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Measurements of PEM conductivity by impedance spectroscopy

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Abstract

The methodology of PEM conductivity measurements is discussed for examples of literature data and results of the experiments, carried out in this study. It is shown here that a simple two-electrode cell proposed in this work, operated at frequencies of 1 to 10^7 Hz reproducibly gives a response typical for a solid electrolyte, and therefore is easily rationalised in terms of equivalent circuits. The obtained impedance diagrams are compared with the ones described in the literature for 4-probe experiments. It appears from this comparison that the cell geometry and electrode arrangement play important roles in the formation of the frequency dependent response. In some cases, two-electrode cells may have an advantage over the four-probe technique, as they are less complicated and therefore involve less stray effects in the resulting impedance spectra. In this study, the proposed configuration, which we have previously utilized for some of our measurements, proved to be efficient at producing reproducible, reasonable and reliable results, related to the expected values of PEM conductivity.

Keywords: Proton conductivity; PEM; Impedance spectroscopy

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1. Introduction

Currently, the thriving field of proton exchange membranes (PEM) is attracting ever growing attention for the development of new types of solid polymer electrolytes. A most important functional characteristic of these materials is their proton conductivity, which is measured using a variety of techniques, the choice being dependent mostly on their availability and convenience. The methodology of these tests was discussed for instance in an article [1], entitled “Importance of Proton Conductivity measurements in PEM for FC application”. As the subject matter of this paper is of primary importance for the whole field of PEM, we present herein some considerations based on our comparative analysis of published work and our own data, dealing with acquisition and interpretation of results of experiments, undertaken in order to determine the PEM's conductivity. These considerations might be of help for the numerous presently emerging research groups focusing their scientific interests in this domain and seeking suitable equipment configuration for their studies.

It is worth mentioning, that among existing techniques the impedance spectroscopy and four-electrode cell configuration (as used in ref. [1]) are commonly considered as the best combination. However, it is important to realize, that merely using this approach does not guarantee against severe errors. The main goal of the present work is to underline not only the importance of the correct choice of technique and instrumentation but also the significance of sensible results and their rational interpretation.

2. Brief literature review

Accurate measurement of the proton conductivity of electrolyte membranes presents a non-trivial experimental challenge. As protons are the sole mobile charge in these electrolytes, their conductivity can be measured by a DC technique only using the H/H^+ reversible electrodes, which is

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expensive and too complex for a routine test. An AC technique allowing polarization effects at the electrodes to be avoided is commonly considered as the most appropriate for solid electrolytes. Impedance spectroscopy is the most widespread method, where analysis of a complex-plane frequency dependent response of a sample may allow estimation of its proton conductivity.

Another problem is concerned with the strong dependence of PEM conductivity on its hydration state. Several experimental schemes have been used to control the measurement conditions, each one having its own merits and limitations.

Sandwiching membrane specimens between flat electrodes (transverse measurement), employed for example in refs. [2–4], hinders them from equilibration with the environment, even if the assembly is then immersed in water as was undertaken in ref. [5]. Immersing a membrane in a liquid electrolyte solution, where it separates two half cells as in refs. [6–8], can affect its chemistry due to ion exchange. This approach appears justified when the membrane is for utilization in electrodialysis, however in FC application the conductivity measured in such a manner would not be very reliable. In other works [9,10], two additional pieces of carbon cloth were introduced into transverse measurement cell for the purpose of facilitating equilibration of the sample with the environment atmosphere. However, this arrangement adds more complexity to the electric circuit under measurement by involving two additional resistances, often comparable in magnitude with the bulk resistance of the membrane, as well as two interfaces with their capacitances. These additional electrical elements evidently make measurement results less precise. Perhaps the most correct approach is to use gas-diffusion Pt/C electrodes instead of pure carbon cloth, and to carry out the measurements in an atmosphere of humidified H_2, under conditions closely imitating a hydrogen FC, as in refs. [11,12]. However, this is a rather expensive and cumbersome technique, as it requires a large and expendable piece of membrane, hot-pressed electrodes etc. Still further, all techniques estimating the transverse conductivity, suffer from the problem of precise measurement of very low resistance (<1 Ohm), often comparable with the resistance of interconnecting wiring. In order to make the membrane resistance dominant over the response of the whole system, and at the same time to ensure equilibration of the specimens in situ, a frame cell has been proposed in the work [13], where conductivity is measured in the longitudinal direction on one membrane side along a face, exposed to environment. This method is obviously suited only to isotropic membranes with surface properties undistinguishable from the bulk, because only in this case longitudinal conductivity will not differ from transverse one, which is an applicative target of these measurements. Longitudinal measurements are widely used [1,14–16]. However the issues of cell geometry and electrode configuration, as factors having a substantial impact on the impedance response, have subsequently attracted much attention. In ref. [17] it was shown that in two-electrode geometry, interfacial impedances dominate the response in the employed frequency range (≤100 kHz), and to avoid this spurious signal a four-electrode configuration was proposed. There the voltage drop is measured by a separate pair of wires connected to the high impedance input of the apparatus, eliminating any current flows across the interfaces. A special four-electrode cell allowing conditioning of the membrane sample under a stream of humidified gas is described in ref. [18]. In studies [15,19] however it was demonstrated that a two-probe configuration may also ensure reliable results, provided they are obtained at higher frequency range. Yet another approach, employed apparently since 1977 [20], is to use a coaxial cell where the impedance is measured between inner and outer rings, thereby avoiding stray inductances and capacitances. Later similar measurements using a coaxial probe were carried out in refs. [21,22].

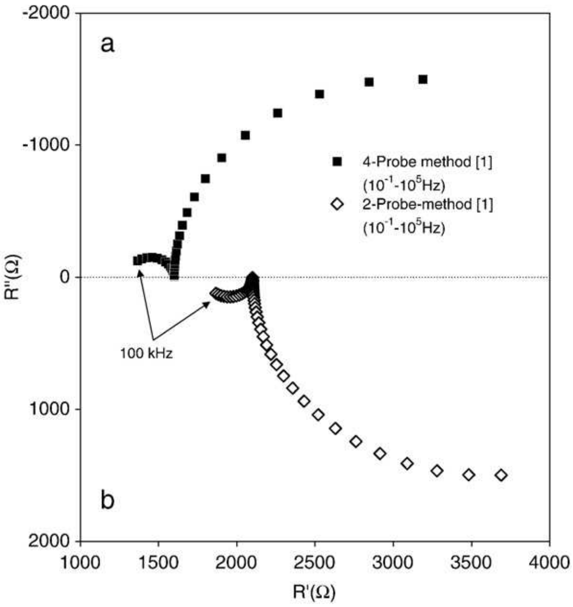

Fig. 1. Imitation of the diagrams, shown in Fig. 5 of ref. [1]). These responses were acquired in ref. [1] using Solartron 1260 analyzer coupled with 1287 interface. The circuit depicted in Fig. 2 was used for simulation. The parameters of the circuits are presented in Table 1. a) Simulation of four-probe impedance responses using a circuit shown in Fig. 2, capacitive impedance. b) Simulation of two-probe impedance responses using a circuit shown in Fig. 2, effective negative capacitance. The frequency range of a) and b) was 0.1–10^5 Hz, corresponding to that used in ref. [1].

As follows from the abundance and diversity of measurement techniques in current use, a standard method for PEM conductivity measurements is still awaited. Viewing the problem from this frame of reference, article [1] is of great importance, as it proposes a complete system for carrying out measurements under controlled humidity. The system comprises a cell consisting of four Pt wire electrodes, mounted on an insulating frame with windows between wires with a membrane enclosed between this frame and a similar insulating frame without electrodes. In the following we discuss its results in comparison with ones acquired in our laboratory.

3. Results and discussion

Strictly speaking the electrochemical response of a system under measurement is best rationalised in terms of an equivalent

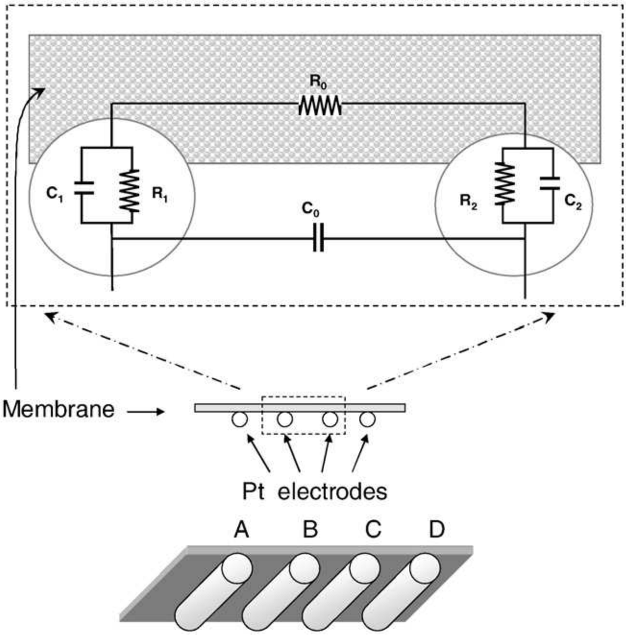

Fig. 2. The equivalent circuit used for simulation of the responses obtained for Nafion membrane in ref. [1] using four-probe and two-probe arrangements. A home made cell comprised 4 linear (~2 cm Pt wire) probes spaced 1 cm apart, fixed on a Teflon plate with windows between the electrodes. Measurements were carried out on one side of the membrane, which was pressed to the electrodes by another plate. R_1C_1 and R_2C_2 sub-circuits correspond to electrode–membrane interfaces, R_0 is the sample resistance, C_0 is inter-electrode capacitance.

circuit, comprised of elements whose electrical parameters should be fitted to the experimental diagram. As this was not performed in ref. [1], we tried herein to simulate the complex impedance responses, shown in Fig. 5 of ref. [1] in the same frequency range of 0.1 to 10^5 Hz. In Fig. 1, one can see the impedance spectra are visually undistinguishable from the ones in the cited work.

First let us consider the four-probe test, which gave a capacitive response, whose simulation is shown in the Fig. 1a. Simple equivalent circuit, suggested in ref. [1], comprises only one RC sub-circuit with a resistance in series and obviously could not provide such a response. The small high frequency semicircle in Fig. 1a does not start at the origin of the coordinates, and if extrapolated to intersect with the Z' axes, will cross it at ~1300 and ~1600 Ohm. As there is another arc signal corresponding to a higher resistance and yet a further one is understood to exist between 0 and 1300 Ohm, the simplest equivalent circle should consist of at least three reactive elements and might be assumed to be represented as shown in Fig. 2. The RC sub-circuits (1 and 2) originate from the interfaces between metal electrodes and electrolyte media, inevitably formed at the points of contact, even if the probes carry no current. There should be also a capacitance C_0 between the electrodes, and a resistance of the membrane R_0. The simulation of this circuit fits very well (Fig. 1a) with the results of the experiment, carried out in ref. [1]. The parameters of the elements of this equivalent circuit are shown in Table 1. It may be assumed from this analysis that experiment in ref. [1] was carried out in such a manner, that some measurable current passed through electrodes B,C.

The same membrane sample in two-probe configuration (current generator connected to B,C instead of A,D electrodes, Fig. 2) produced a flipped signal shifted to the right as seen from Fig. 1b. The authors of ref. [1] explained this behaviour by “inductive impedance derived from PBO connectors, Pt electrodes and leads including coaxial cables”. At the same time they marked left-hand side points of the signal (low Z') as the high frequency limit of the response. This obviously contradicts to the hypothesis of inductive character of the response with $Z''>0$. An inductance dominated signal normally exhibits inverse frequency sequence and should show low Z' at low frequency. If the frequency assignment in ref. [1] is correct, then the assumption of predominant role of inductive impedance in this response is invalid. A suitable solution may be found in assumption of effective negative capacitance (C_1 and C_2 values are shown in Table 1), caused by some chemical reactions or adsorption phenomena, involving probably water molecules. A simulation, performed using circuit parameters shown in Table 1, gave a response (Fig. 1b) which visually undistinguishable from the one obtained in ref. [1].

The increase in R_0 in this case over R_0 of Fig. 1a may be accounted for by a larger distance between the electrodes in the 2-probe method. It was not mentioned in ref. [1], whether the left or right intersection of the first semicircle was taken as the resistance of the sample, in order to use it to extract the conductivity estimate. According to the equivalent circuit proposed here (Fig. 2), it is more reasonable to assume that R_0 is the membrane related value. It might look unclear, why a symmetrical cell, shown in Fig. 2, exhibits a strongly asymmetrical response (R_1, C_1 different from R_2,C_2 Table 1). This, however, can be explained by non-parallel alignment of the plate supporting the electrodes and the plate holding the membrane down. If the clamping pressure is not equal for all 4 electrodes (which is difficult to attain with flexible Teflon plates and extended electrode wires) then electric parameters of interfaces between membrane and electrodes would be inevitably different. The high contact resistances revealed by complex impedance spectra are supposed to be due to insufficient rigidity of Teflon plates. As the screws are outside the cell working area, the inner pair of electrodes probably is less tightly pressed to the membrane and humidity may form an insulating interface between metal and solid electrolyte. Thus, the advantages of the four-probe cell

Table 1
Electrical circuit parameters, used for simulation of the responses, shown in Fig. 1

Element	Equivalent circuit for Fig. 1a	Equivalent circuit for Fig. 1b
R_0 (Ohm)	1300	1800
C_0 (F)	10^{-11}–10^{-12}	10^{-12}
R_1 (Ohm)	300	300
C_1 (F)	3×10^{-8}	-1×10^{-8}
R_2 (Ohm)	3000	3000
C_2 (F)	5×10^{-4}	-5×10^{-4}

The circuit is shown in Fig. 2.

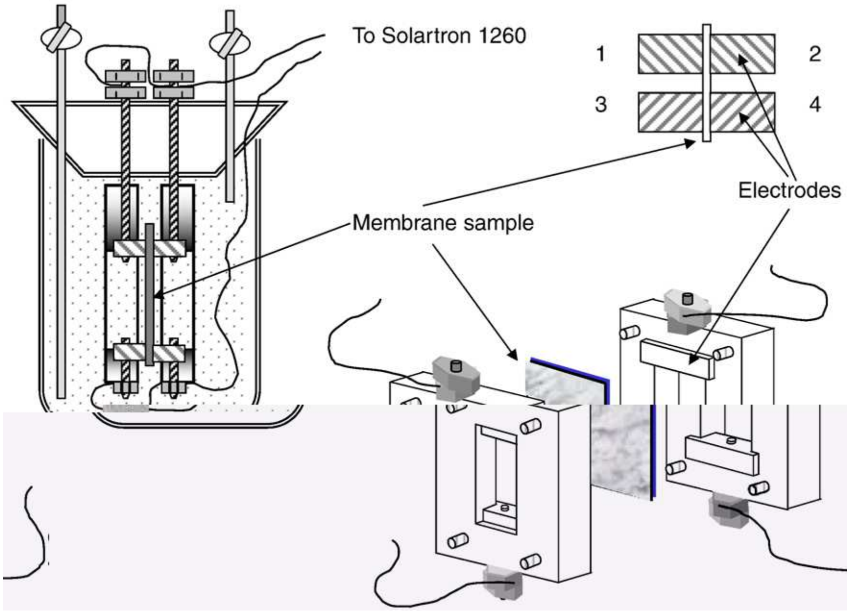

Fig. 3. Schematic drawing of a two-electrode cell, used for measurements of membrane conductivity in longitudinal direction.

were not brought into effect while its more complicated geometry caused the problems with electrode-material contacts.

It is interesting to note, that as was reported in ref. [1], an “inductive” response (positive Z'') obtained in humid air in the two-electrode cell, transforms into a totally capacitive one (negative Z'') in the whole frequency range when the cell is filled with liquid water. This may be accounted for the strong impact of water adsorption phenomena on the adsorption capacitances C_1, C_2.

It should be understood that this attempt of analysis of the literature data was performed on the illustrative drawings and does not represent a real data fit, but rather an effort of attaining a visual resemblance of the responses reported in ref. [1]. In any case the results, obtained in four and two-probe cells used in ref. [1], shows that the cell geometry used by the authors does not appear to be optimal, resulting in a complicated response with significant stray impacts. This makes it difficult to extract the required conductivity values. Moreover, these cells are overly sensitive to the conditioning atmospheres, resulting in completely different impedance diagrams depending on environmental specifics.

At the same time an inexpensive two-electrode cell (Fig. 3) built in our laboratory allows obtaining reproducible and reasonable results. It was used for measuring conductivity of various materials with conductivities from 10^{-8} to 1 S/cm in dry or humid atmospheres or filled with liquid water. In distinction with the cell described in ref. [1], in the present one a membrane

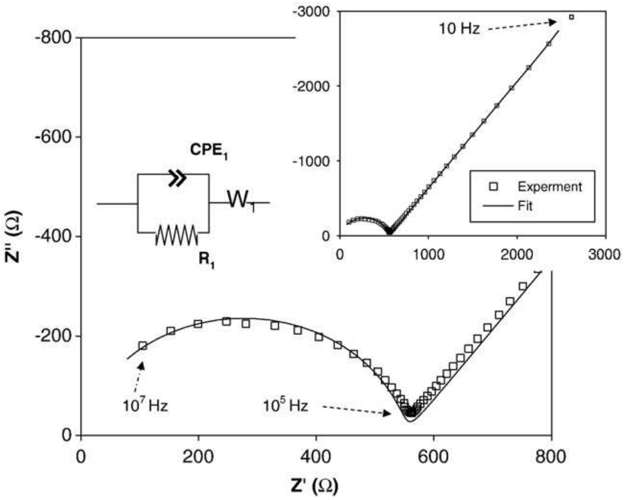

Fig. 4. Complex impedance responses of wetted Nafion in the frequency range of 10–10^7 Hz. Squares — experimental data; solid line — fitting results. Equivalent circuit parameters are shown in Table 2. Corresponding conductivity of the sample $\sigma = 0.083$ S/cm.

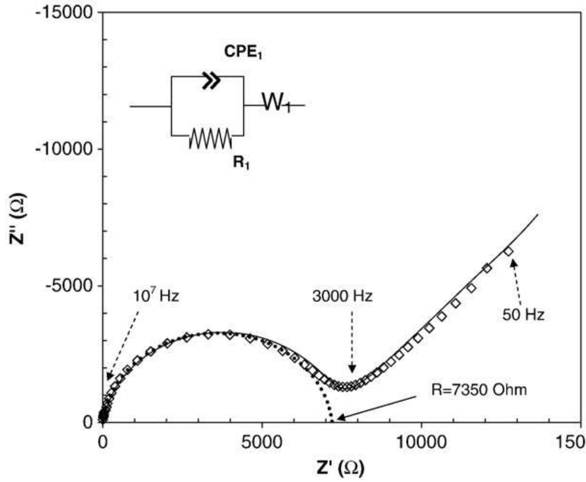

Fig. 5. Complex impedance responses of Nafion membrane, conditioned in room environment ($t = 23$ °C, RH = 65%) in the frequency range of 50–10^7 Hz. Squares — experimental data; solid line — fitting of the whole spectrum; dotted line — fitting of the first semicircle with an R-CPE circuit in the range 10 kHz–10 MHz. Equivalent circuit parameters are shown in Table 2. Corresponding conductivity of the sample $\sigma = 0.023$ S/cm.

sample is tightly secured between two pairs of flat stainless-steel electrodes, thereby ensuring negligible contact resistance. As shown in Fig. 3 electrodes 1,2 and 3,4 are connected pair-wise, with a sample placed between two capacitor plates, one comprises electrodes 1,2 and the other of 3 and 4, (see Fig. 3). This configuration proved to be satisfactory, as evidenced by minimizing stray signals and always giving typical responses, examples of which are illustrated by Figs. 4 and 5.

The complex impedance spectrum, shown in Fig. 4 for instance represents a response of hydrated Nafion membrane at 100%RH at room temperature, and Fig. 5 illustrates impedance of a Nafion sample at ambient room conditions (24 °C, 65% RH). These diagrams are much simpler, being comprised of only two elements: a suppressed semicircle in the high frequency domain and a straight line at lower frequencies. This behavior is typical for an electrolyte, whose bulk resistance is responsible for the high frequency semicircle, while the low frequency response is controlled by the diffusion of charged particles with some impact of electrode polarization if slope angle of the straight line differs from 45°. Thereafter the equivalent circuit comprises R-CPE combination, where constant phase element (CPE) is a substitute for the conventional capacitor C in order to reflect the fact that the semicircle is suppressed. The CPE is a generalisation of a capacitor, which produces an impedance $Z_{\mathrm{CPE}}=1/[T(j\omega)^{\alpha}]$ having a constant phase angle in the complex plane. The exponent α determines this angle and when $\alpha=1$ phase angle is 90° and CPE degenerates into pure capacitor with $T=C$. One more equivalent circuit component in series with R-CPE combination (insets in Figs. 4 and 5) is a generalised Warburg element. Its impedance is $Z_{\mathrm{W}}=R_{\mathrm{W}}{*}\,\mathrm{ctnh}\,([j*T_{\mathrm{W}}*\omega]^{\alpha})/(j*T_{\mathrm{W}}*\omega)^{\alpha}$ and at $\alpha=1/2$ reflects charge carrier diffusion through a material, the depth of which increases inversely with the frequency. Fitting of the experimental curves with this equivalent circuit gave very congruent responses, as shown in Figs. 4 and 5. From Table 2, where the parameters of the circuit are shown, one can see that the exponent α for Warburg element is close but not exactly equal to 0.5, which means that at lower frequencies the response is controlled mainly by proton diffusion, with some impact (larger for hydrated membrane) of interfacial relaxation.

The high frequency semicircle is associated with membrane resistance in parallel with the cell capacitance. Depression of the response probably has the physical meaning of a certain distribution of capacitances in the vicinity of the specimen and along its thickness. It should be noted here that capacitances in both cases of wet and dry membranes are very low (on the order of pF) and capacitance distribution is rather narrow (α is close to unity, Table 2).

Table 2
Equivalent circuit parameters, determined by fitting of the responses, shown in Figs. 4 and 5

Element		Equivalent circuit for Fig. 4	Equivalent circuit for Fig. 5
R_1 (Ohm)		571	7010
CPE_1	T (F)	5×10^{-10}	9×10^{-10}
	α	0.9	0.93
W	R (Ohm)	18,000	40,000
	T (F)	0.25	0.04
	α	0.61	0.54

R values retrieved from the fitting of the high frequency semicircles, corresponding to membrane's bulk DC resistances were then converted into conductivities using membranes geometrical dimensions according to $\sigma\ =L/(R*d*b)$. Here L is a distance between electrodes 1 and 3 (Fig. 3), d and b are specimen thickness and width respectively. The calculation results (specified in figure captions) are consistent with those reported in literature [15,23]. Thus, a response, which is typical for a solid electrolyte, is obtained in the suggested measurement cell. It might be mentioned that this kind of response was consistently and reproducibly obtained in these cells for various materials with conductivities from as low as 10^{-8}S/cm and up to as high as about 1 S/cm. When frequencies of at least 1 MHz are used, in good accordance with the literature [15,17] the acquisition of almost a complete signal, associated with PEM bulk conduction becomes possible.

For practical purposes the required R value might be evaluated without fitting the whole experimental curve by an equivalent circuit, but simply from fitting of high frequency semicircle (the option usually existing in impedance software) or even from inflection point, where a semicircle converts into a straight line. Usually the difference in not large: for instance in the diagram illustrated in Fig. 5 the value of R retrieved from fitting of the whole curve was about 5% lower than obtained from the fitting of semicircle only and about 7% less than the point of inflection. For conductivity of the materials this error is perhaps not significant.

4. Conclusion

From the comparison of two kinds of measurement cells for evaluation of PEM conductivity by the impedance method, one can see that the cell geometry and the electrode arrangements play an important role in the formation of the frequency dependent response. In some cases, two-electrode cells may have an advantage over four-probe techniques, as they are less complicated and therefore involve less stray effects in the resulting impedance spectra. Consequently more simple geometry makes this configuration less prone to experimental error. The configuration proposed in this study proved to be efficient at producing reasonable and reliable results. Higher frequencies required for obtaining the required measurements from these kind of cells are readily available in many commercial apparati such as Solartron 1260 (30 MHz), Autolab PGSTAT302/FRA2 (1 MHz), Novocontrol Alpha-A series (20 MHz), Hewlett-Packard 4194a (100 MHz). Using the suggested cell at 10^{1}–10^{7} MHz allows the acquisition of a simple response, related to the required value of bulk DC conductivity of PEM.

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