Effect of Introducing Nonideal Capacitance in the Estimation of the Solution Resistance for Accurate Electrolytic Conductivity Measurements

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ABSTRACT: The standardization of secondary electrolytic conductivity cells requires the use of a certified reference material. The accepted certification method involves electrochemical impedance spectroscopy (EIS) to estimate the material’s solution resistance. This method normally assumes that the impedance’s imaginary component can be neglected; and hence, the measured impedance approximates the real impedance. Thus, a linear extrapolation of the impedance versus the period (inverse frequency) yields solution resistance. However, experimental impedance data usually do not exhibit a linear behavior over the spectra of frequency, which strongly suggest that the ideal capacitive assumption may not strictly apply. To account for the observed nonlinear behavior, we have proposed to introduce the concept of a constant phase element (CPE) to the analysis of impedance. This approach leads to the development of a relationship that improves the accuracy of the estimation, by establishing a critical frequency where extrapolation should be done. Finally, we are presenting simulated results to demonstrate how sizeable capacitive effects can influence the determination of solution resistance, and a final analysis to estimate the impact on constant cell or electrolytic conductivity values.

1. INTRODUCTION

Electrolytic conductivity \( \kappa \) is one of the parameters that are most widely used in industrial, environmental, and pharmaceutical fields. Its measurement uses devices that require calibration with certified reference materials (CRMs). These CRMs are certified using primary or secondary systems, provided mainly by National Metrology Institutes or other designated institutes.

From the scientific and metrological points of view, this measurement is interesting and actually stands under investigation, because some problems remain unsolved when solutions with very high (like seawater) or very low (like high-purity water) ion content are used, particularly in the solution resistance value estimation.\(^1\)\(^2\)

During typical electrochemical experiments, solution resistance is almost eliminated, leading to neglect of its value, by adding an excess of ions that transport charge from an interface to another. In this way, practically, only processes and overpotentials at electrodes are considered and deeply studied.\(^3\)\(^4\) For \( \kappa \) measurements, this action cannot be used because solution resistance represents the variable of interest.\(^5\)\(^6\)

In practice, solution conductivity \( \kappa \) is determined from a cell constant \( K_{\text{cell}} \) previously known, and solution resistance \( R_s \) by using eq 1.

\[
\kappa = \frac{K_{\text{cell}}}{R_s}
\] (1)

For primary systems, the cell constant can be determined by precisely measuring cell dimensions, and for secondary systems by using a certified reference material (CRM). The solution resistance is obtained from electrochemical impedance spectroscopy (EIS) measurements.

From these EIS measurements, real and imaginary impedance components are obtained. Resistances as \( R_s \) are mainly associated with the real part of impedance. These measurements need a prior evaluation of the frequency interval and the sinusoidal signal amplitude to assess the optimal measurement conditions.\(^7\) Usually, \( R_s \) is obtained from a linear extrapolation to an infinite frequency of the real part of impedance versus period (inverse of frequency).\(^8\) That linear extrapolation comes from Hoover investigation,\(^8\) where different equations were used to fit resistance measurement. However, in all cases, an ideal capacitor was considered. This introduces deviations that affect the accuracy of the estimation, as shown in the discussion, because solid electrodes do not present ideal capacitances.\(^3\)

This paper explores the effects of using a different approach that is censed to improve the accuracy of the internationally accepted method for the estimation of \( R_s \) by considering the
nonideality of capacitance. Here, we introduce the use of equivalent circuits containing nonideal capacitive behavior to account for deviations in measured impedance and propose the use of such circuits for the best fitting of the experimental impedance data. We also discuss the implications that the nonideal capacitance has on the solution resistance evaluation; i.e., its estimation obtained from the accepted methodology. An important contribution that helps specialists to improve regression values by introducing the concept of a critical frequency is included. Finally, simulated spectra are presented, which could explain some behavior observed in experimental data represented in Nyquist and Bode plots.

2. MATHEMATICAL MODEL

Our proposed approach uses equivalent circuits; such circuits are frequently used to estimate electrochemical parameters. In this case, the suitable elementary circuit is a simple and common one (Figure 1a).

The above circuit intrinsically assumes that the electrodes possess flat and homogeneous surfaces of well-defined geometries; hence, its model treats the double-layer capacitance as an ideal capacitor. However, in electrochemical systems with solid electrodes, this assumption does not hold, and the revised model circuit, shown in Figure 1b, better approximates the true behavior.3,9–11

Here, R, and denote the same meaning as indicated above. CPE or the constant phase element represents the nonideal capacitance, which has been empirically defined as follows3

\[ Z_{\text{CPE}} = \frac{1}{\omega \alpha C_{\text{dl}}^\alpha} \]  

(2)

where \( \alpha \) accounts for the nonideal behavior of the capacitance and typically represents an exponent less than 1 and in the range of 0.70–0.99.3 \( \omega \) is the angular frequency, and \( \omega \) stands for the frequency in Hertz. Thus, the use of a CPE introduces an additional parameter and generally improves the model’s fitting, and it is censed to represent the dispersive behavior of the capacitance with frequency in solid electrodes.3

3. RESULTS AND DISCUSSION

3.1. Analysis of Total Impedance When the CPE is Included. By Kirchhoff’s laws, the total impedance of the equivalent circuit containing the CPE is

\[ Z = Z_R + \frac{1}{Z_R + Z_{\text{CPE}}} \]  

(3)

where \( Z \) represents the total impedance, \( Z_R \) and \( Z_{\text{CPE}} \) are the impedances of solution and charge transfer contributions, and \( Z_{\text{CPE}} \) represents CPE impedance.

By decomposing \( Z_{\text{CPE}} \) into its real and imaginary components, applying the De Moivre’s theorem and introducing this result in the expression of \( Z \), eq 3, we get the real (\( Z' \)) and imaginary (\( Z'' \)) components as12

\[ Z' = R_s + \frac{1}{R_s} + \frac{1}{\omega^\alpha C_{\text{dl}}^\alpha \cos \left( \frac{\alpha \pi}{2} \right)} \]  

(4)

\[ Z'' = -\frac{\omega^\alpha C_{\text{dl}}^\alpha \sin \left( \frac{\alpha \pi}{2} \right)}{\left( \frac{1}{R_s} + \frac{1}{\omega^\alpha C_{\text{dl}}^\alpha \cos \left( \frac{\alpha \pi}{2} \right)} \right)^2 + \left( \omega^\alpha C_{\text{dl}}^\alpha \sin \left( \frac{\alpha \pi}{2} \right) \right)^2} \]  

(5)

It is important to note that both the real and imaginary components depend on the resistances as well as on the nonideal capacitance. It is easily evidenced from eq 4 that a no-simple linear relationship exists between \( Z' \) and \( \omega \) when nonideal capacitance is taken into account. Thus, a plot of \( Z' \) vs \( 1/\omega \) or equivalently, \( Z' \) vs \( 1/f \) is not going to give a strict line with \( R_s \) as the y-intercept, as assumed by the accepted method.3 Instead, a more complex relationship is expected. A deeper analysis of eq 4 leads to the conclusion that this expression can be simplified if the term \( 1/R_{\text{ct}} \) is negligible when compared to the term depending on the frequency. Thus, we can define two cases, depending on whether \( 1/R_{\text{ct}} \) is negligible or not, compared to the frequency-dependent term. We are identifying this term as \( Y_{\text{CPE}} \) according to the equation

\[ Y_{\text{CPE}} = \omega^\alpha C_{\text{dl}}^\alpha \cos \left( \frac{\alpha \pi}{2} \right) \]  

(6)

Thus, it can be established that there exists a cutoff or critical frequency \( \omega_c \) that can be obtained by setting the following equation, which compares the terms where \( R_s \) is involved in eq 4

\[ \frac{1}{R_{\text{ct}}} = Y_{\text{CPE}} = \omega_c^\alpha C_{\text{dl}}^\alpha \cos \left( \frac{\alpha \pi}{2} \right) \]  

(7)

or in terms of frequency

\[ \omega_c = \left( \frac{1}{R_{\text{ct}} C_{\text{dl}}^\alpha \cos \left( \frac{\alpha \pi}{2} \right)} \right)^{1/\alpha} \]  

(8a)

\[ f_c = \frac{1}{2\pi} \left( \frac{1}{R_{\text{ct}} C_{\text{dl}}^\alpha \cos \left( \frac{\alpha \pi}{2} \right)} \right)^{1/\alpha} \]  

(8b)

This relationship permits us to estimate the frequency above which the term \( 1/R_{\text{ct}} \) becomes lower than \( Y_{\text{CPE}} \) and even negligible. It is important to remark that this frequency should be the lower limit to make an extrapolation assuring linear behavior.

3.2. Case 1: \( 1/R_{\text{ct}} \) is Negligible. This first case implies that \( R_s \) is high. This usually occurs when the measurement is made at an open circuit potential or when an applied overpotential does not favor electrochemical reactions; i.e., low polarization potentials and low amplitude signals. In these conditions, the term \( 1/R_{\text{ct}} \) becomes negligible as compared to \( Y_{\text{CPE}} \) and eq 4 simplifies into

\[ Z' = R_s + \frac{\cos \left( \frac{\alpha \pi}{2} \right)}{\omega^\alpha C_{\text{dl}}^\alpha} \]  

(9)
Or in terms of \( f \)

\[
Z' = R_{ct} + \frac{\cos\left(\frac{\alpha f}{2}\right)}{(2\pi)^{\alpha} C_{dl} f} \quad (10)
\]

It is clearly seen that under this assumption, there is a linear correlation between \( Z' \) and \( f^{-\alpha} \), but not on \( f^{-1} \). As a consequence, a graph of \( Z' \) vs \( f^{-1} \), as currently done, is going to produce deviations of the linear behavior and, thus, inaccurate estimations of \( R_{ct} \). This is illustrated in Figure 2 with an example of spectra simulated with the equivalent circuit that includes the CPE.

![Figure 2](image_url)

**Figure 2.** Example of simulated spectra with an equivalent circuit that includes the CPE. \( R_{ct} = 10 \, \Omega \), \( C_{dl} = 1 \times 10^{-5} \, \text{F} \), \( \alpha = 0.9 \), \( R_{ct} = 1 \times 10^{6} \, \Omega \), a frequency range from 1 Hz to 100 kHz, and 15 points per decade. Nyquist plot (a) Bode module and phase (b upper and lower) and \( Z' \) regression (c).

Assuming as a first approach that \( 1/R_{ct} \) is going to be negligible above one hundred times this value, it can be established that eq 10 is going to be more precise for \( f > 35 \, \text{Hz} \). This frequency is marked in Nyquist and Bode diagrams. A graph of \( Z' \) vs \( f^{-\alpha} \), above this frequency, Figure 2c, shows a very good fitting to a straight line, getting a regression coefficient \( (R^2) \) of unity and y-intersection = 9.9833 \( \Omega \), i.e., an error of \(-0.167\% \) relative to the exact value (10 \( \Omega \)). In contrast, as also evidenced in Figure 2c, a graph of \( Z' \) vs \( f^{-1} \) shows obvious deviations from the linear tendency for the same frequency range and gives a lower regression coefficient (0.9979) and a higher error (3.42\%) in the \( R_{ct} \), estimated value of 10.3417 \( \Omega \). It is important to remark that the frequency range employed for the linear regression was the same in both cases, ranging from 35 and 39.8 Hz (the next immediate frequency from 35 Hz) to 100 kHz.

It is worth noting that the relevance of having a way to calculate a critical frequency that lets us to define the frequency range, where the linear approximation is going to be more precise. Until now, the way to define this range in practice was arbitrary and dependent on the appreciation of the analyst, with the added drawback of using a wrong correlation in \( f^{-1} \). The results showed in this work permits us to suggest concrete improvements to the current methodology for accurate \( R_{ct} \) measurements.

### 3.3. Case 2: \( 1/R_{ct} \) is Not Negligible

This corresponds to situations where \( R_{ct} \) is low so a clear semicircle tendency in the Nyquist plot is observed. This implies the presence of electrochemical reactions at the surface of the electrodes, like evolving of \( \text{H}_2 \) or \( \text{O}_2 \) that are produced by high polarization potentials or high amplitude signals.

In this case, reciprocal of \( R_{ct} \) cannot be neglected and complete real component mathematical expression, eq 4, should be considered. This makes the correlation of \( Z' \) with the frequency more complex. As an example to illustrate this situation, we have simulated spectra considering the same parameter values used in simulation on case 1 (\( R_{ct} = 10 \, \Omega \), \( C_{dl} = 1 \times 10^{-5} \, \text{F} \), \( \alpha = 0.9 \), a frequency range from 1 Hz to 100 kHz, and 15 points per decade) but changing \( R_{ct} = 50 \, \Omega \), i.e., a low value. The resulting spectra are shown in Figure 3.

Here, we can see in the Nyquist plot a well-defined semi loop, whose diameter corresponds to the value of \( R_{ct} \) and the high-frequency limit is \( R_{ct} \). The height is slightly lower than the half of the diameter because of the nonideal capacitance (\( \alpha = 0.9 \)). Respective Bode plots confirm the predominance of the capacitive contribution in the mid-frequency range and the resistive contribution in the lowest and highest frequency range. These are the typical spectra obtained in real systems when electrochemical reactions are taking place at the surface of solid electrodes. The plot of \( Z' \) against \( f^{-\alpha} \) and \( f^{-1} \), Figure 3c, shows that both traces are remarkably nonlinear in the whole range of frequencies: Up to three regions of different and variable slopes are evidenced, making uncertain any extrapolation. The estimation of \( f_c \) for this set of simulation parameters shows that the linear approach for \( f^{-\alpha} \) will be more precise for \( f > 162 \, \text{kHz} \), which is beyond the simulated high-frequency limit (100 kHz) and is difficult to obtain experimentally without the influence of measurement artifacts. As a consequence, it is not recommended to obtain \( \kappa \) estimations by this method in the presence of reactions on the electrodes. This means that measurements should be made at the open circuit potential OCP or low polarization and small amplitudes on inert electrodes.

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linear another parameter with the same value as depicted above. Then, kHz to obtain as demonstrated in previous sections, we decided to evaluate its fitting comprises low frequencies that are out of the range, where f−α is negligible. To confirm this, new simulations were done with the same parameters than the above, but this time, fs was estimated and employed for each simulated spectrum to define the appropriate frequency range to apply the linear approach with f−α. Once this range for each spectrum is defined, linear fitting was applied on it to estimate Rc. The results are shown in Figure 5.

It is evidenced that in this case, the new proposed fitting for f−α gives always better results compared with the actual estimation with f−1. Here, we observe that the estimation of Rc by using the extrapolation with f−α is very close to the exact value, while the extrapolation with f−1 gives larger deviations when Rc is high. These deviations are reduced with small values of Rc and become close to that produced by the f−α extrapolation. The fact that the deviations are lower for low Rc is attributed to the fact that Rc is the high-frequency limit of Z′, so that the higher the frequency, the more accurate the approximation should be. However, the number of frequencies that can be included in the fitting, according to this method, is lower for the lower values of Rc (see Table 1), making it, as a consequence, less robust. Another drawback is that, in practice, measurements with conventional potentiostats usually present artifacts that introduce additional experimental deviations for f > 10 kHz. Thus, the recommendation is to do the fitting in the frequency range, where 1/Rc becomes negligible but including if

3.4. Influence of Rc. Because Rc is an important parameter, as demonstrated in previous sections, we decided to evaluate its effect in a wide range of Rc estimations. Thus, we simulated impedance spectra with Rc ranging from 100 Ω to 100 kΩ, and another parameter with the same value as depicted above. Then, linear fitting was applied for all of the spectra between 1 and 100 kHz to obtain Rc. The results are presented in Figure 4.

In this graph, it is worth remarking that the estimation using f−α is significantly more precise for high Rc values (Rc ≥ 1 kΩ), but it presents large deviations for the low ones. It is attributed to the fact that the range of frequencies considered to do the linear fitting comprises low frequencies that are out of the range, where

![Figure 3. Simulated spectra with an equivalent circuit that includes the CPE. R = 10 Ω, C = 1 × 10−5 F, R = 50 Ω, α = 0.9, a frequency range from 1 Hz to 100 kHz, 15 points per decade. Nyquist plot (a) Bode module and phase (b upper and lower) and Z′ regression (C).](image1)

![Figure 4. Effect of Rc on Rc estimation at simulated spectra (R = 10 Ω, C = 1 × 10−5 F, α = 0.9, a frequency range from 1 Hz to 100 kHz, and 15 points per decade).](image2)

![Figure 5. Effect of Rc on Rc estimation at simulated spectra (R = 10 Ω, C = 1 × 10−5 F, α = 0.9, a frequency range from 1 Hz to 100 kHz, and 15 points per decade), using fs to define the appropriate frequency range to apply the linear approach with f−α.](image3)

| Table 1. Calculated fs Values, the Number of Frequencies Included at Regression, Intercept Values, and Errors against Nominal Values |
|---|---|---|---|
| Rc (Ω) | fs (Hz) | number of freqs included | error % |
| 100 000 | 0.35 | 34.17 | −0.1670 |
| 31 600 | 1.3 | 10.0139 | 9.9927 | 44 | 1.3989 | −0.0731 |
| 10 000 | 4.5 | 10.0597 | 9.9966 | 36 | 0.5969 | −0.0339 |
| 3160 | 16 | 10.0245 | 9.9986 | 27 | 0.2447 | −0.0137 |
| 1000 | 58 | 10.0117 | 9.9992 | 19 | 0.1167 | −0.0079 |
| 316 | 209 | 10.0059 | 9.9995 | 11 | 0.0587 | −0.0054 |
| 100 | 750 | 10.0031 | 9.9995 | 3 | 0.0307 | −0.0046 |

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possible the lowest frequencies in this range. Table 1 reports the calculated $f_c$ and the relative error in the estimation of $R_s$.

It is worth remarking that errors for the $f^\alpha$ extrapolation method are, for all of the $R_s$ values tested here, at least one order of magnitude smaller than those observed for the $f^{-1}$ method. This leads us to the confirmation that the inclusion of the concept of nonideal capacitance (by including a CPE) in the modeling and treatment of impedance measurements permits us to obtain a more accurate estimation of $R_s$ and, as a consequence, a more accurate estimation of $\kappa$. This is a very relevant issue for $\kappa$ measurements of certain systems like high-purity water.2,6 These results also remark the relevance of obtaining the cutoff or critical frequency to establish the adequate frequency range to do the linear fitting.

### 3.5. Influence of $\alpha$.

To make analysis of nonideal capacitance, particularly $\alpha$ effects on impedance spectra, simulations were carried out at similar conditions to that in case 1a ($R_s = 10 \, \Omega$; $R_{ct} = 100 \, k\Omega$; $C_{dl} = 10^{-5} \, F/cm^2$, frequency range from 1 Hz to 100 kHz, and 15 points per decade), but changing $\alpha$ from 0.95 to 0.7 (lowest typical value for solid electrodes in aqueous media). Figure 6 shows the resultant spectra.

**Figure 6.** $\alpha$ effect on simulated impedance spectra: Nyquist plot (a); Bode module and phase (b upper and lower).

Slight changes are observed in the size of the spectra, getting smaller when $\alpha$ is reduced. In experimental spectra, it occurs when surface roughness increases, provoking a more heterogeneous solid–liquid interface. Some authors have also related this parameter $\alpha$ to the fractal dimension parameter.13 Data treatment similar to that already employed above, calculating $f_c$ for each spectrum from the parameters of the equivalent circuit and then selecting from the highest $f_c$ the frequency range (44 points, from 136 Hz to 100 kHz) to do linear fitting, the values of which are presented in Table 2.

### Table 2. $\alpha$ Effect on the Calculated $f_c$ Values, Intercept Values, and Errors against Nominal Values

| $\alpha$ | $f_c$ (Hz) | $f^{-1}$ method | $f^{-\alpha}$ method | $f^{-1}$ method | $f^{-\alpha}$ method |
|---------|-----------|------------------|----------------------|------------------|----------------------|
| 0.95    | 1.2653    | 10.0399          | 9.9964               | 0.399            | −0.0361              |
| 0.90    | 0.3479    | 10.1440          | 9.9977               | 1.440            | −0.0231              |
| 0.85    | 0.1156    | 10.2767          | 9.9986               | 2.767            | −0.0145              |
| 0.80    | 0.0388    | 10.4178          | 9.9991               | 4.178            | −0.0089              |
| 0.75    | 0.0153    | 10.5542          | 9.9995               | 5.542            | −0.0053              |
| 0.70    | 0.0035    | 10.6782          | 9.9997               | 6.782            | −0.0030              |

It is evidenced that linear fitting with the $f^{-\alpha}$ method is always superior in accuracy to that based on the $f^{-1}$ method: Relative error for the $f^{-\alpha}$ method is one up to three orders of magnitude smaller than that for the $f^{-1}$ method. In addition, $f^{-\alpha}$ is more accurate for lower values of $\alpha$. It means that the more nonideal the capacitance is, the better results the proposed method gets. On the contrary, the $f^{-1}$ method gives larger errors for smaller values of $\alpha$, and only works well for ideal capacitances.

### 3.6. Experimental Example.

This methodology was applied to experimental data, whose spectra are shown in Figure 7.

The studied solution was a calibrated solution of KCl with a certified value of 1000.3 ± 1.0 $\mu$S/cm. Impedance plots show spectra with a similar form than that of Figure 2, but more depressed (smaller slope) and in a narrower frequency range. Fitting of the spectra gives the following values for the parameters of the equivalent circuit model: $R_s = 2127 \, \Omega$; $R_{ct} = ...
1.2 × 10^7 Ω, \( C_0 = 4.3 \times 10^{-5} \text{ F} \), \( \alpha = 0.82 \). From these, the estimation of the critical frequency gives \( f_c = 4.1 \times 10^{-5} \text{ Hz} \). Thus, the graph of \( Z' \) vs \( f^{-\alpha} \) for \( f > 4.1 \times 10^{-3} \text{ Hz} \) should give a linear trend. Such a low cutoff frequency means in this case that all of the available experimental data are in the frequency range that makes valid the assumption that 1/\( R_0 \) is negligible. Indeed, as expected, a line with \( R^2 = 0.9956 \) and y-intercept = 2192.9 Ω is obtained, Figure 7c. In contrast, linear fitting with \( f^{-1} \) for the same range gives a lower correlation (\( R^2 = 0.9858 \)) and y-intercept = 2205.3 Ω.

A difference of 12 Ω approximately can in two possible ways:

1. Constant cell: By using certified value and both \( R_0 \), there is a difference of constant cell of 0.012 cm^−1, which is important and could represent significant bias.

2. Electrolytic conductivity: Considering that this value is employed to estimate \( \kappa \) of an unknown solution, measuring with a cell with a nominal value of 1 cm^−1, \( \kappa \) could be modified from 453.45 to 456.02 μS/cm. This difference is similar to uncertainty reported for some secondary reference materials.14

As a consequence, the recommendation is to use the \( f^{-\alpha} \) approach as an improvement of the \( f^{-1} \) method. Even if from a practical point of view, errors in \( R_0 \) measurements for the \( \kappa \) estimation will be reduced because these are obtained by measuring at two different conditions, additional improvement can be achieved if accuracy in the \( R_0 \) estimation is also improved, as it has been identified as an important issue since Hoover’s work.6,8

4. CONCLUSIONS

Actual methodology to estimate solution’s resistance only considers ideal capacitive contributions to impedance measurements; however, from a more rigorous point of view, neglecting the nonideal capacitive contribution to the real part is not correct and leads to inaccuracy. An improvement is obtained by considering the contribution of a nonideal capacitance (CPE) on the real component and the estimation of a critical frequency that permits us to define a suitable frequency range to do a linear fitting. Analysis indicates that linearity is observed only at the open circuit potential or no electrochemical reaction conditions, by using \( f^{-\alpha} \) instead of \( f^{-1} \) in the abscissa axis. Thus, this condition should be assured to improve accuracy.

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Notes

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