Relazione sull'attività svolta dal Dott. Ulises Cano Castillo presso il CNR-ITAE nell'ambito della STM nel periodo dal 05/05/2011 al 18/05/2011.

L'attività sperimentale svolta dal Dott. Cano Castillo svolta ha riguardato principalmente la messa a punto di un sistema e di una metodologia di caratterizzazione di membrane, sviluppate presso il CNR-ITAE, attraverso l'utilizzo della spettroscopia ad impedenza (EIS) per la misura della conducibilità protonica. In questa attività è stato affrontato il problema dell'individuazione delle condizioni di misura adatte alle membrane innovative. Poiché le membrane innovative sono membrane composite contenenti materiali inorganici, in prima approssimazione si è discussa la possibilità di utilizzare la tecnica a 4 elettrodi, ma poi si è scelto di modificare la cella di misura e di effettuare le misure con la tecnica a 2 elettrodi. Dopo aver realizzato la cella a 2 elettrodi sono state effettuate le misure sulle membrane. Inizialmente è stata caratterizzata una membrane di Nafion recast e successivamente una membrana composita a base di Nafion e Zirconia. Le misure sono state effettuate per trovare una metodologia per l'interpretazione dei risultati specialmente nei casi in cui le membrane contengono dei filler inorganici. Le fasi della misura hanno riguardato:

- La definizione dell'hardware della cella sperimentale
- La configurazione delle connessioni
- Il range di frequenza e l'ampiezza del segnale a.c. per le nuove membrane

Inoltre è stata condotta una analisi della letteratura riguardante:

- Confronto fra i metodi di misura
- Misure su membrane a conduzione ionica attraverso EIS
- Limiti dell'uso della tecnica EIS su elettroliti polimerici (a causa delle proprietà dielettriche)

I risultati preliminari ottenuti hanno mostrato un comportamento particolarmente capacitivo delle membrane in cui la bassa frequenza produce elevate valori della componente immaginaria ed una diminuzione di quella reale.

Un'altra questione da risolvere è quella delle condizioni sperimentali in relazione alla necessità di utilizzare H_2 per la formazione dei protoni in modo che questo non sia un fattore limitante per la misura di conducibilità protonica, specialmente in questo caso in cui quest'ultima è il parametro più interessante da studiare.

In base a questa esperienza il Dott. Cano Castillo ha stilato una guida per le misure EIS riportata in Appendice 1.

Oltre al lavoro sperimentale, il Dott. Cano Castillo ha presentato le attività del suo gruppo di ricerca presso l'IIE di Cuernavaca, attraverso questa presentazione sono stati individuati gli interessi comuni di ricerca per i due gruppi da parte italiana e messicana. Inoltre, sono stati individuati dei topics per una eventuale presentazione di un progetto comune insieme alla TRE-DW nella prossima call FCH JU 2011-1 del JTI Fuel Cells & Hydrogen.

APPENDICE 1 - Guida per le misure di impedenza

There is a huge amount of information on impedance theory explained in books and other sources, explaining the basics of the technique, its potential and its limitations, as well as how to use or extract information from results obtained by impedance measurements. This is not such a document. Instead, it is intended as a quick guide for those wanting to use this technique and are not experienced or have limited knowledge on the use of it. Impedance is a way to get insight information of systems under study so the better we understand the technique and the precautions needed to make good use of impedance results, the more correct statements we will do.

Experimental Measurements

Initial measures (not measurements)

Impedance assumes that the **system under study is linear**, which means that if you apply a sinusoidal perturbating signal (e.g. voltage) you will obtain from the system a resulting sinusoidal signal too (e.g. current). A simple voltage-current curve can tell you if your system is linear and under which conditions. In many cases when using very small amplitudes of a perturbating signal you get linear response.

Noise cancelling is necessary. When using a commercial instrument **always read the manual** to follow recommendations on how to avoid and hopefully cancel external noise as this technique is very sensitive. Typical recommendations are the use of a Faraday cage, place your system far from electronic and electric devices and use blinded wire connectors that will pick any noise in the surrounding space near your experiments. Crossing your cables and keeping them short also help.

Depending on the instrument you are using, on the amount of current expected from your system being tested or on the type of information you are looking for, you may use different electrodes connecting configurations. Check the differences in the instrument manual, to see the differences and the use of such connecting configurations. In general typical configurations could be 2, 3 or four electrodes. The difference in each connection is related to the path the current will follow and the reference used for voltage measurement or control. These two conditions are defined by what type of information you are looking for. Most of the time **it is better to first define your need for the measurement**, the limitations and possibilities of the technique and then plan your experimental work.

Setting up your instrument

If you are ready to carry out your experiments, ***do not perform them yet*** until you understand the parameters related to the impedance test that you can or that should carefully define in your instrument (via software most of the time). Some important parameters are:

Amplitude of the perturbing signal. This value depends on the linear response of the system but sometimes you have to find out yourself. Some systems (probably most of them in electrochemistry) are in the order of mV or mA, but others can go even far larger than that. Often, depending on the sensibility of the instrument, you need to impose larger amplitudes to

gain a larger response signal value so the instrument picks it up easier and with better resolution. Just remember to make sure you are in the linear region of the system.
Voltage or current as a perturbing signal? As a general rule if you are not sure you can initially use voltage as a perturbing signal. In theory there should not be a difference in linear systems, but if you imagine that they can have different slopes (in a V-I curve), the gradual change of either variable when planning your experiments, will be different for one signal compared to the other. Also, sometimes you could be interested in what happens at a specific value of potential or current, which will also define the convenience of using one or the other.
Frequency range to be used: remember that most of the time you will explore a range of frequencies, as each frequency value can be thought of as a window through which you can "see" different events in your system (e.g. high frequencies relate to fast processes such as electron transfer, while low values can be associated to mass transport processes). High frequency values can easier detect capacitances and inductances than lower values. That is why for some less conductive materials (with high dielectric properties) you often need to use higher frequency values. If your system is reasonably steady you can explore low frequencies but this will take long time. That is why is important to have steady state conditions when measuring impedance.
Number of points to be taken: as a general rule is good to have several points per frecuency decade. As we normally want to explore several orders of magnitude in frequency, a logarithmic scale is always used, therefore make sure that if you change your frequency range when doing experiments, you adjust the total number in the frequency scan so as to have at least 5 frequencies per decade (generally equally spaced in the log scale).
Number of cycles before the measurement is actually taken. To ensure the quality of measurements, instruments normally provide (through software) the possibility of selecting a number of cycles (or full wave length of the perturbing signal) before it does the actual calculation of the response of the system. Also, sometimes when the calculation is performed some testing systems allow you to choose the technique to perform the actual measurement (check the manual as different mathematical techniques could produce different error levels although just from the strict point of view).
Impedance testing systems also allow the selection of certain *time* for the system under test *to allow steady state before the measuring* of each point. This is necessary as some systems have initial (when first connected to the perturbing signal) transient response, different from the steady state behavior. You do not want to add both during the measurement

The Measurements

Now you are ready to do the measurements. Prepare your rig (other hardware and preparations you need to bring your system to experimental conditions). Select the right electrical connections for your cell. Take care by cancelling any potential source of external noise and choose appropriate parameters for the impedance measurement. Now you are ready to go for it.

The Results

Once you get your initial results you have to ask yourself if they “make sense”. By saying this, it means that you should ask yourself if, based on previous knowledge from your system (properties, literature, etc.), these are what you expect. As an example, often the impedance measurements are used to determine conductivity/resistivity or dielectric properties (e.g. capacitance), see if the order of magnitude of what you get is in the range as other reference information.

As the uses of impedance measurements can go from simple systems where you want to determine simple information, to very complex systems, this guide does not cover this aspect. Instead, a series of recommendations follow:

Know as much as possible your system; imagine your system as an electrical circuit full of components which also include (beside your system) the wires you use to connect. Think of the structure of your system; will it influence an electrical response such as an a.c. perturbing signal? If yes, how?. Think also that different materials (electrodes, electrolytes, fillers, etc.) have different electrical properties and therefore will respond different. If your system is already composed by different materials, remember that most responses are additive, that is, the response of one material will add to the effect of another, etc. Use this as a general rule only but not as a norm, as sometimes the interaction of materials are more complex than that. Think if your system has solid or porous structure or if there are liquids such as electrolytes or other conductors (either electronic or ionic or both). Think if they are affected by the experimental conditions you use (T, P, voltage, etc.). Remember that electric conductors (such as metals) behave very different from semi conductors (for example oxides) or insulators or even traditionally insulators that become conductive by some treatment.

Only you can use the best conditions while taking impedance measurements and make the most out of your results. Carrying out impedance measurements can be simple (very often is not), but obtaining errorless results and interpreting them correctly cannot be assured by anyone but you.