ECYT
PROGRAMA DE DOCTORADO INTERUNIVERSITARIO

Programa de Doctorat
Electroquímica Ciència i Tecnologia

PROJECTE DE TESI DOCTORAL

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Tutor (*si s'escau*)**:**

Línia de recerca: ELECTROQUÍMICA DEL MEDI AMBIENT

Títol de la Tesi: SYNTHESIS AND CHARACTERIZATION OF NANOPARTICULATED SUPPORTED CATALYSTS FOR POROUS ELECTRODES AND ENVIRONMENTAL APPLICATIONS

El projecte ha de constar de les següents parts:
1. Introducció: interès del tema
2. Objectius
3. Pla de treball i cronograma.
4. Bibliografia

Màxim 1000 paraules (sense comptar la bibliografia)

1. Introduction and general interest of the subject

The development of eco-friendly, sustainable and cost-effective energy sources is a present need because the use of fossil fuels causes negative effects such as the climate change and environmental pollution. Hydrogen is a clean energy vector that can be satisfactorily used in fuel cells, which have higher efficiency than other competing devices [1]. Water electrolysis is considered to be one of the most promising techniques to obtain pure and green H_2 from renewable energy sources (i.e., solar and wind power) [2]. In addition, the production of H_2 can be combined with water decontamination because the organic compounds can be oxidized at the anode in concomitance with cathodic hydrogen production. The H_2 released could then be stored to be used in a fuel cell and hence, part of the energy consumed in the electrolysis could be recovered.

Platinum is known to be the best catalyst for the H_2 oxidation and the hydrogen evolution reactions and, therefore, it is the preferred catalyst for polymer electrolyte fuel cells and water electrolyzers, respectively. However, Pt is expensive, scarce and susceptible to poisoning, especially when the hydrogen gas used as fuel is produced by reforming [3]. Accordingly, reducing the cost and improving the catalyst activity and stability are currently active research areas. One possibility is to use core-shell nanostructures, in which a core of a sacrificial metal is covered by a shell of Pt [4]. The nanoparticles have a large active surface area with low Pt loading, thus allowing saving the amount of precious metal and, in addition, the metal core can modify the electronic properties of the surface Pt to be a more active catalyst than the pure metal. As shown in previous studies, polymetallic catalysts such as Pt(Cu) core-shell nanoparticles can contribute to the reduction of the cost and to the CO poisoning in fuel cells [5-9].

A step forward is also planned in the case of obtaining new good anode catalysts for the oxidation of organic pollutants, since its combination with a gas-diffusion cathode would finally yield a fuel cell for water decontamination. Using a specialty electrode as gas-diffusion electrode for hydrogen peroxide generation, the addition of Fe^{2+} or purpose-made Fe-based heterogeneous catalysts to the solution in catalytic amounts could promote Fenton's reaction, thus enhancing the degradation of contaminants [10-11]. Note that in such Fenton-based systems, Pt and platinized anodes are typically employed, but they represent a high cost for practical implementation and hence, less expensive anodes are needed.

2. Objectives

The general objectives of the PhD thesis are:

1. To update the existing bibliography.
2. To synthesize core-shell Pt(Cu)/C electrodes using the electroless reduction of Cu^{2+} and galvanic exchange. The metal content can be modulated, being about 20 wt.% for fuel cells. Variables foreseen in the synthesis are the bath composition and temperature. The support would be carbonaceous or not.

3. To determine the electrochemical performance of the catalysts. The electrochemical characterization techniques, in particular the cyclic voltammetry, allow showing their catalytic activity and determining the electroactive surface areas through the hydrogen sorption and the CO stripping.
4. To determine the crystalline structure, metallic composition, total metal percentage, size and distribution of nanoparticles and states of oxidation of the elements in the electrocatalyst. The appropriate characterization techniques are X-ray diffraction, atomic absorption, low and high resolution transmission electron microscopy, X-ray energy dispersive microanalyses and X-ray photoelectron spectroscopy.
5. To study the kinetics of the hydrogen oxidation and the oxygen reduction reactions, using cyclic and linear sweep voltammetry and electrochemical impedance spectroscopy, on the glassy-carbon surface of the rotating disk electrode modified by the appropriate catalysts.
6. To compare the structural and electrochemical characteristics of the electrocatalysts prepared with those of the Pt/C commercial electrocatalysts of reference.
7. To perform degradation tests of organic pollutants with the supported core-shell catalysts as the anodes and a H_2-producing cathode.
8. To perform degradation tests of organic pollutants in fuel cells. The anodes will be H_2-diffusion ones or electrodes able to oxidize the organic matter. The cathode will be an O_2-diffusion one for H_2O_2 production with the addition of Fe species to promote Fenton's reaction.

3. Working plan and schedule

The aforementioned work is planned according to the schedule summarized in Table 1.

Table 1.- Chronogram for the PhD development, considering 4 years (16 terms). One or two stays in a foreign centre (6 months or 3 months and 3 months, respectively) and presentations in national and international meetings (2 per year) are forecasted.

Activity	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1. Development of methods and techniques	x															
2. Objective 1	x	x	x	x												
3. Objective 2		x	x	x	x	x	x	x	x							
4. Objective 3				x	x	x	x	x	x							
5. Objective 4				x	x	x	x	x	x							
6. Stay in a foreign centre										x	x					
7. Objective 5					x				x	x	x	x				
8. Objective 6									x	x	x	x				
9. Objective 7											x	x	x	x		
10. Attendance to congresses				x				x				x				x
11. Writing and defense of Thesis														x	x	x

4. Bibliography

[1] Daud, W.R.W.; Rosli, R.E.; Majlan, E.H.; Hamid, S.A.A.; Mohamed, R.; Husaini, T. PEM fuel cell system control: A review, *Renew. Energy* 113 (2017) 620–638.
[2] P. V. Kamat, Meeting the clean energy demand: Nanostructure architectures for solar energy conversion, J. Phys. Chem. C 111 (2007) 2834–2860
[3] Wang, Y.; Chen, K. S.; Mishler, J.; Cho, S. C.; Adroher, X. C. A Review of Polymer Electrolyte Membrane Fuel Cells: Technology, Applications, and Needs on Fundamental Research. Appl. Energy 88 (2011) 981–1007
[4] Hunt, S. T.; Roma, Y. Principles and Methods for the Rational Design of Core − Shell Nanoparticle Catalysts with Ultralow Noble Metal Loadings. Acc. Chem. Res. 51 (2018) 1054–1062
[5] Caballero-Manrique, G.; Nadeem, I.M.; Brillas, E.; Centellas, F.; Garrido, J.A.; Rodríguez, R.M.; Cabot, P.L. Effects of the electrodeposition time in the synthesis of carbon-supported Pt(Cu) and Pt-Ru(Cu) core-shell electrocatalysts for polymer electrolyte fuel cells, *Catalysts* 6 (2016) 125.
[6] Liu, Y.; Huang, Y.; Xie, Y.; Yang, Z.; Huang, H.; Zhou, Q. Preparation of Highly Dispersed CuPt Nanoparticles on Ionic-Liquid-Assisted Graphene Sheets for Direct Methanol Fuel Cell. Chem. Eng. J. 197 (2012) 80–87.
[7] Mintsouli, I.; Georgieva, J.; Armyanov, S.; Valova, E.; Avdeev, G.; Hubin, A.; Steenhaut, O.; Dille, J.; Tsiplakides, D.; Balomenou, S.; et al. Pt-Cu Electrocatalysts for Methanol Oxidation Prepared by Partial Galvanic Replacement of Cu / Carbon Powder Precursors. "Applied Catal. B, Environ. 136-137 (2013) 160–167
[8] Georgieva, J.; Valova, E.; Mintsouli, I.; Sotiropoulos, S.; Armyanov, S.; Kakaroglou, A.; Hubin, A.; Steenhaut, O.; Dille, J. Carbon-Supported Pt(Cu) Electrocatalysts for Methanol Oxidation Prepared by Cu Electroless Deposition and Its Galvanic Replacement by Pt. J. Appl. Electrochem. 44 (2014) 215–224.
[9] Dimitrova, N.; Georgieva, J.; Sotiropoulos, S.; Boiadjieva-Scherzer, T. Z.; Valova, E.; Armyanov, S.; Steenhaut, O.; Hubin, A.; Karashanova, D. Pt(Cu) Catalyst on TiO2 Powder Support Prepared by Photodeposition-Galvanic Replacement Method. J. Electroanal. Chem. 823 (2018) 624–632.

[10] Brillas, E.; Sirés, I.; Oturan, M.A. Electro-Fenton process and related electrochemical technologies based on Fenton' s reaction chemistry, Chem. Rev. 109 (2009) 6570–6631.
[11] Liu, X.; Zhou, Y.; Zhang, J.; Luo, L.; Yang, Y.; Huang, H. Insight into Electro-Fenton and Photo-Fenton for the Degradation of Antibiotics : Mechanism Study and Research Gaps. Chem. Eng. J. 347 (2018) 379-397

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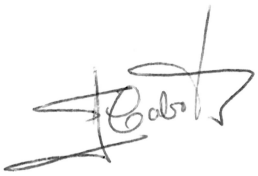

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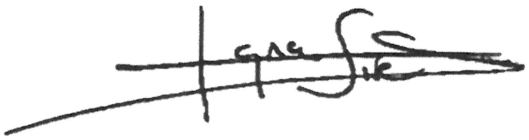

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