

## Electronic Supplementary Material

to the

## Determination of the Diffusion Coefficient of Hydrogen Ion in Hydrogels

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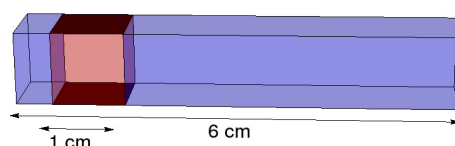
### A Electric Properties of the Conductometric Cell

In Harned and French's method, the conductance and conductivity values expressed at an  $\frac{a}{6}$  distance from top and bottom of the cell are used for evaluation. In our custom-made cell, the electrodes are centered at these locations, however, their  $1 \text{ cm}^2$  area is not negligible considering the concentration gradient developing during the experiments. By solving the differential form of Ohm's law

$$0 = \nabla j = \kappa \nabla^2 U \quad , \quad (1)$$

where  $j$  and  $U$  are the electric current density and the electric potential, respectively, we can compare the conductivity values at the center of the electrode, *i.e.*, in  $1 \text{ cm}$  distance from the end of the cell ( $\kappa_{1\text{cm}}$ ) to those calculated over the electrode area ( $\kappa_{\text{mean}}$ ) for concentration gradients obtained in the calculations. The use of Eq. (1) on a cell with homogeneous concentration distributions, *i.e.*, with constant  $\kappa$  also provides us with the theoretical cell constant  $C$ . Equation (1) is solved with a finite volume method by using the potential solver in OpenFOAM on a  $300 \times 50 \times 50$  mesh with a physical size corresponding to the experimental cell with no flux boundary conditions at the wall except at the electrode surface, where the potential is set to be constant (see Fig. 1).

The theoretical cell constant, obtained from a spatially homogeneous field with constant conductivity, is found to be  $C = 0.71 \text{ cm}^{-1}$ . This value is then applied for further comparative calculations where the computation yields the total current through the electrode surface and hence provides an  $R$  resistance value used to calculate the mean conductivity ( $\kappa_{\text{mean}} = \frac{C}{R}$ ). Table 1 shows examples out of 48 comparisons where  $\kappa_{1\text{cm}}$  associated with the center of the electrode is compared to  $\kappa_{\text{mean}}$  obtained from the corresponding concentration profiles in our previous calculations of ionic diffusion. It can be observed that the differences are considerably small—the highest value does not exceed 0.2%. This agreement implies that electric current patterns between the two electrode surfaces in a pair are close to an ideal parallel form and, therefore, average conductivity measured this way may be validly used for obtaining effective diffusion coefficients.



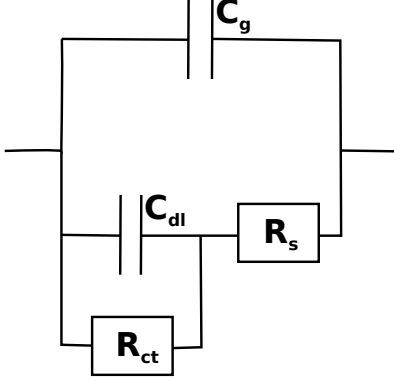
**Fig. 1** Geometry of the  $6 \text{ cm} \times 1 \text{ cm} \times 1 \text{ cm}$  inner space of the conductometric cell. Only one pair of electrodes (dark top and bottom faces in the highlighted red area) is shown for simplicity. Electric currents may flow between these two surfaces while the electrolyte diffuses from left to right lead by its concentration gradient.

**Table 1** The acquired  $R$  resistance values and  $\kappa_{1\text{cm}}$  conductivity calculated from  $R$  and the theoretical cell constant.  $\kappa_{\text{mean}}$  is the average conductivity at the given electrode pair corresponding to the concentration profile used for calculation. The percentage difference between the two conductivities is also shown.

$R$	$\kappa_{1\text{cm}}$	$\kappa_{\text{mean}}$	difference (%)
1992	$3.549 \cdot 10^{-2}$	$3.550 \cdot 10^{-2}$	0.02
1031	$6.859 \cdot 10^{-2}$	$6.859 \cdot 10^{-2}$	0.01
1869	$3.784 \cdot 10^{-2}$	$3.790 \cdot 10^{-2}$	0.16
2047	$3.454 \cdot 10^{-2}$	$3.455 \cdot 10^{-2}$	0.03
1736	$4.072 \cdot 10^{-2}$	$4.076 \cdot 10^{-2}$	0.09
2062	$3.430 \cdot 10^{-2}$	$3.428 \cdot 10^{-2}$	0.06
2242	$3.154 \cdot 10^{-2}$	$3.148 \cdot 10^{-2}$	0.19
1799	$3.931 \cdot 10^{-2}$	$3.931 \cdot 10^{-2}$	0.01

## B Impedance Measurements

The impedance is a complex function,  $Z = Z_{\text{real}} + iZ_{\text{im}}$ , where both the real and imaginary parts could depend on the frequency of the measurement. An equivalent circuit diagram of the conductometric cell is illustrated in Fig. 2 detailing the connections between the elements. The electric double layer evolving at the electrode surfaces is also taken into account by the Constant Phase Element (CPE) model. Summarizing all the parallel and series connec-



**Fig. 2** Equivalent circuit diagram of the conductometric cell illustrating the ohmic resistance of the solution  $R_s$ , the ohmic resistance and the capacitance of the electric double layer,  $R_{ct}$  and  $C_{dl}$ , respectively, and the capacitance  $C_g$  caused by the cell geometry.

tions, a formula can be derived for the net impedance:

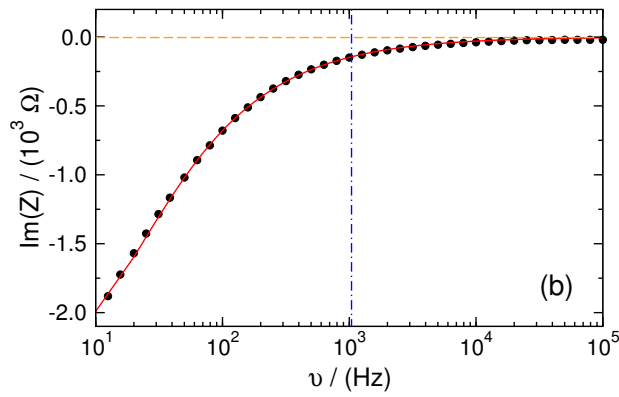
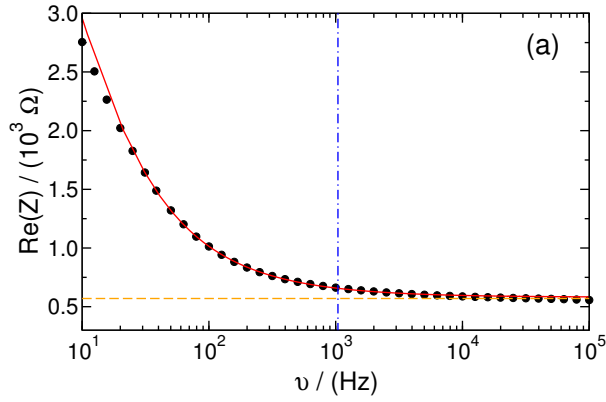
$$Z = \left( \frac{1}{Z_g} + \frac{1}{Z_{dl} + Z_s} \right)^{-1} = \left( i\omega C_g + \left( \frac{1}{\frac{1}{R_{ct}} + (i\omega)^n C_{dl}} + R_s \right)^{-1} \right)^{-1}, \quad (2)$$

where  $R_s$  stands for the ohmic resistance of the solution,  $R_{ct}$  is the charge transfer resistance due to the possibility of the decomposition of water or the reduction of dissolved oxygen,  $C_{dl}$  is the capacitance of the electric double layer,  $C_g$  is the capacitance caused by the cell geometry, and  $n$  has a value  $0.5 < n < 1$  introduced in the CPE model attributed to the roughness of the electrode surface.

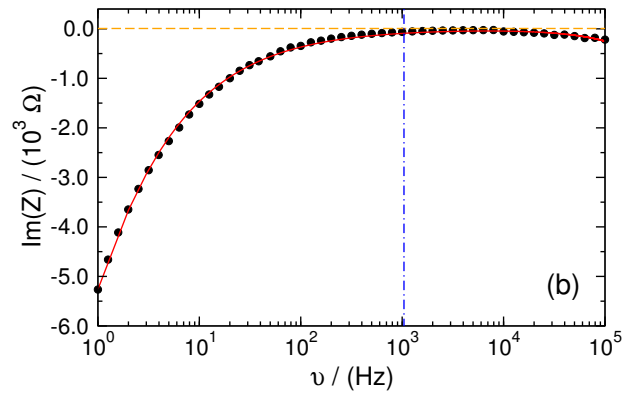
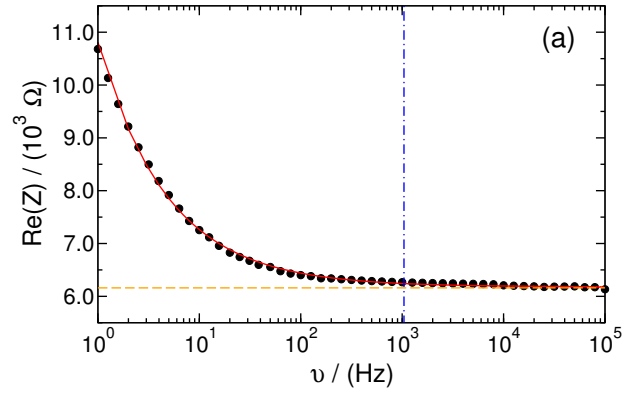
Since at different frequencies the contribution of each circuit element to the net impedance can significantly vary, a re-

liable method was to be found to analyse the system. Therefore, the cell's inner space was filled with a 692 ppm sodium chloride standard solution (NaCl Calibration Standard for Orion Thermo Scientific conductometer) which had a conductivity of  $\kappa = 1413 \mu\text{S}/\text{cm}$ , then the cell was closed and subjected to measurement. Impedance spectra were recorded using a Gamry PS3 potentiostat and a Stanford Research System Phase Sensitive Lock-in Amplifier. 10 mV rms voltage signal was applied at around the open circuit potential of the electrode pairs in the frequency range of 1 – 10000 Hz. It was also found previously that the conductometer in use (Orion Thermo Scientific) performs measurements at 1033 Hz preset frequency according to the actual ohmic resistance of the system (in the interval of 100 – 10000  $\Omega$  or, equivalently 0.1 – 10 mS). The real and imaginary parts of  $Z$  are plotted on individual graphs indicating the actual frequency of the conductance measurement as well (see Fig. 3). The figure also shows the nonlinear function fitted to the plotted data (solid red line) using the net impedance formula given in Eq. (2). Wolfram Mathematica is used for nonlinear complex curve-fitting with restrictions that the fitted parameters  $R_s$ ,  $R_{ct}$ ,  $C_{dl}$ , and  $C_g$  remain real. The most significant quantity, the ohmic resistance of the solution between the electrodes ( $R_s$ ) is obtained as a fitted parameter for both electrode pairs (orange line in Fig. 3 (a)):  $R_{s,\text{top}} = 577.5 \Omega$  and  $R_{s,\text{bottom}} = 491.8 \Omega$ . The experimental cell constants  $C$  are then calculated from those values since  $C = \kappa \cdot R$  resulting in  $C_{\text{top}} = 0.82 \text{ cm}^{-1}$  and  $C_{\text{bottom}} = 0.69 \text{ cm}^{-1}$  for the electrode pairs. Those values are in satisfactory agreement with the theoretical one obtained from calculating the electric properties of the conductometer cell ( $C = 0.71 \text{ cm}^{-1}$ , see Sec. A).

In a next step, similar impedance measurements were performed using 2 w/v% agarose hydrogel (instead of the NaCl standard) to fill the conductometric cell; the results are shown in Fig. 4. (We would like to highlight here that at this step no main diffusing electrolyte was involved in the system, only the homogeneously distributed background electrolyte of the hydrogel was subjected to the measurement.) It can be observed both in Fig. 3 and even more remarkably in Fig. 4 that the real part of  $Z$  closely approaches the obtained  $R_s$  value, moreover, the imaginary part of  $Z$  becomes almost zero. Therefore, we would like end with the concluding remark that, especially in hydrogel medium, the impedance measured by the electrode pairs is sufficient for evaluation of conductance measurements.



**Fig. 3** The real part (a) and the imaginary part (b) of impedance  $Z$  as the function of frequency shown by the black points. The solid red line denotes the nonlinear function fitted to the points, the blue vertical line marks the 1033 Hz preset frequency of the conductometer in use, and the orange dashed line represents  $R_s$ , obtained from the nonlinear curve-fitting in graph (a) and the constant zero value in graph (b).



**Fig. 4** The real part (a) and the imaginary part (b) of impedance  $Z$  as the function of frequency shown by the black points for measurements with agarose hydrogel. The solid red line denotes the nonlinear function fitted to the points, the blue vertical line marks the 1033 Hz preset frequency of the conductometer in use, and the orange dashed line represents  $R_s$ , obtained from the nonlinear curve-fitting in graph (a) and the constant zero value in graph (b).