Hydrogen mass transfer through micro and nano-structured electrodes for energetic applications

A research activity is in progress, to study hydrogen mass transfer through micro and nano-structured electrodes for energetic applications. The research is mainly oriented to the improvement of the technological application of hydrogen as energy vector.
The main objective of the study is to develop suitable layers of palladium based materials to be used as coating for fuel cells electrodes. Material characterization is performed by means of electrochemical impedance spectroscopy (EIS), atomic force and electronic microscopy

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Trasporto di idrogeno attraverso elettrodi micro e nanostrutturati per applicazioni energetiche

È in corso un'attività di ricerca per studiare il trasporto di idrogeno attraverso elettrodi micro e nanostrutturati per applicazioni energetiche. La ricerca è orientata principalmente al miglioramento delle applicazioni tecnologiche dell'idrogeno come vettore energetico.
Obiettivo principale dello studio è quello di sviluppare layer di materiali a base di palladio da utilizzare come rivestimento degli elettrodi per fuel cell.
La caratterizzazione dei materiali è stata realizzata mediante spettroscopia ad impedenza elettrochimica, microscopia a forza atomica ed elettronica

Materials properties at micro and sub-micro scale are gaining a mounting attention because of their very large application spectrum. The interest towards such a kind of materials is originated by both scientific and technological perspectives.

The application field is ranging between catalysis, selective absorption, gas storage and technologies for developing electrodic materials for energetic applications. These materials are widely studied and characterized by means of electrochemical techniques.

An experimental activity has been activated, in cooperation with US research Institutions, to study hydrogen mass transfer through micro and nano-structured electrodes for energetic applications.

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The research Project, supported by the Italian Ministry of Foreign Affairs, is mainly oriented to the improvement of the electrochemical processes involved in the technological application of hydrogen as energy vector.

The research program is focused on developing suitable layers of palladium based materials to be used as coating for fuel cells electrodes. The coating will characterized by a very high specific surface given by a proper roughness or by porous/nano-porous structures that will ensure an enhancement of the hydrogen kinetics.

The focus of the research is the study of the hydrogen absorption/adsorption mechanisms across the electrodic interface.

The materials characterization will be performed by merging microscopy techniques and electrochemical spectroscopy to correlate the surface morphology and the electrochemical interface structure that may be translated in terms of kinetics properties.

The first period of the research activities has been mainly oriented to realize the experimental set-up and to the preliminary tests. Material samples have been realized by means of a proper metallurgical treatments and chemical process.

The experimental set-up

The first task was to realize a thermostatic system able to guarantee the electrolyte set-point temperature for a given electrochemical current density. Such a working condition is fundamental to have reliable and reproducible electrochemical impedance spectroscopy (EIS) measurements.

Therefore some thermally insulated copper cylindrical vessel, housing the cell, has been realized in order to operate the electrochemical cells within the proper thermally controlled frame.

A well dimensioned heat sink has been applied on the bottom of the cylindrical vessel and the whole system has been located into a thermostatic box a Tset-point± 0.15 °C (Figure 1).

A PID thermal control has been applied by using a PT100 temperature sensor reading the temperature of the thermostatic box and the temperature gradients inside the box are minimized by means of an air circulation system.

The electrochemical characterization of the palladium
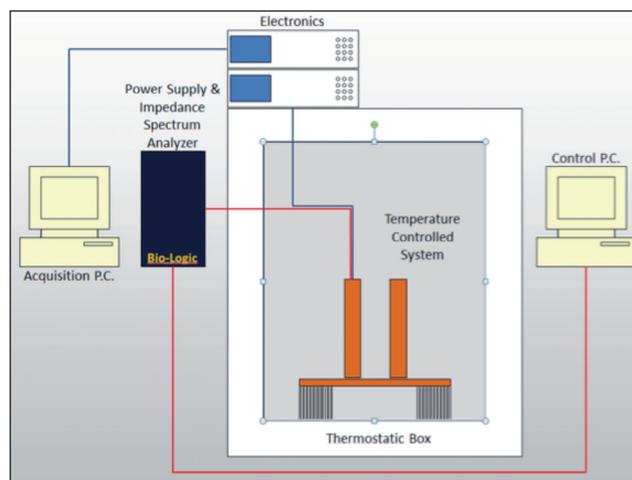
FIGURE 1 Diagram of the experimental apparatus composed by the thermostating system, the power supply connected to a control computer equipped with software to carry out the impedance spectroscopy measurement (Bio Logic system) and the data acquisition system

based materials is performed by operating an electro chemical cell containing the sample that is cathodically polarized within an aqueous solution of lithium hydroxide. The electrodic configuration is symmetric: the cathode (palladium foil) is located between two platinum anodes. The electrochemical cell consists of a pyrex vessel with a vacuum seal. The presence of a catalyst ensures the recombination of the gases produced during electrolysis, with consequent control of the level of cell pressure. A diagram of the electrochemical cell is shown in Figure 2.

The experimental apparatus is constituted by the thermostating system, by a power supply connected to a control computer equipped with software to perform the impedance spectroscopy measurement (Bio Logic system) and from the data acquisition system based on a Data Logger Agilent model 34970A.

The experimental data are the voltage and current of the cell, the electrolyte temperature, pressure of gases in the electrochemical cell, hydrogen concentration in the electrode, the temperature in the thermostatic chamber and the coolant temperature.

The absorption of hydrogen in the electrode with cathodic polarization was performed by a measure of
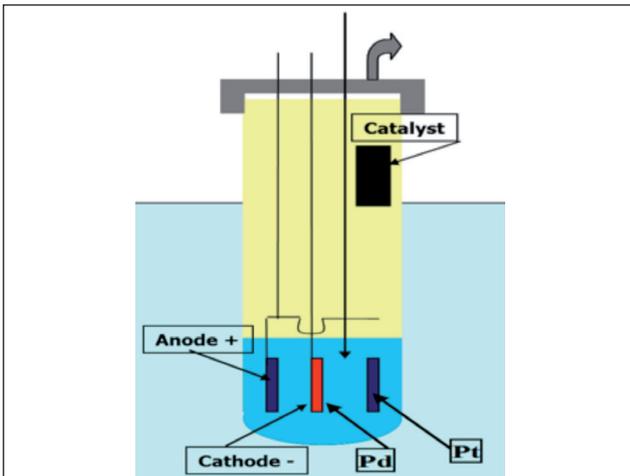
FIGURE 2 Scheme of the electrochemical cell

variation of electrical resistance carried out with an Agilent LCR model4263B.

The software interface between the computer acquisition and instrumentation acquisition is realized by LabView software (version 2011). The communication between the computer acquisition and the instrumentation is achieved by means of GPIB interface.

Bio-Logic power supply control is obtained by a dedicated computer on which is installed the software EC-Lab Bio Logic. This software not only manages the
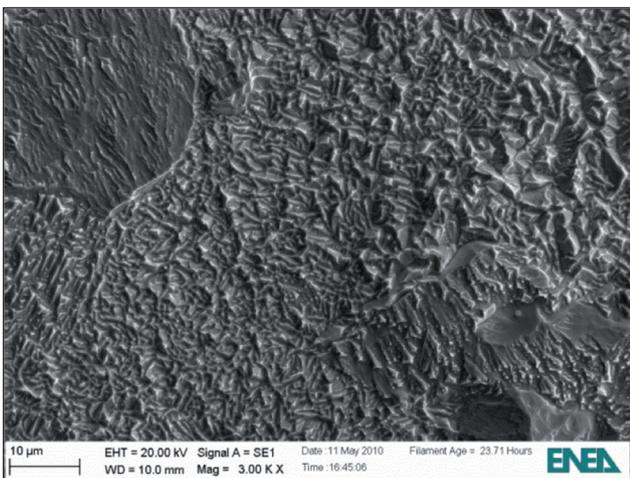
FIGURE 3 EM picture of a test sample

power supply also allows the characterization by electrochemical interphase EIS. The impedance spectroscopy is a tool able to identify, through the definition of the equivalent circuit, the morphological characteristics of the electrode, such as the porous structure.

Samples preparation

In the first period of activity, some electrodes were prepared rolling commercial palladium and putting it first through thermal treatment (annealing with controlled temperature slope to 850 °C for one hour) and then through chemical etching in Aqua Regia (HCL/HNO3 = 3/1). The finished samples dimensions are 10 mm x 40 mm x 50 micron. The chemical etching was performed for the purpose of increase the specific surface of the palladium electrode.

Analyses through electronic microscopy (SEM, EDX, EBSD) allowed to identify the polycrystalline state and the surface features of some samples.

Figure 3 shows a SEM picture of a palladium electrode that underwent both thermal treatment and chemical etching as described before. The analysis highlights the effect of the chemical etching on the surface, that appears to be dendritic with micrometric and sub-nanometric dendrites dimensions.

Figure 4 shows the results of the EBSD analysis performed on a test sample, in which the preferential orientation (100) of the surface crystals is clearly visible.

Electrochemical Impedance Spectroscopy Measurements

The Electrochemical Impedance Spectroscopy (EIS) is an analytical technique that allows to study the electrode/electrolyte interface and the chemical and physical processes occurring at that interface (charge transfer, mass transport, intercalation, conductivity etc.). Then, it is a very suitable method to analyze the electrochemical behavior of an electrochemical cell.

A first set of tests have been performed on the produced samples to check the stability of the measurements, in order to verify the reliability of the experimental setup and identify the proper operating conditions and setting parameters of the system. The tests have been
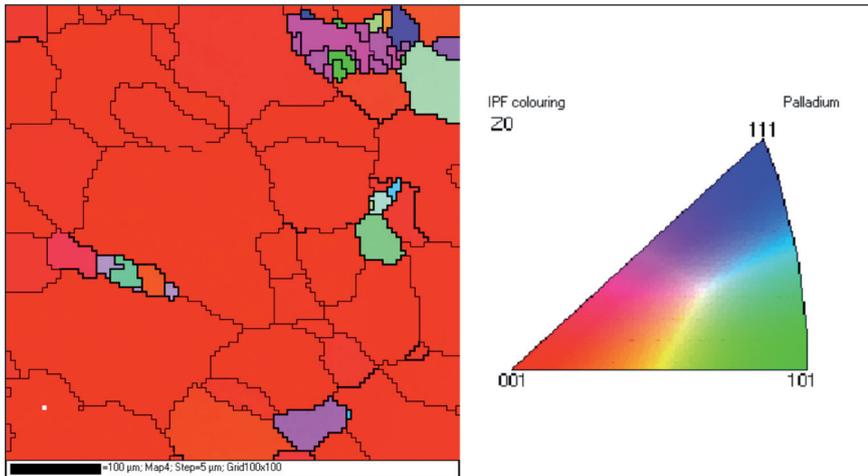
FIGURE 4   EBSD analysis of the sample

carried out on hydride samples, operating in galvano-static mode, with a cathodic polarization current of 20 mA, at a constant temperature of 25 °C.

The images of Figure 5 and Figure 6 show the surface morphology by scanning electron microscopy (SEM) of samples L26 and L39, respectively. These samples have received a different chemical etching.

The EIS spectra have been acquired in the galvanostatic mode by using 20 mA polarization current and 1 mA probe current in the frequency range from 10 mHz to 400 kHz. The corresponding impedance spectra have been shown in Figure 7, in the Nyquist representation.

It can be observed that the two samples are characterized by different surface morphologies and, correspondingly, by different impedance spectra.

The effect of the surface morphology on the impedance spectra appears mainly through the different values of the pseudo-capacitance and the depression-angle.

The EIS experimental data have been best fitted by assuming the electrical circuit drawn in Figure 8 to simulate the electrode/electrolyte interface (Randles circuit).

The best fitting parameters refers to the following circuital elements: the in series ohmic resistance (Rs), which represents the ohmic drop due to the electrolyte;

FIGURE 5   SEM image of the surface of sample L26
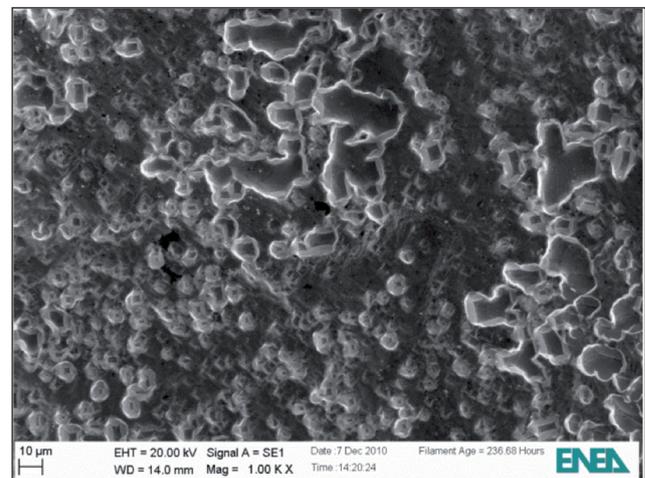
FIGURE 6   SEM image of the surface of sample L39
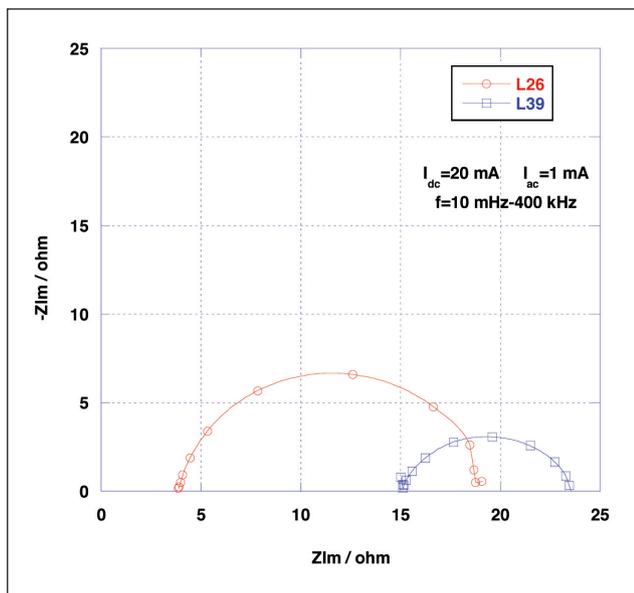
FIGURE 7 Nyquist Impedance plots of samples L26 and L39

FIGURE 8 Modified Randles circuit applied to fit EIS data

the polarization resistance (Rp), which accounts for the charge and mass transfer; the constant phase element (Q), which represents the not-ideal capacitive behavior of the electrochemical double layer. The time constant of the electrodes can be deduced by the frequency at which the phase of the impedance shows a maximum.

The constant phase element, which is characteristic of rough/porous electrodes, produces a depression of the impedance spectrum below the real impedance axis, defined by a depression angle that is dependent on the specific morphology of the electrode and is expressed in terms the of its percent deviation from 90° (α).

The other parameter associated to the Q element is the pseudo-capacitance, which can be also deduced from the impedance spectrum.

All the best fitting parameters have been reported in Table 1.

The values of the best fitting parameters are indicative of the different electrochemical behavior of the two electrodes.

Sample L26 shows a lower ohmic resistance (Rs), a higher polarization resistance (Rp) and a lower time constant (τ) than sample L39. This result suggests that the electronic charge transfer is faster in electrode L26 than in L39, while the electrochemical and diffusion processes are slowed down.

Furthermore, the parameter α of the Q element is closer to 1 in the case of sample L26 than for sample L39, indicating lower roughness/porosity, to which corresponds lower specific surface. Such a behavior is in agreement with the surface morphologies showed by the SEM images, which report a much more porous surface for sample L39. The higher value of specific surface area of electrode L39 is confirmed by the higher value of the pseudo-capacitance of this electrode (2.7 mF respect to 0.7 mF).

This first results show that it is possible to connect the surface features of the electrodes to the electrochemical behavior, correlating surface morphology and electrochemical interface structure, by means of equivalent circuit representation. ●

Parameter	L26	L39
R_s/ohm	3.9	15.1
R_p/ohm	15.3	8.6
α	0.9	0.8
τ/ms	36	111
C_{eq}/F	$0.7 \cdot 10^{-3}$	$2.7 \cdot 10^{-3}$

TABLE 1 Best fitting parameters of the experimental impedance spectra