposition of carbon mesogel de carbon on a flat glassy carbon was made from a stable dispersion of carbon in water/ethanol/Nafion®. We used 25 mg of milled carbon, 0.5 ml f distilled water and 0.3 ml of a Nafion® solution (5% in polymer). The mixture was ultrasonicated during 1 hr.

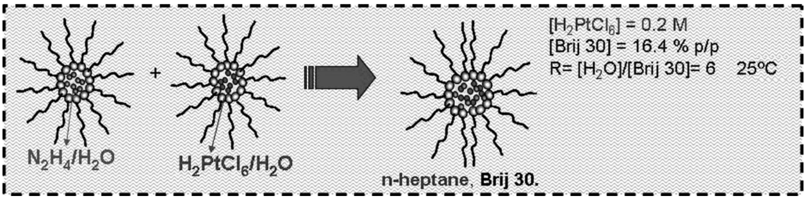
Characterization

The electrochemical performance of the mesogel carbon electrodes was analyzed with a three electrode configuration. The monolithic samples were machined with a thickness of 0.3 mm and ca. 10 mg of weight. A carbon aerogel (Maketech, of a geometrical area 5 times of the working electrode) and a silver/silver chloride electrode (saturated KCl) were used as counter and reference electrode. Cyclic voltammetry (CV) and the AC impedance measurements were performed using a PC4 Potentiostat-Galvanostat-ZRA (Gamry Instruments, Inc). The electrolyte was aqueous 1.0 M H_2SO_4 unless otherwise specified. The current in the resulting cyclic voltammograms was divided by the scan rate and the electrode mass to obtain specific capacitance vs. voltage profiles. The surface area and pore size distribution were calculated from nitrogen adsorption isotherms (Micrometrics, ASAP 2000) using the Brunauer, Emmett, and Teller (BET), and Barrett, Joyner and Halenda (BJH) methods, respectively. The morphology of the carbons was observed with a scanning electron microscope (SEM, Philips 515). DEMS experiments have been performed using an experimental set-up as described before [21]. The working electrode (electrochemical area ca. 5.5 cm^2), consists of a Pt sputtered on a microporous semipermeable membrane (Scimat, average thickness 60 μm, porosity 50%, mean pore size 0.17 μm). The electrochemical cell was completed with a Pt wire as counter electrode and a reversible hydrogen electrode (rhe) in the same acid electrolyte as reference electrode. All potentials in the text are referred to this electrode. The DEMS cell is directly attached to the vacuum chamber containing the mass spectrometer (Balzers QMG 112) with a Faraday cup detector. Volatile species generated at the electrode evaporate at the pores of the membrane into the vacuum and are detected by the mass spectrometer with a time constant of ca. 1s. This time constant is small enough to allow mass spectrometric cyclic voltammograms (MSCVs) for selected mass-to-charge ratios (m/z) to be recorded in parallel to cyclic voltammograms (CVs) at a scan rate of 0.01 V s^{-1}.

Results and Discussion

The Pt nanoparticles were produced by reduction of H_2PtCl_6 with hydrazine inside an inverse micelle. Both the Pt ion and the reductant are made into inverse micelles (water in hexane) with Brij as surfactant (Sch. 1). A dynamic light scattering measurement of the micelles (Fig. 1) reveal diameters of ca. 20 nm for the micelle before reaction and ca. 16 nm for the one after formation of Pt.

While it is tempting to assume that all the micelle core is filled with Pt and the size of the nanoparticles depends directly on the micelle size, STM measurements of



Scheme 1. Synthesis of Pt nanoparticles inside inverse micelles.

the particle size, show particles of ca. 5 nm [20]. Therefore the micelle is not filled completely with the Pt nanoparticle. The nanoparticles are adsorbed into porous carbon microparticles. The porous carbon is obtained by carbonization (800 oC, Ar atmosphere) of dry porous RF resin. (Sch. 2) While resorcinol-folmadehyde polymerization produces a porous wet gel, simple drying creates a compact xerogel trough gel collapse by surface tension forces. However addition of cetyl,trimethylammonium bromide (CTAB) produces stable spherical micelles which stabilize the negatively charged RF nanoparticles [22]. The resulting carbon has a BET area of $634 \pm 30\,\mathrm{m}^2/\mathrm{g}$ as measured by N_2 adsorption. The monolithic porous carbon is milled, sieved to obtain particles of 25–35 μm diameter and dispersed using Nafion® [23]. The resulting ink is deposited onto flat glassy carbon electrodes, giving modified electrodes. The electrochemical response of an electrode modified with Pt nanoparticles adsorbed on porous carbon (Fig. 2) show an enhanced current for proton reduction at ca. 0.0 Vrhe (upper panel). Restricting the potential excursion to avoid bulk hydrogen formation show clearly the two peak systems (at ca. 0.15 and 0.23 Vrhe) due to weak and strongly adsorbed H_2 (lower panel). The response in absent in porous carbon since hydrogen could not be adsorbed.

To understand better the behavior, we apply Differential Electrochemical Mass spectroscopy. The electrode surface is set in a thin layer cell very close (<10 μm) to a porous hydrophobic membrane, made of Teflon®. On the other side of the

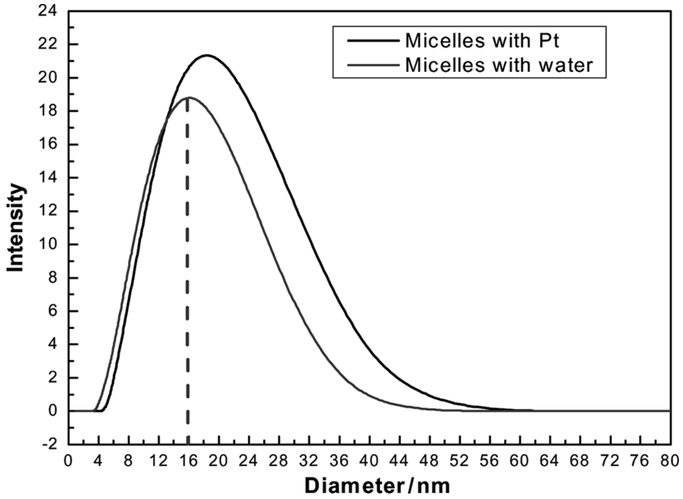


Figure 1. Dynamic light scattering measurements of inverse micelles before and after Pt nanoparticle formation.

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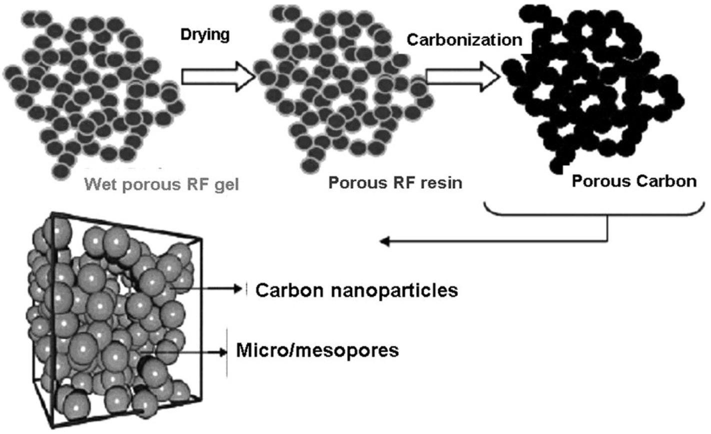

Scheme 2. Mechanism of carbon formation by carbonization of a resorcinol-formaldehyde porous gel.

membrane, high vacuum is applied into a chamber holding a mass/charge detector, such as a magnetic quadrupole. Since the membrane is hydrophobic, water is scarcely transferred across it while less polar volatile substances cross the membrane and are detected by the mass/charge detector. To improve the signal/noise ratio there are two detectors in tandem, one set to the dominant (water) signal and the other t the mass/charge of interest. In that way, the differential signal represents the amount of either volatile reactants (e.g., methanol) or volatile products (e.g., CO_2) against the background water signal. Using the device, the substance of interest can be detected with high sensitivity (nanomoles) and selectivity (given by the mass/charge ratio (m/z)). Since the electrode is under potential control, the amount of reactant consumed or product produced at each potential can be determined.

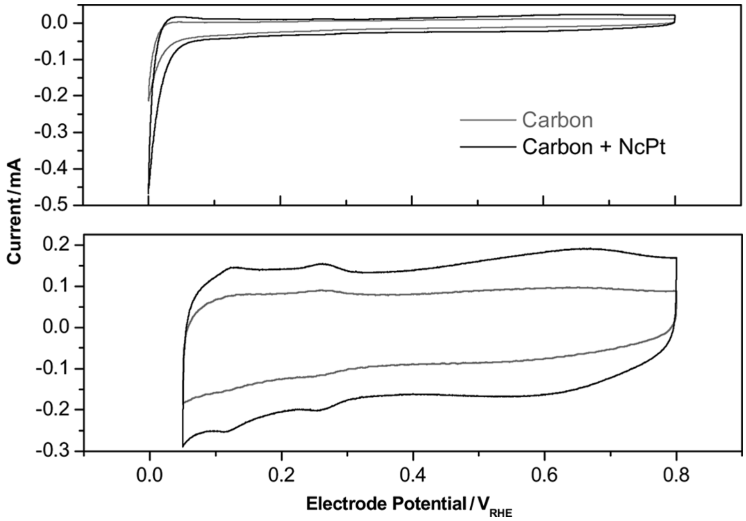

Figure 2. Cyclic voltammograms of porous carbon electrodes with (black line) and without (gray line) adsorbed Pt nanoparticles. Scan rate = 10 mV/s. Electrolyte = 1 M H_2SO_4.

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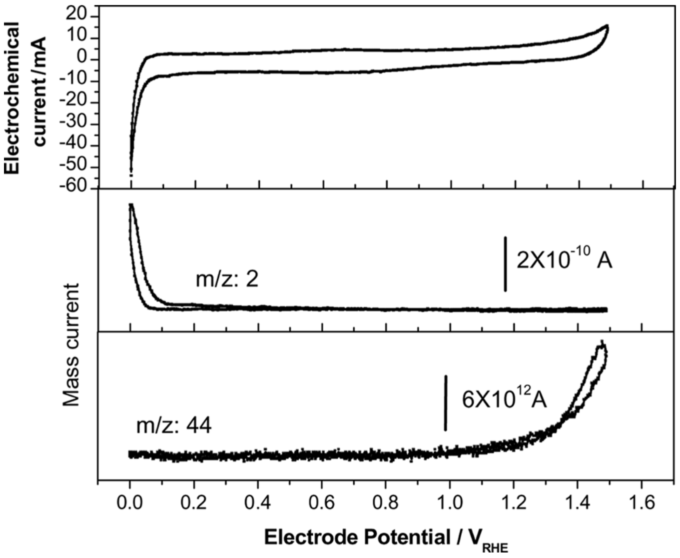
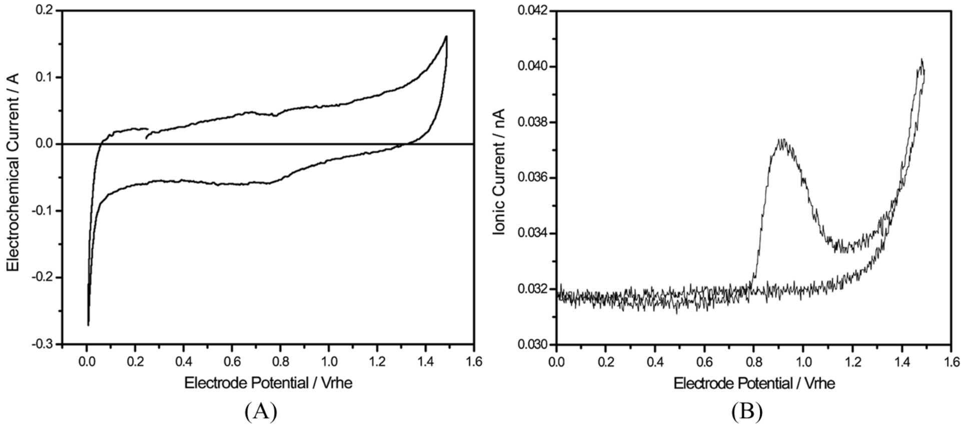


Figure 3. Comparison of the cyclic voltammogram of PC/PtNp (upper plane), the DEMS signal for H_2 (medium plane) and the one of CO_2 (lower plane). Scan rate = 10 mV/s. Electrolyte = 1 M H_2SO_4.

The DEMS response of a glassy carbon electrode covered with porous carbon particles containing Pt nanoparticles is shown in Figure 3. At ca. 0.0 Vrhe H_2 is evolved, as denoted by the clear m/z = 2 signal. On the other hand, at ca. 1.4 V a clear signal of m/z = 44 indicates that CO_2 is evolved. The later is likely to come from surface oxidation of the carbon electrode.

It is possible to adsorb CO on the Pt surface and oxidize it electrochemically. Interestingly, the electrochemical response (Fig. 4A) does not show noticeable current due to adsorbed CO oxidation. On the other hand, a clear DEMS signal for m/z = 44 can be seen at ca. 0.95 V (Fig. 4B). The different sensitivity can be due to



(A) (B)

Figure 4. (A) Cyclic voltammogram and (B) DEMS signal of adsorbed CO on a porous vitreous carbon electrode loaded with Pt nanoparticles.

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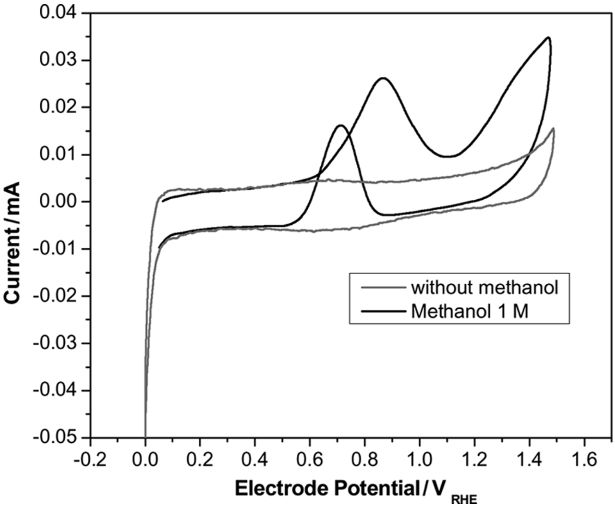

Figure 5. Comparison of the cyclic voltammogram of PC/PtNp without methanol (grey line) and with methanol (back line). Scan rate = 10 mV/s. Electrolyte = 1 M H_2SO_4.

the fact that electrochemical current contains the capacitive and faradaic contribution. In a high surface area electrode, the capacitive part is large and obscures the faradaic current. On the other hand, DEMS is only sensitive to the volatile species produced during electrochemical reaction. Therefore, there is no DEMS signal associated with double layer charging where no volatiles species is produced. Therefore, the CO_2 signal can be easily detected. Such capability is quite important to study electrocatalysts supported on porous conductors.

On the other hand, a clear electrochemical signal is measured when methanol is oxidized onto porous carbon loaded with Pt nanoparticles (Fig. 4). In the case of H^+ reduction to H_2, both CV and DEMS signal show a clear signal. It seems clear that the large double layer capacitance of porous vitreous carbon does not allow detecting the redox response of adsorbed couples but not of solution species.

Finally, the Pt NP supported electrode is tested for methanol oxidation (Fig. 5). As it can be seen, while no current due to methanol oxidation is observed, a clear electrochemical response is observed when Pt NP is present.

Conclusions

- The Pt nanoparticles (Np), synthesized by chemical reduction inside inverse micelles, absorbed into the pores of carbon electrodes can detected by proton reduction and hydrogen adsorption.
- The electrodes modified with porous carbon microparticles which are inserted with Pt Np are able to electrochemical oxidize CO and methanol.
- While DEMS detects adsorbed CO, electrochemistry could not resolve the signal from the background current due to capacitance inherent to the large surface area carbon.
- DEMS is the technique of choice to detect products of fuel electroxidation in fuel cells.

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References

[1] Hoogers, G. (Ed.), (2002). *Fuel Cell Technology Handbook*, CRC: Boca Raton.

[2] (a) Lu, G. Q., Wang, C. Y., Yen, T. J., & Zhang, X. (2004). *Electrochim. Acta*, *49*, 821; (b) Stone, C. (2007). *Fuel Cells Bulletin*, *2007*, 12.

[3] Zhou, L. (2005). *Renewable and Sustainable Energy Reviews*, *9*, 395.

[4] Demirci, U. B. (2009). *Environment International*, *35*, 626.

[5] García, M. F., Sieben, J. M., Pilla, A. S., Duarte, M. M. E., & Mayer, C. E. (2008). *Int. J. Hyd. Energy*, *33*, 3517.

[6] Tian, J., Sun, G., Jiang, L., Yan, S., Mao, Q., & Xin, Q. (2007). *Electrochemistry Communications*, *9*, 563.

[7] Liu, Z., Ming Gan, L., Hong, L., Chen, W., & Yang Lee, J. (2005). *Journal of Power Sources*, *139*, 73.

[8] Moreira, J., del Angel, P., Ocampo, A. L., Sebastián, P. J., Montoya, J. A., & Castellanos, R. H. (August, 2004). *International Journal of Hydrogen Energy*, *29*(9), 915–920.

[9] Ding, J., Chan, K.-Y., Ren, J., & Xiao, F.-S. (2005). *Electrochimica Acta*, *50*, 3131.

[10] Pekala, R. W. (1989). *J. Mater. Sci.*, *24*, 3221.

[11] Mayer, S. T., Kaschmitter, J. L., & Pekala, R. W. (1995). US Patent No. 5,420,168.

[12] Yamamoto, T., Sugimoto, T., Suzuki, T., Mukai, S. R., & Tamon, H. (2002). *Carbon*, *40*, 1345.

[13] Darmstadt, H., Roy, C., Kaliaguine, S., Joo, S. H., & Ryoo, R. (2000). *J. Am. Chem. Soc.*, *122*, 1071.

[14] Antonietti, M. (2001). *J. Colloid Interface Sci.*, *6*, 244.

[15] Kresge, C. T., Leonowicz, M. E., Roth, W. J., Vartuli, J. C., & Beck, J. S. (1992). *Nature*, *359*, 710.

[16] Beck, J. S. *et al.* (1992). *J. Am. Chem. Soc.*, *114*, 10834.

[17] Patarin, J., Lebeau, B., & Zana, R. (2002). *J. Colloid Interface Sci.*, *7*, 107.

[18] Soler-Illia Galo, G., Sanchez, C., Lebeau, C. B., & Patarin, B. (2002). *J. Chem. Rev.*, *102*, 4093.

[19] Bell, W. & Dietz, S. (2001). US Patent, 6,297,293.

[20] Guillén-Villafuerte, O., García, G., Anula, B., Pastor, E., Blanco, M., López-Quintela, M., & Hernández-Creus, A. (2006). *G. Angewandte Chemie*, *45*, 4266–4269.

[21] (a) Planes, G., Moran, E., Rodriguez, J. L., & Pastor, E. (2001). *Portugaliae Electrochim. Acta*, *19*, 377; (b) Zinola, C. F., Rodriguez, J. L., Arevalo, M. C., & Pastor, E. (1998). *J. Electroanal. Chem.*, *454*, 161.

[22] Bruno, M. (2007). Ph.D. thesis, Universidad Nacional de Rió Cuarto, Argentiona.

[23] Ramdutt, D., Charles, C., Hudspeth, J., Ladewig, B., Gengenbach, T., Boswell, R., Dicks, A., & Brault, P. (2007). *Journal of Power Sources*, *165*, 41.

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