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PLA DE RECERCA / PLAN DE INVESTIGACIÓN
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Programa de doctorat / Programa de doctorado Electroquímica. Ciencia y Tecnología	
Línea de recerca / Línea de investigación Electrocatálisis fundamental y aplicada	
Títol de la tesi / Título de la tesis Estudios fundamentales y electrocatálisis en superficies bimetálica monocristalina de PtPd.	

MEMÒRIA DEL PLA DE RECERCA
MEMORIA DEL PLAN DE INVESTIGACIÓN

1. Antecedents i estat actual del tema / Antecedentes y estado actual del tema

The search for alternative energy sources, in the last years, has concentrated high support of capital and research from the scientific community, in order to eliminate dependence on fossil fuels as a source of energy, which, in addition to being non-renewable, generate pollutants. In this context, converters of wind, thermal, solar, hydro, etc. into electrical energy have become popular[1,2]. However, the storage of this energy becomes a problem, since such sources are seasonal in many regions, which would not allow a continuous supply. One of the ways to store such energy is in the form of chemical bonds, to be used later through controlled reactions, such as those that occur in fuel cells, where the conversion of chemical energy into electrical energy occurs with high efficiency[1].

In a fuel cell, the reaction that takes place at the anode is the oxidation of fuel, being hydrogen the simplest one, and the reaction that takes place at the cathode is the reduction of oxygen, usually from the air. In acidic media the reactions are:

$$H_2 \rightarrow 2H^+ + 2e^- \qquad \text{(Reaction 1)}$$

$$^1/_2\ O_2 + 2H^+ + 2e^- \rightarrow H_2O \qquad \text{(Reaction 2)}$$

thus, the overall fuel cell reaction is:

$$H_2 + {}^1/_2\, O_2 \rightarrow H_2O \qquad \text{(Reaction 3)}$$

The anode is fed with molecular hydrogen (H_2) or hydrogenated compounds and the cathode uses oxygen (O_2) from the air, , being able to theoretically supply 1.23 V with a yield of up to 83% (energy available to do work / total energy), with only water as a residual product[3]. Table 1 show the standard free energy (ΔG°), the number of electrons transferred (n), for the complete oxidation and reduction of hydrogen and oxygen, respectively, at 25 ºC and 1 bar and the thermodynamic open-circuit voltage (U^0_{cell}) for the complete fuel cell and the theoretical standard potential (E^0) for the anodic reaction.

Table 1. Thermodynamic data for the total electro-oxidation of Hydrogen (H_2) and Oxygen (O_2) reduction under normal conditions of temperature and pressure (NTP)[4].

Theoretical cell reaction	ΔG° / kJ mol^{-1}	n	U^0_{cell} / V	E^0 / V
$H_2 + {}^1/_2\, O_2 \rightarrow H_2O$	-237	2	1.23	0.00

Although hydrogen belongs to the class of "green gases", its majority is still obtained from fossil fuels and its transportation requires additional care due to the high risks of explosion. In this context, the use of small organic species, such as formic acid, has been a plausible idea, aiming at the electrochemical conversion of these species into more oxidized products[5–7]. thus, this idea has become attractive for cells that directly use organic molecules to replace hydrogen (DLFCs - direct liquid fuel cells). Table 2 presents a thermodynamic overview regarding the complete oxidation of different organic molecules, with 1, 2 or 3 carbons (CX, with X = 1, 2 or 3, respectively), against the oxidation of hydrogen shown in table 1.

Table 2 Thermodynamic overview for the complete oxidation of formaldehyde (CH_2O), formic acid ($HCOOH$), methanol (CH_3OH), ethanol(C_2H_5OH), ethylene glycol ($C_2H_4(OH)_2$) and, glycerol ($CH_5(OH)_3$) under normal conditions of temperature and pressure (NTP)[4,8].

Theoretical cell reaction	ΔG° / kJ mol^{-1}	n	U^0_{cell} / V	E^0 / V
$CH_2O + O_2 \rightarrow CO_2 + H_2O$	-522	4	1.35	-0.12
$HCOOH + {}^1/_2\, O_2 \rightarrow CO_2 + H_2O$	-285	2	1.48	-0,25
$CH_3OH + {}^1/_2\, O_2 \rightarrow CO_2 + 2H_2O$	-698	6	1.21	0.02
$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$	-1325	12	1.14	0.09
$C_2H_4(OH)_2 + 5/2\, O_2 \rightarrow 2CO_2 + 3H_2O$	-1349	10	1.22	-0.01
$C_3H_5(OH)_3 + {}^7/_2\, O_2 \rightarrow 3CO_2 + 4H_2O$	-1850	14	1.25	-0.02

Observing the data shown in tables 1 and 2 and the physical characteristics of these molecules, such as: toxicity, inflammability, volatility, etc., thermodynamic and logistical advantages of the systems that operate with such organic molecules at the anode are evident. Another point that makes this cause attractive is the high energy density of these molecules, where methanol (C1), ethanol (C2) and glycerol (C3) present 4047, 5442 e 6269 KWh L^{-1}, respectively. However, the presence of processes parallel to the total and direct oxidation of the molecule can lead to the formation of strongly adsorbed species, which acts as a poison in the catalyst, causing kinetic impediment in the use of available energy in these systems. As a consequence of these undesirable processes, powers higher than the standard potential are necessary for the reaction rate of these systems to have considerable values, which may be a limitation of the use of these fuels in DLFCs[9].

Despite the negative points and difficulties pointed out in the use of organic molecules to replace hydrogen in fuel cell anodes, the formic acid oxidation reaction continues to be widely studied[10–13]. The motivation for these continuous studies stems from the high-power density found in the oxidation of formic acid, which can result in considerable yields in low temperature direct fuel cells. From a fundamental point of view, the structural simplicity of the formic acid molecule has been used as a model system to study and elucidate the electro-oxidation of molecules in solid catalysts (electrodes)[14–16].

Pd electrodes present higher catalytic activities than Pt in the formic acid electro-oxidation reaction, however this reaction is much more elucidated for Pt catalysts[17–20]. Thus, the use of PtPd bimetallic electrodes, with well-defined surface, can be a good strategy to study the formic acid oxidation reaction both from an applied and fundamental point of view.

2. Bibliografia més rellevant / Bibliografía más relevante

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3. Objectius de la investigació / Objetivos de la investigación

Objetivo general:

The present research project has the general objective to study fundamental aspects of the electrochemical behavior of monocrystalline bimetallic PtPd electrodes (MBE-PtPd), as well as their catalytic activity in the formic acid oxidation reaction (FAOR). Specifically, it intended to elucidate at a fundamental level the effect of the surface structure and Pt/Pd ratio of the electrodes, in the catalysis of the FAOR, making it possible to establish a relationship between the electrochemical behavior and the physical structure of the electrodes in the mechanisms that govern the FAOR.

Objetivos específicos:

i. Evaluation of the electrochemical behavior of the monocrystalline surface of Pt-Pd bimetallic and Pd monometallic electrodes.
ii. Evaluation of the electrocatalytic activity of bimetallic electrodes in the formic acid oxidation reaction in voltammetric regime.
iii. Monitoring of FAEO by Infrared Spectroscopy (FTIR) in order to evaluate the formation of organic species on the electrode surface.
iv. Monitoring of the FAEO by Differential electrochemical mass spectroscopy (DEMS), in order to evaluate the formation of gaseous species.
v. Identify soluble FAEOR intermediates by HPLC.
vi. Determine FAEOR kinetic parameters through numerical simulation coupled with experimental results.

4. Metodologia, hipòtesi i planificació temporal / Metodología, hipótesis y planificación temporal

Metodologia

i. **Fabrication and Characterization of the monocrystalline surfaces of Pt/Pd bimetallic electrodes.** Bimetallic Pt/Pd electrodes with a monocrystalline surface will be made using the protocol developed by Clavilier[21]. The physical characterization will be performed by low energy electron diffraction (LEED) and Auger electron spectroscopy (AES), according to the procedure used in the reference[22]. The electrochemical characterization of the electrode surfaces will be carried out in perchloric acid, sulfuric acid and sodium hydroxide, by cyclic voltammetry, following the protocol developed by Clavilier et al.[21], making it possible to evaluate the electrochemical behavior of the electrodes in different reaction media.

ii. **Evaluation of the catalytic activity of bimetallic electrodes and mechanistic elucidations in the FAOR**. Based on the results of characterization of the electrodes by cyclic voltammetry, the supporting electrolyte that presents less interaction with the electrodes will be chosen and used in this step. The electrooxidation reaction of formic acid will be studied by classical cyclic voltammetry, high-speed scanning and pulsed experiments. In order to eliminate undesired effects by ohmic drop and diffusion processes, the experiments of pulsed voltammetry and high scanning speed will be

carried out in an electrochemical cell in the hanging-meniscus rotating disk configuration[23] with compensation corrected ohmic value (previously determined by electrochemical impedance spectroscopy[24]).

iii. **In-situ monitoring of FAOR by infrared spectroscopy**. In order to make it possible to use an electrode with a monocrystalline surface, a spectro-electrochemical cell will be used in the configuration of reflection of external absorbance[25]. Spectra with a resolution of 8 cm^{-1} and composed of 64 interferograms will be collected concomitantly with the potential scan, according to the procedure traditionally used in our research group[26].

iv. **Online monitoring of CO_2 production during the FAEOR.** The experiments will be carried out in a spectro-electrochemical cell in the Capillary imle[27] configuration. The CO_2 formation will be monitored concomitantly with the linear potential sweep, according to the experimental procedure described in the reference[28].

v. **Monitoring the production of soluble intermediates during the FAEOR.** Due to the high vapor pressure of some soluble organic species, such as formaldehyde, that are possibly produced during the oxidation of formic acid, infrared (FTIR) and mass spectroscopy (DEMS) experiments may not be the ideal technique for these studies. The monitoring of soluble species produced during the oxidation of formic acid will be carried out by electrochemical measurements coupled with liquid chromatography (HPLC) analysis, according to the procedure used in the reference[29].

vi. **Modeling the electro-oxidation of formic acid to Pt and Pd**. Based on the electrochemical and spectroscopic results obtained in the FAEOR study, a kinetic model will be proposed and tested by numerical simulation. For this, a schematic of chemical and kinetic reactions will be elaborated that describe the oxidation of formic acid on the surface of Pt and Pd, which later will be translated into differential equations. Finally, the differential equations will be numerically solved using mathematical software and reevaluated, to obtain better congruence between the experimental and simulated results.

Hipotesis

Through the presence of two metals in the electrode composition, it is possible to modify the catalytic activity and the selectivity of intermediates in the electro-oxidation reaction of formic acid. The presence of experimental and numerical studies will allow us to propose kinetic information on the mechanisms that govern the reaction for FAEOR in Pt and Pd.

Planificación Temporal

The forecast for the execution of the investigation plan is 3 years, the schedule being divided into 6 parts (P1-P6), where each part represents the period of 1 semester. Initially, a bibliographic review will be carried out, with exclusive dedication in the first semester, but that will be understood by the entire investigation plan. The experimental activity, described in items i-v of the methodology, is divided into three main stages, namely: making, characterizing and evaluating the catalytic activity of bimetallic electrodes. Finally, a kinetic model for FAOR on PtPd will be proposed and the doctoral thesis will be elaborated, reporting the results obtained during the execution of the research project. The following table summarizes the forecast for the execution of each activity.

Actividad	**Semestre**					
	1	**2**	**3**	**4**	**5**	**6**
Bibliographic review	X	X	X	X	X	X
Fabrication and characterization of electrodes.	X					
Evaluation of the catalytic activity of electrodes		X				

In-situ monitoring of FAEOR by infrared spectroscopy			X	X		
On-line monitoring of CO_2 production during the FAEOR.			X	X		
Identification of soluble intermediates during the FAEOR			X	X		
Modeling the electro-oxidation of formic acid to Pt and Pd.					X	
thesis writing.			X	X	X	X

5. Impacte esperat/ Impacto esperado

- That the student has acquired high knowledge in electrochemistry, as well as in solving scientific problems;
- Publication of results in scientific journals;
- Presentation by the student of the results obtained by the scientific community through conferences.

6. Implicacions ètiques o de bioseguretat/ Implicaciones éticas o de bioseguridad.

Indique si la memòria contempla algun dels següents aspectes que puguen tenir implicacions ètiques o relatives a la bioseguretat:

Indique si la memoria contempla alguno de los siguientes aspectos que puedan tener implicaciones éticas o relativas a la bioseguridad:

A. Recerca en humans o utilització de mostres biològiques d'origen humà
Investigación en humanos o utilización de muestras biológicas de origen humano
Si ☐ No ☒

B. Utilització de cèl·lules troncals embrionàries humanes, o línies derivades d'elles
Utilización de células troncales embrionarias humanas, o líneas derivadas de ellas
Si ☐ No ☒

C. Assaigs clínics
Ensayos clínicos
Si ☐ No ☒

D. Ús de dades personals, informació genètica, uns altres
Uso de datos personales, información genética, otros
Si ☐ No ☒

E. Experimentació animal
Experimentación animal
Si ☐ No ☒

F. Utilització d'agents biològics de risc per a la salut humana, animal o per al medi ambient
Utilización de agentes biológicos de riesgo para la salud humana, animal o para el medioambiente
Si ☐ No ☒

G. Ús confinat d'organismes modificats genèticament (OMG)
Uso confinado de organismos modificados genéticamente (OMG)
Si ☐ No ☒

H. Alliberament d'OMG
Liberación de OMG
Si ☐ No ☒

Si ha contestat afirmativament en alguna de les qüestions anteriors, explique els aspectes ètics referits a la recerca que es proposa, les consideracions, procediments o protocols a aplicar en compliment de la normativa vigent. En tot cas, la recerca en aquestes àrees requerirà de l'autorització del comitè d'ètica de la UA i/o dels organismes preceptius. Aquesta autorització, que ha de ser prèvia a l'inici dels treballs experimentals, serà exigible per al dipòsit de la tesi.

Si ha contestado afirmativamente en alguna de las cuestiones anteriores, explique los aspectos éticos referidos a la investigación que se propone, las consideraciones, procedimientos o protocolos a aplicar en cumplimiento de la normativa vigente. En todo caso, la investigación en estas áreas requerirá de la autorización del comité de ética de la UA y/o de los organismos preceptivos. Esta autorización, que tiene que ser previa al inicio de los trabajos experimentales, será exigible para el depósito de la tesis.