(57) Abrégé/Abstract:
This invention consists in a device and a method to determine the ionic, electronic and mixed (electronic-ionic) conductivity in polymer, ceramic and composite (polymeric-ceramic) membranes. The invention device may work from room temperature to 300 °C and the method includes the collection and analysis of electrochemical impedance spectra during cell operation.
ABSTRACT

This invention consists in a device and a method to determine the ionic, electronic and mixed (electronic-ionic) conductivity in polymer, ceramic and composite (polymeric-ceramic) membranes. The invention device may work from room temperature to 300 °C and the method includes the collection and analysis of electrochemical impedance spectra during cell operation.
MODULAR DEVICE TO MEASURE IONIC, ELECTRONIC AND MIXED
CONDUCTIVITY IN POLYMERIC AND CERAMIC MEMBRANES

DESCRIPTION

TECHNICAL FIELD OF THE INVENTION

The actual invention is a useful device to detect ionic, electronic and mixed
conductivity in polymeric, ceramic and composite membranes. The main objective of
this invention is to simulate real operating conditions at work, that is to say those that
prevailed in fuel cells, batteries, electrochemical sensors and pseudo-capacitors,
where electrical conductivity plays an important role in the operation of these
systems. The modular device permits the work of two electrodes, either blocking or
no blocking electrodes and with one or two different atmospheres (gases), or one/two
different liquids in each compartment divided by the same membrane.

The device is a conductivity cell composed of two inlets and two outlets to convey gas
or liquid, a heating system conformed by electric resistances, and an opening for the
temperature control thermocouple. The cell is fabricated in aluminum to have a high
corrosion resistance and an improved heat transfer. The two compartments are
divided by the same membrane, which is isolated from aluminum by silicon or glass
seals as needed and depending on use. This array allows the cell to keep in direct
contact with gases or liquids and this way monitor the charge carriers throughout the
membrane. As a result of cell modularity, it is possible to carry out interfacial studies
of electrochemistry type by means of the cell connection to a potencióstat-galvanostat
or to an impedance spectrometer.
BACKGROUND OF THE INVENTION

The electric conductivity is a material’s capability of allowing the flow of electric current through itself. It is also defined as a natural property to measure the capacity of providing electrons (or electronic holes as it is the case of semiconductors), ions or both types of species that can flow through a material.

An electrolyte is a substance composed of ions; there exist different types of electrolytes such as liquids, solids and gases (plasma: highly ionized gas). Solid electrolytes can be made of a polymeric, ceramic and composite (polymeric-ceramic) material. A family of materials in constant growth is that of ionic solids, in which certain ions exhibit a quick transport. These materials are commonly named as fast ion conductors FIC. In certain cases, the rapid transport of ions is accompanied by a considerable increased in electronic conduction (mixed conductivity).

There exists a large interest in the science and technology of FIC due to their potential to be used as electrodes and electrolytes in conversion devices of electrochemical energy. These solid electrolytes have in turns another application in industry, including sensors to detect insulin and oxygen, the latter used in automobiles. Other applications involved power systems such as electrochemical super-capacitors, fuel cells, batteries and accumulators such as those based on lithium.

In order for a solid to have fast ion conduction it must fulfill the following criteria [West A. R., Solid State Chemistry and Its Applications, John Wiley & Sons Essex, 1984]:

1. To have a high concentration of charge carriers or potential charge carriers.
2. To have a high concentration of vacancies for ion movement or interstitial sites.
3. To have a low activation energy for ion movement.
4. To have the presence of a set of energetically equivalent sites partially occupied by other mobile ions.
The FIC is not a new discovery, in 1914, Tubandt and Lorenz observed this behavior in certain silver compounds. These researchers discovered, for example, that ionic conductivity of AgI before fusion was approximately 20% higher than that of the melted solid. The FIC was also observed in other two iodine compounds and AgSI. As it was mentioned in FIC one of the groups of ions, cations or anions is free to move. That group is called sub-reticle and generally it is in a melted state. That model was proposed by Strok in 1936 based on structural and thermodynamic data of AgI. In most of the FIC, entropy for transition to the FIC state is higher than that of a non-conducting FIC. For example, in the AgI, the transition entropy from form b (non-conducting) to a (fast conducting) form at 420 K is 14.7 JK⁻¹mol⁻¹, while the fusion entropy at 861 K is hardly of 11 JK⁻¹mol⁻¹.

The especial electric properties of α-Agl led to an unavoidable search for other solids that exhibited a high ionic conductivity, mainly at temperatures lower than 420 K. The most successful solid at present, despite the existence of others, involved the partial change of silver by rubidium to form an RbAg₄I₅ compound. This compound has an ionic conductivity of 2,500 Sm⁻¹ at room temperature, which is higher than that of a NaCl sodium that has an activation energy of just 0.07 eV (1.12x10⁻²⁰ J). The crystalline structure is different from that of α-Agl, but similarly, the ions of Rb⁺ and I⁻ form a rigid reticle, while those of Ag⁺ are randomly distributed in a grid of tetrahedral sites in which they can move [Smart, L.; Moore, E., Solid State Chemistry: An Introduction. Chapman & Hall, Londres, 1993].

To be useful as a solid electrolyte in a battery, an ionic conductor not only must have a high electrical conductivity but also negligible electronic conductivity to avoid that the battery undergoes a short circuit. Electrons have to cross the external circuit where they can be used to make a useful work. The electronic conductivity of RbAg₄I₅ is considerably small (10⁻⁷ Sm⁻¹) so that it has been used as a solid electrolyte in batteries with electrodes made of Ag and Rbl₂. Such cells operate in a wide range of
temperatures 217-473 K (-55 to 220 °C), require a long time to store energy and provide a high mechanical resistance.

The most promising application of FIC it is in the solid state batteries, there exist two types of batteries:

1. Small primary cells, they must have a long lasting live and must not be discharged during this period
2. Rechargeable secondary batteries, they are used when a high density of energy is the selection criterion.

The batteries of the first type find application as miniature cells; they operate at room temperature and have a long lasting live in the order of years instead of a high density of energy or a high outlet voltage. They are used in watch clocks and photographic machines, pacemaker and military applications. The secondary batteries manage a lithium anode, lithium iodine as electrolyte and the complex as cathode:

Anode (Li): \( 2\text{Li}(s) \rightarrow 2\text{Li}^+ + 2 \text{electrons} \) \hspace{1cm} Equation (1)

Cathode (I\(_2\)): \( \text{I}_2(s) + 2 \text{electrons} \rightarrow 2\text{I}^- \) \hspace{1cm} Equation (2)

Total: \( 2\text{Li}(s) + \text{I}_2(s) \leftrightarrow 2\text{Ii} \) \hspace{1cm} Equation (3)

As \( \text{Ii} \) has vacancies in the reticle and as a result of the small size of Li\(^+\) cations, these are able to migrate through the solid electrolyte whereas electrons flow through the circuit.

There are several devices and equipment suitable to measure the conductivity of solid electrolytes but most of them have their application in liquid solutions. For solid systems, devices based on the Van der Pauw’s method are used (Figure 1).
Other equipment in use for the measurement of resistivity is that of Van der Pauw, in which the simple on use can have an arbitrary form (though homogeneous in composition and thickness) and electric contacts can be taken on any point of its profile. The only restriction is that sample must be thin. Figure 2 shows a diagram corresponding to the set up of equipment.

At first, the potential difference between C and D, \( V_{CD} = V_D - V_C \) is measured by passing an electric current between A and B to calculate R1:

\[
R_1 = \frac{V_{CD}}{I_{AB}} \quad \text{Equation (4)}
\]

The voltage difference between A and D, \( V_{DA} = V_A - V_D \) is measured by passing an electric current between B and C to calculate R2:

\[
R_2 = \frac{V_{AD}}{I_{BC}} \quad \text{Equation (5)}
\]

In agreement with Van der Pauw’s method, resistivity \( \rho \) is given by the expression:

\[
\rho \approx \frac{\pi \cdot d \cdot (R_1 + R_2)}{Ln(2)} \quad \text{Equation (6)}
\]

where \( d \) is the sample thickness.

- \( R_1 \) is the vertical resistance
- \( R_2 \) is the horizontal resistance

When resistivity measurements are performed on samples with a form of rectangular parallelogram, the four point method is used (Figure 2). Current is introduced in two parallel faces of the sample, whilst voltage is measured in two intermediate points within this distance, avoiding this way a voltage loss in the points of electric contact (impedance at voltmeter entrance must be much higher than that of the resistance between voltage contacts).
Sample's resistivity is given by expression:

$$\rho = \frac{VA}{IL} \quad \text{Equation (7)}$$

where $V$ is the voltage, $I$ is the current, $A$ is the sample section and $L$ is the distance between the voltage contacts:

Nevertheless, the specific determination of ionic carrier is not identified by means of this equipment so that the application of blocking or selective electrodes (that permit the pass of electrons or ions only) is widely useful in determining carrier type (For example, if a solid electrolyte transport two types of ion carriers such as "A" and "B" then it is possible to have electrodes that permit only the pass of "A" or "B" ion to be determined but not both at the same time).

With the aim of having a cell that measures not only the general electric resistance but also a specific resistivity (or conductivity), it is possible to know from it what type of carrier is having effect on work. The present conductivity cell has been therefore developed with blocking and selective electrodes.

The main difference of the conductivity cell used in the present invention is the capacity to work in a wide range of temperature, form room temperature and up to 300 °C, by means of electric resistances. As it is known, the electronic conductivity decreases as temperature increases but the ionic conductivity increases with temperature. On the other hand, this cell has two compartments separated by the same membrane to be evaluated, which allows the use of different gases such as oxygen in one side and hydrogen in the other (for example, fuel cell application). Alternatively, compartments can be filled with water or any aqueous solution and the other by an aprotic solution. This cell can stand a maximum pressure of 6 atmospheres, which permits changes in gas pressure, or if a certain gas under study is dissolved into an inert gas. For example, the change of partial pressure of oxygen in nitrogen to study the effect on ionic conductivity by carriers (or vacancies), or
changing the partial pressure of hydrogen and observing the effect on the protonic membrane.

Another substantial advance of this cell is the versatility to interchange charge collecting electrodes that are in direct contact with the membrane, on which it can be designed metallic deposits on a graphite mesh that will serve equally. These deposits will permit to have electrodes that are selective, for example, deposits can be made on platinum or palladium on graphite mesh. Platinum is a good catalyze to divide hydrogen in its ionic form, which permits to monitor the charge flow of hydrogen ion within a membrane with charge carriers of the protonic type.

The state of the art in the conductivity cell design is not extensive in regards to patent edition, however, there are different devices described in arbitrated journals. In both cases, charge carriers flow on the membrane surface and not through it. In our case, charge carriers travel through the membrane and not on it, which avoids ohmic falls and consequently a better conductivity is obtained. Several authors and inventors mentioned that when you used four electrodes and charge carriers flow on the membrane and not through it, ohmic losses are avoided to have an improvement in conductivity. However, our device simulated the best working conditions, be it in fuel cells, electrochemical sensors, pseudo-capacitors or electrophoresis systems. In addition, it is well known that the surface at microscopic level in polymer, ceramic and composite membranes is largely different to that one in the membrane bulk, which can modified the data obtained to be higher in the superficial mode than in the transversal one (as it is exemplified below).

In the reference J. Phys. Chem. 1991, 95, 6040-6044, an open cell is shown in a two-electrode set up with charge carriers that flow on the surface, in this cell is not possible to control pressure and relative humidity of input gas to the system, so that membrane was hydrated before placing it in the conductivity cell to obtain values by means of electrochemical impedance.
In the reference *Electrochimica Acta 48 (2003) 4175–4187*, the Van der Pauw's method of four electrodes is used, in which iterations were carried out on equations to obtain a conductivity value, likewise charge carriers flow on the membrane surface.

In the patent application US 2010/0109651 A1, a conductivity cell can work with two or four electrodes, but only with one atmosphere, and conductivity measurement is performed on surface and not through it.

Patent US 4,118, 549 described a solid state cell to measure conductivity, it is of the battery type composed of two electrodes, which does not permit gas entrance, electric charge transportation is through membrane and it does not account with a heating system or a pressure control.

In Patent US 4,871,427, the cell described consists of two electrodes, which can handle liquids only but not gases.

In Patent US 6,228,325 B1, a cell to measure the quantity of carbon by means of electric conductivity is reported, despite having the same principle of operation as the invention cell, this application is different and more specific for this case.

As it was mentioned above, our invention device works in two-electrode mode but it permits the inclusion of ohmic losses that occurred in real systems, which may provide a more realistic idea of the electric conductivity behavior of membrane. Membrane is not only subjected to an AC voltage but also to physical stresses of mechanical tension derived from the pressure system. The actual cell makes use of two different gases in two compartments, respectively, such as hydrogen and oxygen at different pressures, which can be evaluated to observe the effect on the electric conductivity of membrane.

On the other hand, it is possible to obtain data of electric conductivity from the charge carriers in the sample bulk and not only on the surface.
BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a diagram of the conventional method for measuring electrical conductivity known as 4-point method.

where:
FC = source of direct electric current
L = distance between electrodes
V = voltage.

Figure 2 shows a diagram of the Van der Pauw method.
where:
FC = source of direct electric current
V = voltage
A = point A
B = point B
C = point C
D = point D

Figure 3 shows a view in perspective of the invention cell, where symmetric modules are observed along with the heating system composed of electric resistances and a thermocouple. Electric current collectors have been provided with holes to allow a better flow of reactant gas.
where:
1 = two aluminum plates
2 = electric heater
3 = thermocouple
4 = input gas or fluid
5 = output gas or fluid
6 = silicon frames or borosilicate glass type material
7 = electric current collectors
8 = mesh of graphite or platinum
9 = plastic insulation  
10 = membrane to be evaluated  
11 = screws  
12 = nuts and washers  

Figure 4 shows schematically the arrangement of two points to obtain the impedance spectra from which the ionic membrane conductivity is calculated. Where:  
13 = impedance spectrometer  
14 = computer  
15 = temperature controller  
16 = flow controllers  
17 = pressure controllers  
18 = humidifier  

Figure 5 exemplifies an impedance spectrum, whose analysis provides the membrane ionic conductivity made of a sulfonated tetrafluoroethylene copolymer.  

Figure 6 shows the results obtained by the conductivity cell with hydrogen selective electrodes in a sulfonated tetrafluoroethylene copolymer membrane with protonic conductivity as a function of temperature.  

Figure 7 shows a plot of specific conductivity vs. water mol per equivalent (taken from the J. Phys Chem. 1991, 95, 6040-6044)  

Figure 8 shows the graph of $\sigma$ vs. RH (taken from the patent application US2010/0109651).  

Where:  
$\sigma$ = specific conductivity  
RH = relative humidity
DETAILED DESCRIPTION OF THE INVENTION

The new structure of the invention device can be adapted for measurements of ionic, electronic or mixed conductivity type of polymer membranes, ceramics and composites, using a single modular design which allows the use of different types of electrodes blockers, do not blockers or selective.

More specifically the apparatus of the invention is formed by two pieces of aluminum material (1), die-cut 4 to the resistors (2) to allow heating of the cell and an input for a thermocouple (3), which allows the control and temperature measurement. In turn with two vertically aligned apertures in each of the pieces to the input and output, whether gas or liquid (4) and (5). The faces of the pieces that face towards the membrane (type polymer, ceramics and composites) must be perfectly flat and mirror polished. Are placed on the seals in the form of silicone material frames (6) for temperatures up to 150°C and higher temperatures, using glass fiber material or borosilicate glass type (6), or some other material that will withstand temperature changes and temperatures up to 300°C.

The device has two electric current collectors (7) mainly made of stainless steel but can be made of other metals or metal-coated corrosion-resistant as example gold, (resistant corrosion by hydrogen) depending on the gases or liquids to be handled. The device has in turn, with a highly conductive graphite mesh (8) which is in direct contact with the membrane to be evaluated.

The mesh graphite as such, acts as a blocking electrode ion and only allows the passage of the electron flow (pseudocapacitors). For example by depositing platinum on the mesh graphite this allows the passage protons (selective electrodes, together with the membrane) making it possible to value the charge carrier mobility and determine directly through the membrane in question. The graphite mesh can be replaced by one of platinum or gold directly. Also, it may be done another kind of deposit as ionic salts (e.g. lithium salt) which will enhance their selectivity of charge
carrier, in function of membrane type (e.g. lithium batteries or electrochemical sensors) or the blockade of some other charge carrier different than those being evaluated and could interfere in the measurement. On the edge of the graphite mesh, 
the selective or the blocker electrode (as applicable), is placed a silicone-based plastic as an insulator (9) with high electrical and thermal resistance, which holds and 
fixes the graphite mesh that has platinum deposit or any other deposit as the case study require. It prevents direct contact of current collectors with the membrane and 
each other. Finally in the middle is placed membrane-type polymer, ceramic or composite to evaluate (10).

All modules are placed and aligned as shown in Figure 3. The studs (11), in addition to holding the constituent parts of the conductivity measuring device, allows an 
accurate alignment of the device components. Device modules are placed in layers and fastened by nuts and washers (12) by applying a measured pressure to prevent gas leaks from the conductivity measurement system.

Once having assembled the whole device, this is connected to an impedance spectrometer (13) and also to a computer (14) for control. The electrical resistances and thermocouple are connected to a temperature controller (15). The inputs and outputs of gases or liquids are provided with flow (16) and pressure (17) controllers. In the case of gases, a humidifier (18) is required to hydrate them. Figure 4 shows the invention device and auxiliary parts.

The ionic conductivity of a specific material is strictly related to the ohmic loss associated with the membrane during operation. In many cases, the key in research for the development of membranes is in improving the ionic transport in the direction of having a minimum drop potential, particularly in fuel cells operating at high current densities, or in electrochemical sensors, batteries or super-capacitors (pseudo-capacitors) to be evaluated under similar conditions to their work environment.
HANDLING OF INVENTION DEVICE

In view of the comments made to the figures, it is observed that the device is composed of different pieces with a square profile. The invention cell is constructed in its outer modules with aluminum metal with two holes on each side for the input and output of reactant or inert gases or liquids. The faces looking at the membrane must be mirror polished, which allows a better sealing of the system.

The metal plates must contain 4 holes to align the modules and fix them with screws to prevent leaks and displacements. Two square seals made of silicone or silicone mixture of glass fiber or glass for temperatures above 130 °C with dimensions including the input and output of gases having a thickness of 3 mm. Current collectors with a nearly square profile at the ends are made of stainless steel with a gold coating. Its dimensions must match exactly with the dimensions of joints and a thickness of 1 mm. Gas diffusers must be made of paper or porous graphite mesh, or a mesh of platinum, or any other conductive material; similarly, an inert material and conductor such as graphite or platinum coated with material that is dependent on the charge carriers in the membrane to be analyzed. These materials should join together by an adhesive of polymeric type that stands high temperatures and provides electric current insulation. This adhesive must withstand the temperature range of operation with the same dimensions of those of the joints and collecting boards.

The system operation to determine the electric conductivity is based on the following methodology.

- The membrane is placed inside the conductivity cell as shown in Figure 3.
- The relevant connections are made according to the scheme of Figure 4.
- Membrane can be hydrated at one of the different relative humidity values or by using different atmospheres depending on the ionic carriers to evaluate.
• The supply of gases or liquids is opened; fluid is permitted to flow for about 20 minutes for purging the gases present in the cell.

• The operating temperature of the system is selected and regulated by means of a temperature controller.

• The operating pressure of the system is set.

• The gas flow in the system is adjusted.

• Conductivity is evaluated by impedance spectroscopy.

• From the impedance spectra, the ionic conductivity of the membrane is obtained (e.g. protonic membrane) Figure 5.

• The conductivity \( \sigma_m \) is obtained by determining the impedance modulus at the zero phase shift (side of high frequencies) using the following equation.

\[
\sigma_m = \frac{d_m}{A \cdot |Z_m|_{\alpha=0}} \tag{8}
\]

where \( d_m \) is the membrane thickness, \( A \) is the contact area of the membrane/electrode and \( |Z_m|_{\alpha=0} \) is the modulus of the impedance at zero phase shift (Figure 5).

The results obtained in a membrane made of sulfonated tetrafluorethylene copolymer with proton conductivity are shown in Figure 6.
APPLICATION EXAMPLES OF INVENTION AND COMPARISON TO OTHER METHODS AND MEASUREMENT DEVICES

In these cases a membrane commercially known (NAFION® 117) because of its performance can be taken as a reference.

Example 1

Conductivity measurements (σ in S cm⁻¹) of sulfonated tetrafluoroethylene copolymer (Nafion®) activated in different solutions and under different atmospheres for the invention cell is shown in Table 1.

<table>
<thead>
<tr>
<th>Solution to activate Nafion®</th>
<th>H₂</th>
<th>O₂</th>
<th>H₂O (liquid)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O₂ at 5%</td>
<td>0.047</td>
<td>0.066</td>
<td>0.058</td>
</tr>
<tr>
<td>HNO₃ at 65%</td>
<td>0.069</td>
<td>0.077</td>
<td>0.077</td>
</tr>
<tr>
<td>H₃PO₄ at 6M</td>
<td>0.066</td>
<td>0.061</td>
<td>0.053</td>
</tr>
<tr>
<td>HNO₃ 50:50 vol.</td>
<td>0.094</td>
<td>0.099</td>
<td>0.078</td>
</tr>
</tbody>
</table>

Table 1. Conductivity measurements (S cm⁻¹) of invented modular cell.

Example 2

In table 2, the conductivity measurements obtained by the Van der Pauw’s method are shown for comparison in accordance with reference Electrochimica Acta 48 (2003) 4175–4187.
<table>
<thead>
<tr>
<th>Water content (% wt) in Nafion®</th>
<th>σ (S cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.003</td>
</tr>
<tr>
<td>30</td>
<td>0.058</td>
</tr>
<tr>
<td>36</td>
<td>0.03</td>
</tr>
<tr>
<td>43</td>
<td>0.077</td>
</tr>
<tr>
<td>50</td>
<td>0.072</td>
</tr>
<tr>
<td>70</td>
<td>0.02</td>
</tr>
</tbody>
</table>


**Example 3**

In a conductivity cell in two electrode mode where the electric charge carriers flow on the membrane surface and not through it, as it is the case of invention cell, the graph is shown in accordance with reference *J. Phys. Chem.* 1991, 95, 6040-6044 (Figura 7).

**Example 4**

In the patent application US2010/0109651 A1 another example of a conductivity cell in mode of two and four electrodes (Figure 8) is shown. However, in contrast to the invention device the charge carriers flow on the membrane surface and not through it, as it is the case for the invention cell.

The examples above show a ionic conductivity slightly higher than those obtained in the invention cell, this is derived from the ohmic loss in the actual system because of the presence of "neck bottle" in Nafion®, points which are opened and closed as a function of water content in the bulk sample, which many times does not reach to humidify the internal surface membrane. This can produced distorted results because in the other systems charge carriers flow superficially where water greatly humidified
the surface, which results in a membrane with a high ionic conductivity. However, when this membrane is subjected to real working conditions there will be a great decay in the cell performance, as it is the case of fuel cells.
CLAIMS

1. A modular device for measuring ionic, electronic or mixed conductivity of polymeric, ceramics and composites membranes, wherein measuring ionic or electronic conductivity, or both types of conductivity by two electrodes in a perpendicular direction of polymer, ceramic or composite membrane.
   a. two aluminum plates each containing two compartments having two electric heating elements incorporated therein;
   b. Two aluminum plates with two orifices each one of fluid inlet and each other of fluid outlet;
   c. two compartments which can be filled with a liquid or gaseous fluid;
   d. two electrodes having a square flat surface and are separated by the membrane to be measured;
   e. a first current collector made of stainless steel which is in contact with a first electrode square flat surface that is in contact with the surface of the membrane, through which passes an alternating current and voltage at different frequencies;
   f. a second current collector made of stainless steel which is in contact with a second electrode of square shaped flat surface that is in contact with the membrane surface, whereby passing an alternating current and voltage at different frequencies;
   g. a recess in one of the aluminum plates receiving a thermocouple;
   h. two O-ring sealing with shaped frames to prevent the escape of fluids from the apparatus and separating and isolating the two aluminum plates above from the core of conductivity cell;
   i. a first removably conductive mesh of graphite surrounded by a first polymeric, fiberglass or glass insulation material (O-ring sealing) that can endure temperatures up to 300 °C;
   j. a second removably conductive mesh of graphite surrounded by a second polymeric, fiberglass or glass insulation material that can endure temperatures up to 300 °C; and
k. a polymer, ceramic or mixed membrane removably positioned between the first and second graphite meshes.

2. A modular device for measuring ionic, electronic or mixed conductivity for polymeric, ceramic and composite membranes in accordance with claim 1, wherein the device is provided with an input hole and an output hole in each of the aluminum plates, where the input and output holes are vertical aligned, respectively, to allow the input and output of fluids.

3. A modular device for measuring ionic, electronic or mixed conductivity for polymeric, ceramic and composite membranes in accordance with claim 2, wherein the modular device permits the change of the first and second conductive graphite mesh to a mesh having a material selected from the group consisting of platinum, palladium, and gold to control the flow of charge carriers through the membrane.

4. A modular device for measuring ionic, electronic or mixed conductivity for polymeric, ceramic and composite membranes in accordance with claim 3, wherein the graphite electrodes are exchangeable by other type of materials selected from the group consisting of platinum, gold, and graphite mesh coated with conductive materials of ionic or electronic type, which allows selectivity towards the charge carriers in the membrane, or to block the flow of a certain charge carrier to observe the electronic flow in the membrane, or identify the mixed flow of the charge carriers.

5. A modular device for measuring ionic, electronic or mixed conductivity for polymeric, ceramic and composite membranes in accordance with claim 4, wherein the aluminum plates each have one of their faces mirror polished to avoid fluid leaks, and have two compartments each in an upper part to place the two electric heating elements in each plate, and wherein the thermocouple is a type K or a type R thermocouple.
6. A modular device for measuring ionic, electronic or mixed conductivity for polymeric, ceramic and composite membranes in accordance with claim 5, wherein the thermocouple and the electrical heating elements are connected to a temperature controller.

7. A modular device for measuring ionic, electronic or mixed conductivity for polymeric, ceramic and composite membranes in accordance with claim 6, wherein the fluid input holes are connected to a gas or liquid supply, which may be the same source for both inputs or two sources of different gases/liquids or different solutions.

8. A modular device for measuring ionic, electronic or mixed conductivity for polymeric, ceramic and composite membranes in accordance with claim 7, wherein the input gases are wetted by a humidifier.

9. A modular device for measuring ionic, electronic and mixed conductivity for polymeric, ceramic and composite membranes in accordance with claim 8, wherein the device is operatively connected to a flow and pressure controllers that can be automated by an external computer or manually controlled.

10. A modular device for measuring ionic, electronic or mixed conductivity for polymeric, ceramic and composite membranes in accordance with claim 9, wherein the current collectors are connected to an impedance spectrometer.

11. A modular device for measuring ionic, electronic or mixed conductivity for polymeric, ceramic and composite membranes in accordance with claim 10, wherein the aluminum plates, current collectors and membrane to be analyzed are aligned.
12. A modular device for measuring ionic, electronic or mixed conductivity for polymeric, ceramic and composite membranes in accordance with claim 11, wherein four screws are used to fasten, fix, align, and center the modules in order to avoid leaks and losses of ohmic type.

13. A modular device for measuring ionic, electronic or mixed conductivity for polymeric, ceramic and composite membranes in accordance with claim 12, wherein the alignment allows the sealing and connection between the modules and avoids gas leaks.

14. A modular device for measuring ionic, electronic or mixed conductivity for polymeric, ceramic and composite membranes in accordance with claim 13, wherein the placement of the polymer, ceramic or mixed membrane divides the conductivity cell, which is symmetrical, into two separated compartments so that the exchange of fluids from one compartment to the other can only be done through the membrane.

15. A modular device for measuring ionic, electronic or mixed conductivity for polymeric, ceramic and composite membranes in accordance with claim 14, wherein the modular arrangement and the electrode preparation permit selectivity and allow for the flow of charge carriers within the membrane to be identified.
Prior Art

Figure 1
Prior Art

Figure 2
Figure 5
Figure 6

Conductivities

- Sulfonated tetrafluoroethylene 50.50 HNO₃
- Sulfonated tetrafluoroethylene 65% HNO₃

Eₐ=0.11 eV
Eₐ=0.11 eV
Figure 7

SPECIFIC CONDUCTIVITY (1/ohm-cm)

MOL OF WATER PER EQUIVALENT
Figure 8