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Automated setup for impedance measurements of electrochemical cells with two electrodes*

J. R. DYGAS

Instytut Fizyki, Politechnika Warszawska, Chodkiewicza 8, 02-525 Warszawa, Poland

G. FAFILEK, H. DURAKPASA, M. W. BREITER

Institut für Technische Elektrochemie, TU Wien, Getreidemarkt 9, A-1060 Wien, Austria

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An automated setup which allows impedance measurements on cells with two electrodes over a wide frequency range from 1 mHz to 10 MHz combines two impedance analysers and a temperature regulator under the control of a personal computer. Impedance spectra are measured at a programmed set of constant temperatures between room temperature and 1100 K. Alternatively measurements can be made at constant temperature and at specified time intervals. Data are recorded on disk for subsequent analysis by least-squares fitting on a separate computer. Examples for polycrystalline beta″-alumina and sol–gel materials are given.

1. Introduction

Impedance measurements have been successfully applied to the study of electrode processes [1–3] and interfacial phenomena [4–6] in cells with aqueous electrolytes. In the area of solid state ionics the separation of the resistance of a polycrystalline solid electrolyte into a contribution from the grains (intragranular) and from the grain boundaries (intergranular) was accomplished [7] by this technique. The early kinetic studies [1] of the so-called Volmer reaction by impedance measurements were later refined [8, 9] and extended [8, 10] to cathodic overpotentials at which hydrogen was evolved.

Impedance measurements in the early studies [1–7] were time consuming because they were made by a.c. bridges balanced manually. A certain advantage was gained by the use of impedance meters, reading directly either the absolute value and the phase angle of the impedance Z or the ohmic and capacitive components as was done in [9] and [11]. A real breakthrough came in the late 1970s with the availability of commercial analysers for impedance measurements and mini computers for digital recording. The desired frequency range was automatically scanned.

It is the purpose of this communication to describe a setup which performs automatically measurements of impedance spectra on cells with two electrodes at a programmed set of constant temperatures. The frequency scan can be chosen within the range 1 mHz to 10 MHz and impedance measurements are repeated at a selected set of constant temperatures between room temperature and 1100 K or at given temperature at specified time intervals. A provision exists for applying a d.c. voltage across the cell. However, the whole setup does not allow impedance measurements on one electrode the potential of which is controlled by a potentiostat against a separate reference electrode.

The present setup represents a further development of the semi-automatic device described in [12]. It includes two different impedance meters to satisfactorily cover the large frequency range. The use of two meters implies an arrangement for automatic switching the cell from one meter to the other. This is a disadvantage. However, there is also an advantage of using the two meters. Measurements by the two meters can be compared in the overlapping frequency range and malfunctioning of one instrument is easily identified.

2. Description of the setup

2.1. *Impedance meters*

The two impedance meters were a Zahner Elektrik IM5-e and a Hewlett Packard 4192A. Although the IM5-e, a frequency response analyser controlled by a Commodore 8050 computer, was rated by the manufacturer for the frequency range 1 mHz to 1 MHz, the relatively high input capacitance does not allow reliable measurements above an upper frequency of 10 kHz for impedances with absolute values of more than 10 kΩ. The HP 4192A impedance analyser with a frequency range 5 Hz to 13 MHz was used to extend the frequency coverage to the megahertz region. It posseses the highest accuracy between 400 Hz and 1 MHz. A correction had to be applied between 1 and 10 MHz. This correction was incorporated into a simulation procedure for the frequency dependence of

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* This paper is dedicated to Professor Brian E. Conway on the occasion of his 65th birthday and in recognition of his outstanding contribution to electrochemistry.

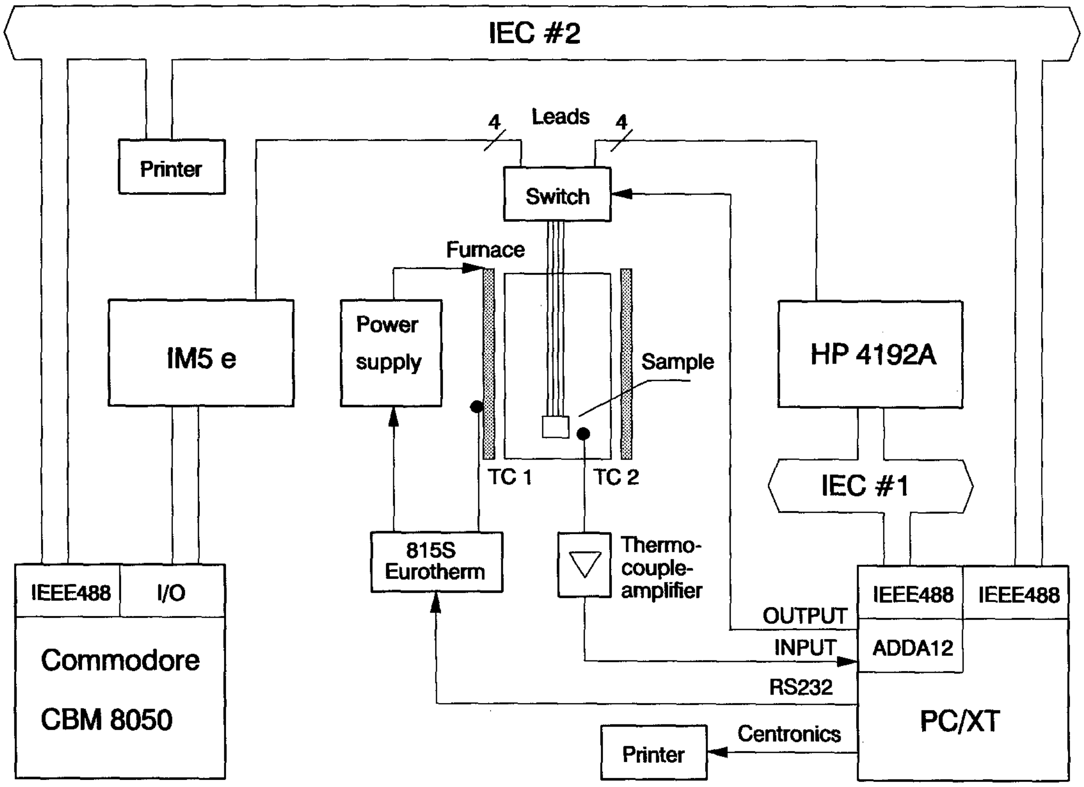

Fig. 1. Schematic diagram of the automated setup for impedance measurements.

the cell impedance. For details on the simulation procedure the reader is referred to [13].

2.2. *Computer control of impedance meters*

Operation of the whole setup, shown schematically in Fig. 1, was controlled by an IBM PC/XT compatible computer. However, the functions of this computer were different for the two meters. It was programmed to conduct, by an IEC-625 bus (IEC 1 in Fig. 1), the impedance measurements with the HP 4192A in a specified frequency range and to store the data on disk. For the IM5-e system the PC/XT computer acted as a peripheral on a second IEC-625 bus (IEC 2) and was programmed to release the measurement cycle and receive the measured data for disk storage at the end of the cycle.

2.3. *Connecting the cell to the meters*

Four shielded leads were used for both impedance meters to connect the cell. Two leads carried the current. The other two leads were the voltage probes. The couple of corresponding leads was put together at the respective electrode. The switching of the two meters was accomplished by eight REED relays, controlled by the PC through the analogue output of an ADDA card. The relays were mounted in two shielded boxes which were separated for low and high terminals. The boxes were close to the sample holder. Test measurements of *RC* circuits were performed through the relays. These tests demonstrated that the influence of the relays on the measured impedance was the same as that produced by an equivalent increase of cable length. The AC signal typically amounted to 50 mV peak-to-peak for the IM5-e where it was controlled by potentiostat. For the HP 4192A the signal was monitored by the use of the Test Level Monitor function of the instrument and adjusted to 17 mV (r.m.s.).

2.4. *Programming and control of temperature*

The PC/XT also supervised the setting and stabilization of the temperature of the furnace and of the sample inside the holder. In order to avoid difficulties associated with the long response time of the sample temperature upon change of heating power, two NiCr–Ni thermocouples and superposition of hardware and software temperature control were applied.

The furnace was heated by d.c. current from an HP-6269B power supply programmed by a Eurotherm Type 815 controller, a digital PID regulator which was used to stabilize the temperature of the furnace provided by the thermocouple placed close to the heating element (TC 1). The setpoint temperature was transferred to the controller from the PC/XT through a serial (RS-232) interface. The furnace temperature was stabilized at a higher value than the desired temperature of the sample, the difference was calculated based on a characteristic curve obtained during a calibration measurement for a given arrangement of the furnace and the sample holder.

After the furnace temperature was stabilized at the setpoint value, a waiting period was established to allow thermal transfer to the position of the sample. The computer monitored the temperature, measured by the second thermocouple (TC 2) placed directly near the sample inside the holder. The amplified voltage of this thermocouple and the voltage proportional to the temperature of the reference junction, obtained from a semiconductor transducer (REF-02), were converted by a 12 bit ADDA card in the PC/XT. When the drift of the sample temperature dropped below a specified limit (typically 0.1 K min^{-1}) it was assumed that the condition of the sample was stabilized and the actual sample temperature was compared with the desired value. If the difference exceeded a specified error limit, the Eurotherm setpoint was adjusted and the stabilization cycle was repeated. Reproducibility of the temperature between different runs with an accuracy of 1 K was possible in this way.

Only when the stabilized temperature of the sample agreed with the desired value within the given error limit, was the measurement of the impedance spectra started. The highest and the lowest values of the temperature of the sample during the measurement were recorded. The temperature variation was less than 0.5 K during typical measurement in the frequency range 10 mHz to 10 MHz which lasted about 30 minutes (4 min with HP4192A and 25 min with IM5-e).

When a temperature program was chosen the sample temperature was stabilized at values specified in terms of several ramps of increasing and decreasing temperature with a constant step. Alternatively, a time program allowed measurements at given temperature to be repeated at specified time intervals.

2.5. *Consistency of measured impedance data*

At a given temperature the impedance spectrum was first measured by the HP4192A, then by the IM5-e and again by the HP4192A. The two spectra measured by HP4192A agreed well with each other when the sample condition was stable, and their comparison allowed discrimination of cases when properties of the cell changed with time, The impedance values measured by the two meters in the overlapping frequency range 5 Hz to 10 kHz agreed typically within 1% of the absolute value and 1 degree of the phase angle, with the exception of the difference caused by considerably higher input capacitance of the IM5-e (about 290 pF including cables and holder) than that of HP4192A (less than 1 pF with properly shielded leads). The agreement was poorer for high impedances with absolute values approaching 1 MΩ: the upper limit of the HP4192A.

2.6. *Sample holders*

A proper sample holder is a crucial part of the impedance measuring setup. Four separately shielded leads were required to minimize spurious impedances at high frequencies. Mechanically stable contact between the sample and the leads had to be maintained. The sample holder varied with the type of experiment.

2.6.1. Measurements on solid electrolytes were performed at high temperatures (up to 800° C) in a specially designed sample holder which permitted contacting the sample with spring loaded platinum plates and separate shielding of the four leads. (Fig. 2). Stainless steel tubes and plates, platinum wires and foils, alumina insulating tubes and supports made of machinable ceramics were used to build the high temperature part of the holder. Four tubes brazed in the holes of two plates formed a rigid construction attached to the brass head of the holder. The longer two of these tubes protruded through the head: one was used as gas inlet; through the other a shielded NiCr–Ni thermocouple was inserted. The shorter two tubes, fitted with alumina insulating tubes, shielded two platinum leads welded to the platinum plate which rested on a ceramic support mounted at their ends. Two more tubes brazed together could move freely in oval holes made in the centres of the plates. This pair of tubes shielded the two leads, welded to the second platinum plate which was placed on a ceramic support fitted to one end of the tubes. At the other end (out of the furnace) springs were attached, which pushed the movable contact plate against the fixed one. Flexible shields were used for these sections of the platinum leads which ran between the stainless steel tubes and BNC jacks in the head of the sample holder. A quartz tube, closed at one end, was fitted with an O-ring to the head of the sample holder and measurements were made under flow of gas, typically nitrogen. The holder was inserted horizontally into a tubular electric furnace at such depth that the sample was in the centre of the hot zone.

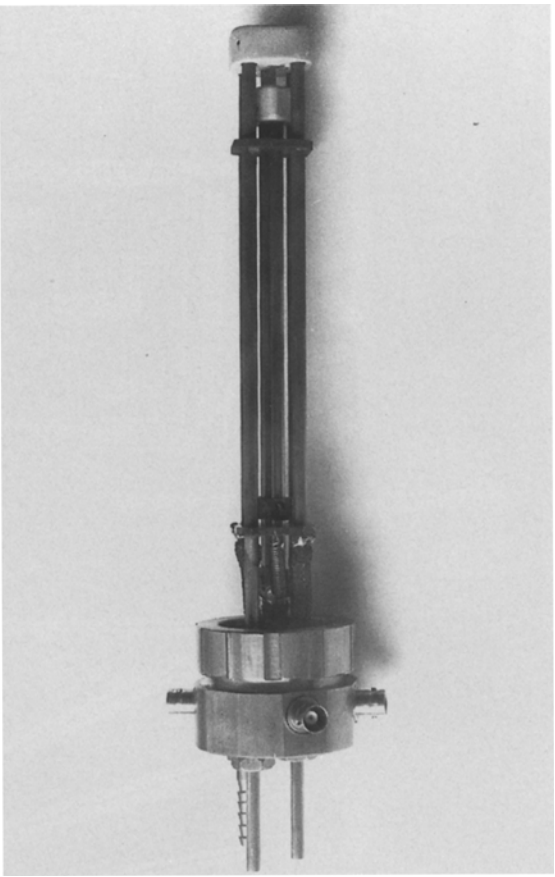

Fig. 2. Photograph of the sample holder used for impedance measurements of solid electrolytes at temperatures up to 1100 K.

2.6.2. Impedance measurements on sol–gel materials

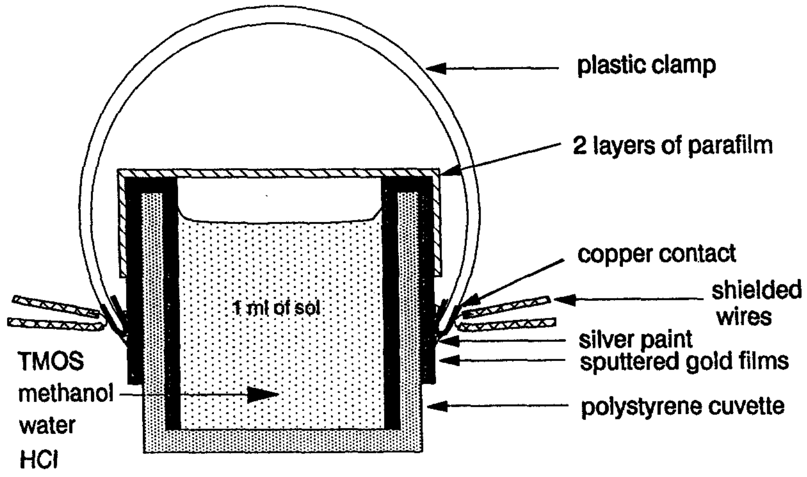

Fig. 3. Cell for impedance measurements of sol–gels.

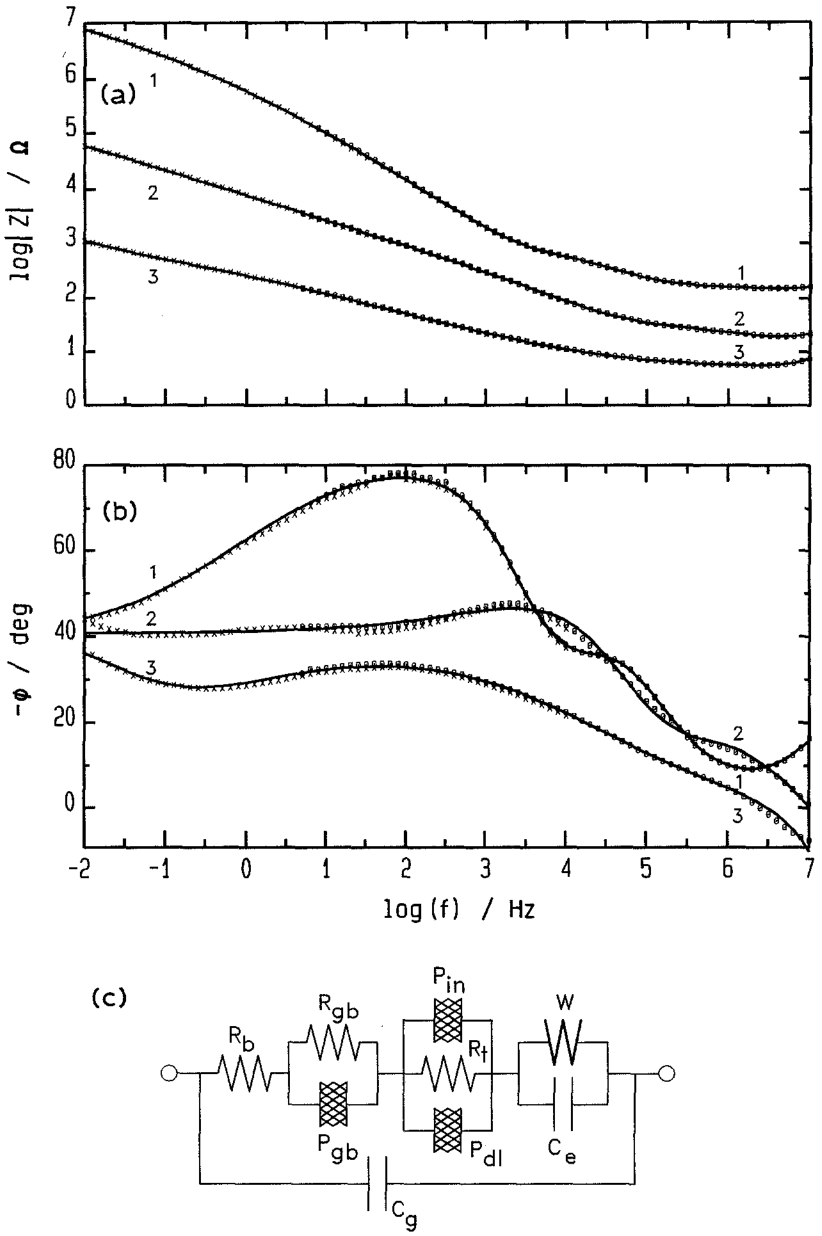

Fig. 4. Absolute value (a) and phase angle (b) of the impedance as a function of the logarithm of the frequency for the cell Au/Ag beta″ alumina/Au measured at (1) −300 K, (2) −471.5 K, (3) −771 K; '*o*'-HP 4192A, '*x*'-IM5e data. Continuous lines represent simulated impedance of the equivalent circuit (c) with parameters obtained by least-squares fit to the data. Cross hatched capcitors in circuit diagram represent CPA elements, W is a Warburg impedance.

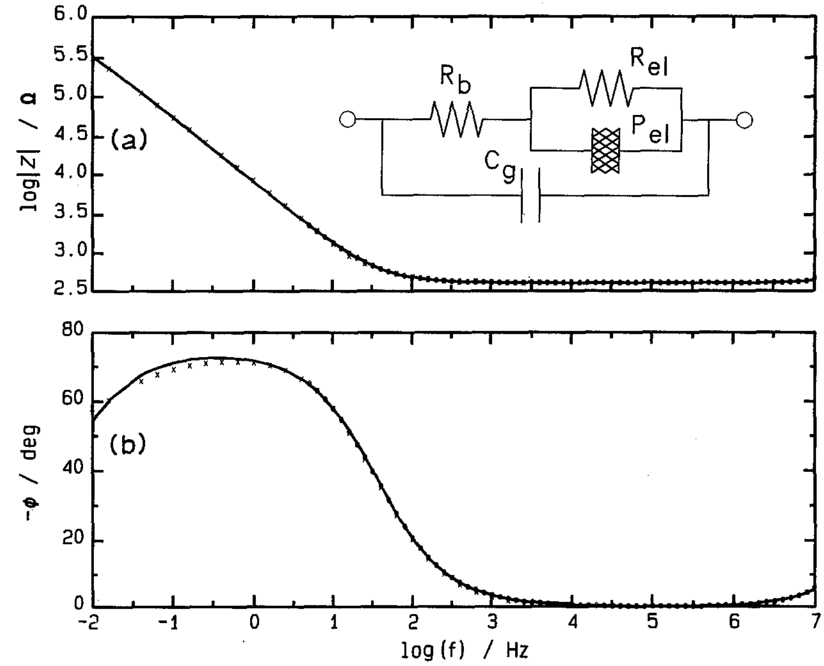

Fig. 5. Absolute value (a) and phase angle (b) of the impedance of the cell Au/sol-gel/Au as a function of the logarithm of the frequency measured at 298 K. Continuous lines represent simulated impedance of the equivalent circuit shown in the insert of (a).

during the gelation process can only be made until electric contact breaks due to shrinkage of the gel. The cells for the impedance measurements used polystyrene cuvettes to hold the sol and were similar to those employed in spectroscopic studies [14]. Several versions of cells using platinum or gold foil or mesh as electrodes were evaluated. These electrodes did not prove satisfactory as they led to cracking of the gels during drying. Sputtering of gold onto two opposite walls of the cuvette, which had been cut to a length of about 1.5 cm, yielded cells with electrodes which did not affect the sol-gel process. The cuvette was masked by using adhesive tape, thus producing a carefully defined surface area. Six cells were sputtered during a single deposition. They were aligned on a small aluminium rack at an angle of about 75° with respect to the gold target of the sputtering system. Thus a gold film was deposited on both the exterior and interior walls of each cuvette. Then the cuvettes were mounted in the reverse fashion to allow sputtering of the opposite wall. The cross section of the cells was 1 cm × 1 cm. The deposition of gold on to the exterior wall provided a convenient means for establishing electrical contact to the cell. A diagram of the cell and the clamp which established electric contact to the gold film are shown in Fig. 3. The cell constant was determined by calibration with 1 M KCl or 0.01 M KCl to be 0.91 cm^{-1} at 298 K.

3. Applications

Two different applications are described subsequently. The cell was of the type metal/solid electrolyte/metal in the first case. In contrast, a liquid electrolyte was used in the second example.

3.1. *Silver beta″-aluminia with gold electrodes*

Gold films were sputtered as electrodes on to Ag beta″ alumina, obtained by ion exchange of commercially available Na beta″ alumina from Ceramatec (USA). Spring loaded foils of platinum made contact with the gold films. Measurements of impedance spectra in the frequency range from 0.01 Hz to 10 MHz were made under flow of dry nitrogen at a series of temperatures up to 800 K. Ten frequencies per decade were taken.

The results of measurements at three temperatures: 300, 471.5 and 771 K are represented by letters ('*o*' for HP 4192A, '*x*' for IM5-e) in Fig. 4(a) and 4(b). The absolute value of Z is plotted as a function of the logarithm of the frequency in Fig. 4(a) and the phase angle in Fig. 4(b). The results, obtained with gold electrodes, differ from those measured with sputtered platinum electrodes [13]. In the case of platinum electrodes a sharp rise of the phase angle at low frequencies was observed at temperatures between 420 and 560 K clearly indicating blocking behaviour. This feature is much less pronounced in the case of gold electrodes.

The experimental spectra were simulated by the impedance of equivalent circuits composed of resistors, capacitors and constant phase angle (CPA) elements. Values of circuit parameters at each temperature were estimated by non-linear least-squares fitting. Several equivalent circuits, corresponding to various models of the interface solid electrolyte/electrodes, were tried. With a few of them a similarly good quality of fit was obtained. The electrical circuit, shown in Fig. 4(c), was finally chosen based on its relative simplicity and smooth, Arrhenius type temperature dependence of the estimated parameter values. This circuit is similar to those used to simulate the impedance spectra of Ag beta″-alumina with platinum electrodes [13]. The solid curves in Fig. 4(a) and (b) correspond to the simulated impedance of the equivalent circuit. The agreement is satisfactory.

It is not the purpose of this communication to attempt an interpretation of the different elements in the electrical circuit used in the simulation. However, based on comparison with results of the four-probe measurements and scaling of the results with geometrical factor [13], it has been demonstrated that the section of the circuit composed of the resistors Rb, Rgb, the CPA element Pgb and the capacitor Cg represent the impedance of the solid electrolyte, while the remaining part of the circuit represents the impedance of the interface solid electrolyte/electrodes.

3.2. *Sol–gel*

The second example involved [15] impedance measurements on cells with sol–gel materials at 298 K. The cells were inside a thermostated aluminum box. The results in Fig. 5(a) and (b) were obtained with a sol, prepared by mixing $Si(OCH_3)_4$ (TMOS: tetramethoxysilane), H_2O and CH_3OH in the ratio 1 : 4 : 3 and adding HCl as a catalyst. The absolute value of Z approaches a constant value at higher frequencies, representing [15] the bulk resistance of the sol. The interfaces become predominant at low frequencies. A simulation of the frequency dependence is achievable by the equivalent circuit shown in the insert of Fig. 5(b). The reader is referred to [15] for details.

Acknowledgement

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