Electrochemical method for measuring corrosion of metals in wood

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Summary

Preliminary studies have shown that electrochemical methods, especially Electrochemical Impedance Spectroscopy (EIS), appear to have great promise for measuring the corrosion rate of metals in wood. One of the major reasons for using these techniques is the ability to maintain moisture content and temperature at conditions encountered in service while measuring the instantaneous corrosion rate. For these reasons, EIS and other electrochemical methods have been investigated at the USDA Forest Products Laboratory in Madison, Wisconsin. This paper discusses progress made and problems encountered in developing electrochemical test methods.

1. Introduction

1.1 Problem

Recently, many designers are choosing to use alternatives to Chromated Copper Arsenate (CCA), including Alkaline Copper Quat (ACQ) and Copper Azole (CuAz). Very little research has been published on the effect of alkaline preservatives on corrosion rates, although researchers think that ACQ and other new preservatives are much more corrosive than CCA, since the percentage of copper in the preservatives has increased. In addition, CCA contains hexavalent chromium and arsenic, both of which typically act as corrosion inhibitors. In contrast, ACQ and other new preservatives do not contain such inhibitors and some formulations of ACQ contain chlorides, which can increase conductivity of wood, increase corrosion rate, and cause pitting corrosion. Unfortunately, no procedure is readily available to quantitatively evaluate the change of corrosion rate with these alternative preservatives. For further information about the effect of new wood preservatives on corrosion and a review of test methods used to measure corrosion in wood, the reader is referred to Zelinka and Rammer (2005a).

1.2 State Of The Art

To the authors' knowledge, only one standard exists that attempts to rapidly assess the corrosion of metal in wood—AWPA E-12 (2004). This standard, developed by the American Wood Preservers' Association, accelerates corrosion by placing a metal coupon between two pieces of preservative-treated wood. This wood–metal assembly is then placed in a conditioning chamber of 49°C ± 1°C (120°F ± 2°F) with a relative humidity of 90% ± 1% for a minimum of 240 h. Whereas this test gives rapid results, it is unclear how the measured corrosion rate relates to performance at ambient temperatures and humidities of wood in service.

2. Preliminary EIS Testing

2.1 Objective

Electrochemical Impedance Spectroscopy appears to have great promise for measuring the corrosion rate of metals in wood (Jack and Smedley, 1987; Bailey and Schofield, 1984). Reasons for using EIS measurements are numerous: ability to maintain moisture content and temperature at conditions encountered in service; ability to measure corrosion rate even if the reaction is diffusion

controlled; ability to design a cell that simulates actual fastener placement; ability to test preservative- and fire retardant-treated wood without polarizing preservative salts; and, most importantly, ability to create an equivalent circuit that models the corrosion process in wood. For these reasons, EIS was investigated as an accelerated test method to determine corrosion rate of metals in contact with wood.

The goal of the preliminary study (Zelinka and Rammer, 2005b) was to prove that EIS could indeed measure corrosion of metals in contact with wood, and therefore only one condition was tested—wood with no preservative treatment, saturated with water.

2.2 Experimental

A schematic diagram for the EIS cell used in the experiment (Zelinka and Rammer, 2005b) is shown in Figure 1. The cell was fabricated from a piece of Southern Pine (*Pinus spp.*) lumber, nominally 100 by 100 mm, to which no preservative treatment had been applied. Before fabrication, the wood was saturated with water by placing it in a pressure chamber. The wood was maintained in this saturated state throughout fabrication and testing. Because the alternating current caused no permanent polarization of the wood, several tests were run in the same wood sample.

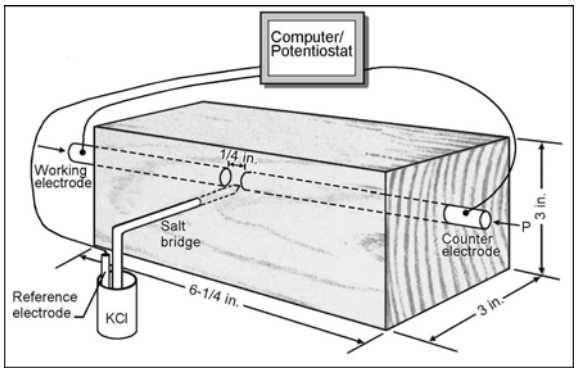

Fig 1 Visual representation of the EIS experiment of (Zelinka and Rammer, 2005b). 1 in. = 254 mm.

The working electrode was made from a plain carbon steel (UNS # G10180) rod with a diameter of 12.7 mm and was only partially exposed. The remainder of the steel rod was insulated by polytetrafluoroethylene (PTFE) tape so that the surface area over which the corrosion was taking place could be measured easily. The PTFE tape was held in place by polymeric heat-shrink tubing. The counter electrode was made from a 12.7-mm diameter graphite rod covered with PTFE tape and heat-shrink tubing. A saturated calomel electrode was used as a reference electrode. The salt bridge was filled with a saturated potassium chloride solution and was fitted with a porous Vycor® (Corning, Incorporated, Corning, New York) tip. The test was run along the grain of the wood because this represented the worse-case scenario for corrosion.

The specimens were conditioned and tested at a temperature of 27°C. The EIS tests were run with a Gamry® potentiostat. The root mean square amplitude of applied voltage was 10mV, and the range of frequencies tested was 3×10^{5}Hz to 1×10^{-1}Hz.

2.3 Results

Impedance from several identical tests confirmed that repeatable data could be obtained using EIS. Figure 2 plots data from one of these replicates in Nyquist format, where the negative of the imaginary (– Im) impedance component is plotted as a function of the real (Re) component. Frequency is plotted implicitly on this type of diagram. The advantage of this format is that, in general, each semicircle on a Nyquist plot represents the time constant of a reaction or a conduction path.

2.4 Discussion

To calculate the corrosion rate from Figure 2, data need to be fit with an equivalent circuit. An

equivalent circuit model treats the material system as a collection of electrical components such as resistors and capacitors placed in series or parallel so that the collection replicates the frequency response of the real system. A key to the equivalent circuit model is that behaviors represented by components in the model can be understood in terms of physical mechanisms.

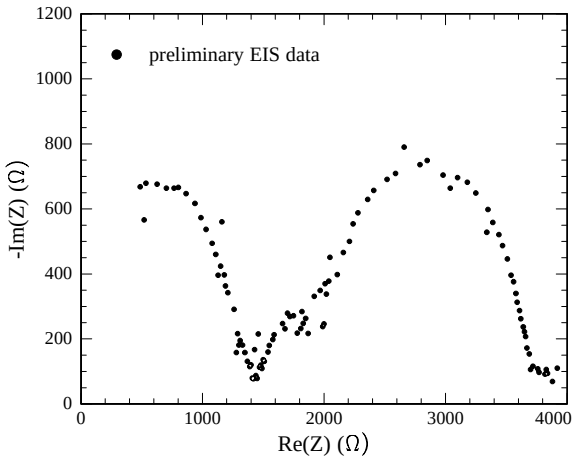

Fig 2 Electrochemical Impedance Spectroscopy (EIS) data, plotted in Nyquist format, from the preliminary EIS corrosion test (Zelinka and Rammer, 2005b)

Since this was a pioneering measurement, it was not known a priori what equivalent circuit model appropriately captured these data. For reference, the simplest possible reaction mechanism for corrosion consists of a single time constant with data appearing as a semicircular arc in the complex plane (Jones, 1996), whereas data (Figure 2) show at least three time constants. From this experiment, it was unclear what these extra time constants represented.

Whereas EIS data (Figure 2) have information about the corrosion reaction on the surface of the metal, this information is convoluted with information about electrical and ionic transport through the wood to the other electrode(s). Separating data into the corrosion reaction and electrical transport is a formidable task and requires a better understanding of the impedance spectra of wood by itself.

2.5 Conclusions

Electrochemical Impedance Spectroscopy measurements were taken on water-saturated wood with a working electrode made of steel to see if this technique could be used to evaluate corrosion of metals in wood. Impedance from several identical tests confirmed that repeatable data could be obtained using EIS. However, the data contained several more time constants than were originally anticipated, and the impedance spectrum could not be correlated to a corrosion rate. Before EIS can become a viable corrosion test method, a thorough understanding of the impedance of wood and wood metal interfaces is needed.

3. Baseline EIS Measurements at 12% Moisture Content

3.1 Introduction

As stated earlier, one key to development of an EIS corrosion test is an understanding of impedance spectra of wood and an equivalent circuit model for the case where no corrosion is occurring. Impedance spectra of Southern Pine (*Pinus spp.*) wood equilibrated to 12% moisture content were taken and an equivalent circuit model was fit to the data.

The primary objective of this series of measurements was to develop an equivalent circuit model of the electrical properties of wood at 12% moisture content, which could be used as a starting point for modeling the corrosion reaction in wood. Furthermore, this experiment was intended to clarify the role of the wood–metal interface in electrical measurements by observing how parameters in the model change with pressure (between the wood–metal interface) and electrode spacing. This understanding of the wood–metal interface could suggest an optimal electrode configuration for electrochemical corrosion measurements in wood.

3.2 Experimental

The experiments were carried out in a manner similar to previous EIS corrosion measurements conducted in wood. A schematic of the test setup is shown in Figure 1. Since the major objective of the study was to measure baseline impedance spectra of wood when no corrosion is occurring, graphite was used for both working and counter electrodes. Also, since the same material (graphite) was being used for both working and counter electrodes, there was no need for a reference electrode (Mansfield, 2003). The lead for the reference electrode was attached to the counter electrode, which resulted in all measurements being taken at zero volts with respect to the open circuit potential. Measurements were made with a Gamry® PCI4-300 potentiostat (Gamry Instruments, Warminster, Pennsylvania). The root mean square amplitude of the applied voltage was 10mV, and the range of frequencies tested was 3×10^{5}Hz to 1×10^{-1}Hz.

Two quantities were varied independently in this study—electrode spacing and contact pressure—and their effects on the equivalent circuit model were studied. Distance between electrodes varied from 3.18 to 25.4 mm and the pressures were varied from 1.55 to 14.0 MPa. In all, 44 impedance spectra were collected. Since preliminary EIS data contained several distinct relaxation times, the authors believed that one of these relaxation times might represent partial charge transfer at the interface because solid electrodes are in imperfect physical contact with a solid material. The authors hypothesized that an increase in pressure would force these electrodes into better contact and minimize the effect of the wood–metal interface. Because it is unclear from the literature whether increasing contact pressure of the electrodes affects the bulk electrical properties of wood, measurements were taken over various electrode spacings at all pressures. By taking measurements at several distances, a resistance vs. distance curve can be generated. Extrapolating this curve to zero electrode spacing gives contact resistance. It would then be possible to compare how this extrapolated contact resistance changes with pressure.

3.3 Results and Discussion

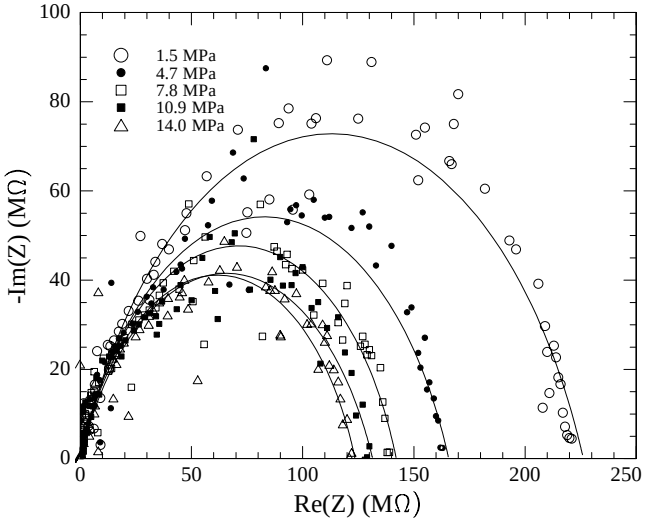

Fig 3 Representative family of impedance spectra (6.35 mm) represented in the complex plane. Data points represent collected data, and solid lines represent predicted behavior from the equivalent circuit model (Fig 4).

In all, 44 impedance spectra were collected, and a representative family of curves with an electrode spacing of 6.35 mm are shown in Figure 3. The solid lines show data fits from the equivalent circuit model discussed below.

Impedance data in Figure 4 all appear as single arcs on the complex plane, which means that each set of data is governed by a single relaxation mechanism (Jones, 1996). Furthermore, that these arcs regress through the origin implies that contact resistance is negligible for all pressures tested.

Data were modeled with a constant phase element (CPE) in parallel with a resistor (Figure 4). The constant phase element acts like a capacitor with a small distribution of relaxation times and is frequently used in electrochemistry to model inhomogeneous systems.

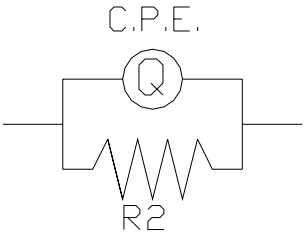

Fig 4 Schematic diagram of 2-Parameter CPE model, the resistor labeled "R2" represents the direct current resistance of the material, and the CPE, represented by a "Q" on the circuit diagram, is a measure of the capacitance of the bulk system

Key parameters of this model are the direct current resistance (R_2) and the mean time constant, τ_o, which is given by Equation 1 where Y_o is the magnitude of the CPE and n is the CPE exponent, which is related to the width of distribution of relaxation times.

$$\tau_o = \left(R_2 Y_o\right)^{1/n} \qquad [1]$$

The mean time constant, τ_o, is a size-independent materials parameter and is a measure of how quickly dipoles can align themselves to the electric field. The R_2 parameter should depend linearly with distance, as resistance, R, of any material is commonly given by Equation 2 where L is the distance between electrodes, A is the cross-sectional area, and ρ is resistivity, a materials parameter.

$$R_2 = \rho \frac{L}{A} \qquad [2]$$

Mean relaxation time, τ_o, is shown as a function of pressure in Figure 5. Given that the dielectric properties of wood are strongly influenced by the presence of water (Skaar, 1988; Brown et al., 1963), it is possible that pressure might be affecting partitioning of water among various chemically and physically distinct sites within cell walls. Significantly, relaxation time, which decreases with increasing pressure, approaches an asymptote at pressures above about 6 MPa. Perhaps saturation is reached as the type of site favored by high pressure becomes fully populated. An alternative explanation would be that pressure directly influences polarization kinetics. By examining effects of both pressure and humidity, we might possibly isolate the degree to which water is involved in this phenomenon. If change in relaxation time indeed is due to a repartitioning of location of water within the cell wall, electrical impedance spectroscopy may be a sensitive method for investigating this partition.

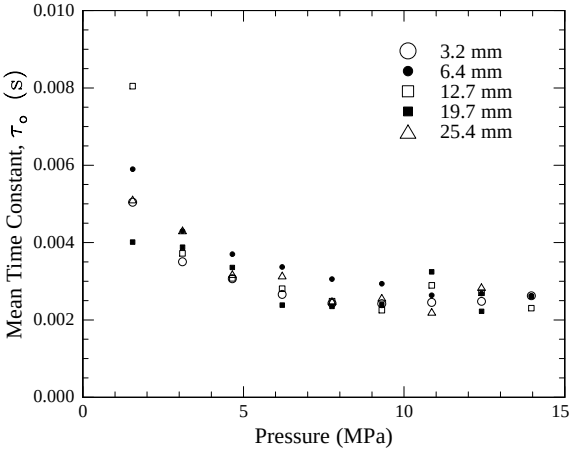

Fig 4 Mean relaxation time, τ_o, as a function of contact pressure for various electrode spacings

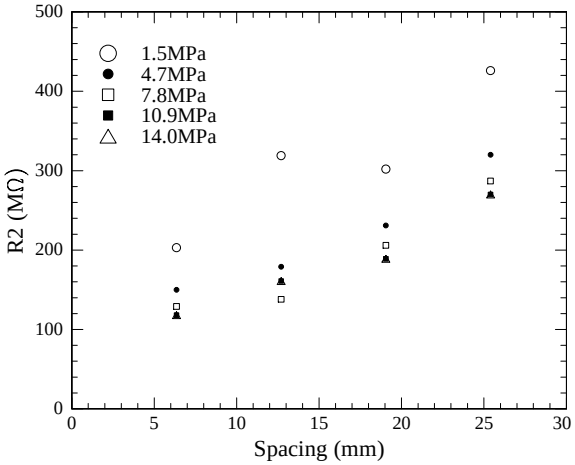

Fig 5 R_2 as a function of electrode spacing for several pressures

As stated earlier, DC resistance of the specimen is determined by R_2. A number of authors have measured DC resistance (Vermaas, 1975; Skaar, 1964; Okoh, 1977) using other methods and have sometimes reported that DC resistance includes an interfacial term. In Figure 5, R_2 is plotted as a function of electrode spacing, and indeed, resistance appears to approach a finite value at zero electrode spacing, consistent with presence of an additional interface resistance. However, a more careful examination of data reveals that a much more likely explanation for this (apparent) intercept is fringe effects associated with electric fields between electrodes.

According to Slogget et al. (1986), the approximate solution for parallel plate capacitors including fringe effects is

$$C = C_{elem}(1 + \frac{2d}{\pi r}\ln(\frac{2e\pi r}{d})) \tag{3}$$

where $C_{elem} = \mathrm{Re}(\varepsilon)\varepsilon_0 A/d$ is the value of capacitance given in elementary treatments. Here, ε_o is the permitivity of free space, $A=\pi r^2$ the area of the plate, and d the spacing between plates. Likewise, we can analyze R_2 with a similar equation, noting that $1/R_2$ has the same dependence on r and d that the capacitance does. Thus, we may write

$$\frac{1}{R_2} = \frac{1}{(R_2)_{elem}}(1 + \frac{2d}{\pi r}\ln(\frac{2e\pi r}{d})) \tag{4}$$

where $1/(R_2)_{elem} = \omega\,\mathrm{Im}(\varepsilon)\varepsilon_0 A/d$ is admittance estimated from an elementary treatment in which current is assumed to flow entirely through the cylindrical region between electrodes. We can show that these equations fit the data well, and that the (apparent) intercept is likely an artifact of fringing effects.

3.4 Conclusions

This research focused on the simple case of electrical contact between wood and metal (graphite) in which there are no added wood preservatives and metal does not corrode. Data generated herein can be used as a starting place for understanding and modeling the more complicated situation of corrosion in the presence of wood preservatives, especially when augmented with additional data exploring effects of humidity and pressure. Specifically, the equivalent circuit model for corrosion in wood under these conditions should contain a CPE in parallel with a resistor representing the underlying electrical transport in wood.

It appears that, for all the parameters that depend on pressure, they become less sensitive at pressures above 6 MPa. Keeping in mind that these parameters depend on pressure, it appears that consistent readings may be obtained if measurements are made at pressures above 6MPa.

4. Baseline EIS Measurements at 20% Moisture Content

4.1 Introduction

To explore the relationship of moisture content on impedance spectra of wood, an identical series of measurements were conducted on Southern Pine equilibrated to 20% moisture content.

4.2 Results and Discussion

In all, 44 impedance spectra were collected and a representative family of curves with an electrode spacing of 6.35mm is shown in Figure 6. Solid lines show data fits from the equivalent circuit model discussed below.

Visual comparison of Figure 6 with data taken at 12% MC (Figure 3) immediately reveals several key differences in the spectra. First, both $-\mathrm{Im}(Z)$ and $\mathrm{Re}(Z)$ are roughly a factor of 100 lower than

their 12% MC counterparts. This is hardly surprising as it is well documented that electrical properties of wood are strongly influenced by moisture content (Skaar, 1988; Brown et al., 1963). Second, 20% MC data appear less noisy than 12% MC data, which is probably because impedances of 12% MC data were on limits of detection by the equipment. Third, data contain a linear region at low frequencies, which is indicative of a diffusive type process (MacDonald and Johnson, 1987). If we treat the diffusion layer as infinite, impedance of diffusion can be represented by the Warburg equation, which relates diffusion coefficients of ions in the wood to impedance response.

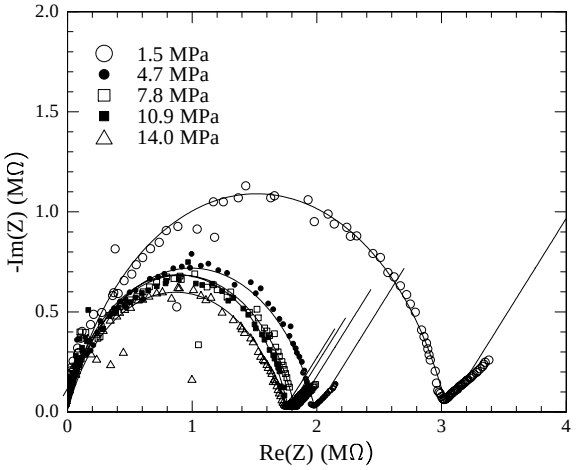

Fig 6 Representative family of impedance spectra (6.35 mm) represented in the complex plane. Data points represent collected data, and solid lines represent predicted behavior from the equivalent circuit model (Fig 7)

Since current data exhibit a similar high frequency response to 12% moisture content data, it makes sense to use the CPE model that described 12% moisture content data and add a Warburg element in series with the resistor to account for low frequency behavior. Adding a Warburg element to this model results in the equivalent circuit shown in Figure 7. The model shown in Figure 7 is standard and often used in literature to describe reactions partially controlled by diffusion (Mansfeld et al., 1993; Jones, 1996; MacDonald and Johnson, 1987). Results of this model are shown as overlays in Figure 6.

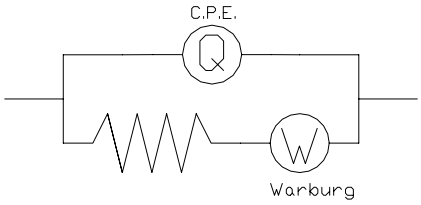

Fig 7 Equivalent circuit model for 20% moisture content data

It may be possible to relate values of the Warburg impedance to diffusion coefficients of ions through wood found with different techniques. If such a relationship could be developed, it would add credence to the belief that wood is an ionic conductor. Also, it may be possible to isolate ions actually involved in electricity conduction.

4.3 Conclusions

This research focused upon the simple case of electrical contact between wood and metal (graphite) in which there are no added wood preservatives and metal does not corrode. We found that to model data at 20% moisture content, the equivalent circuit model that fit the 12% moisture content data needed an additional parameter. This additional parameter, the Warburg impedance, represents a diffusive motion of charge carriers through the wood. Assuming the activation energy for diffusion decreases with increasing moisture content, it is likely that this diffusive behavior was not observed in the 12% moisture content data because ions were not able to dissociate at this moisture content. Further evaluation of the Warburg impedance could lead to a better understanding of electrical conduction in wood.

5. Concluding Remarks

Electrochemical Impedance Spectroscopy appears to have great promise for measuring corrosion rate of metals in wood. Data collected from preliminary testing could not be related to corrosion

rate because of gaps in understanding the impedance properties of wood. Therefore, similar experiments were carried out on wood with inert electrodes. From these experiments, equivalent circuit models of electrical conduction in wood were generated. These models will be the starting point to interpreting future EIS corrosion tests in wood.

6. References

[1] Zelinka, S.L.; Rammer, D.R. 2005a. *Review of test methods Used to determine the corrosion rate of metals in contact with treated wood.* Gen. Tech. Rep. FPL–156. Madison, WI: USDA Forest Service, Forest Products Laboratory.

[2] AWPA. 2004. *Standard Method of Determining Corrosion of Metal in Contact with Treated Wood.* AWPA E12-94. Selma AL: American Wood Preservers' Association.

[3] Jack, E.J.; Smedley S.I. 1987. Electrochemical study of the corrosion of metals in contact with preservative treated wood. *National Association of Corrosion Engineers* 43(5): 266–275.

[4] Bailey, G.; Schofield, M.J. 1984. Corrosion of metal fastenings in CCA-treated timber-the corrosion science assessment. *Journal of Institute of Wood Science* 10(1): 14–18.

[5] Zelinka, Samuel L. and Rammer, Douglas R. 2005b. The Use of Electrochemical Impedance Spectroscopy (EIS) To Measure the corrosion of metals in contact with wood. *TMS Letters* 2(1):15-16.

[6] Jones, Denny A. 1996. *Principles and Prevention of Corrosion.* 2nd ed. Saddle River, NJ: Prentice Hall; 1996. 572 pages.

[7] Mansfeld, F. 2003. Electrochemical Methods of Corrosion Testing. *ASM Handbook Volume 13A. Corrosion: Fundamentals, Testing, and Protection.* Materials Park, Ohio: ASM International; pp. 446–462.

[8] Skaar, C. 1988. Electrical properties of wood. In: Skaar, Christen. *Wood-Water Relations.* Berlin; New York: Springer-Verlag.

[9] Brown, J.H.; Davidson, R.W.; Skaar, C. 1963. Mechanism of electrical conduction in wood. *Forest Products Journal* 13(10): 455–459.

[10] Vermaas, H.F. 1975. Experimental variables affecting the measurement of the DC resistance of wood. *Holzforschung* 29(4): 140–144.

[11] Skaar, C. 1964. Some factors involved in the electrical determination of moisture gradients in wood. *Forest Products Journal* 14(6): 239–243.

[12] Okoh, I.K.A. 1977. Moisture dependence of DC electrical resistivity of some Ghanaian woods. *Technical Bulletin of the Forest Products Research Institute*,-Ghana. 1(2): 33–41.

[13] Slogget, G.J.; Barton, N.G.; Spencer, S.J. 1986. Fringing fields in disc capacitors. *Journal of Physics A: Mathematical and General* 19(14): 2725–2736.

[14] MacDonald, J.R. and Johnson, W.B. 1987. Fundamentals of impedance spectroscopy. In: MacDonald, J. Ross. *Impedance Spectroscopy Emphasizing Solid Materials and Systems.* John Wiley & Sons. A Wiley-Interscience Publication; pp. 1–26.

[15] Mansfeld, F.; Shih, H.; Greene, H., and Tsai, C.H. 1993. Analysis of EIS data for common corrosion processes. Electrochemical Impedance: Analysis and Interpretation, *ASTM STP 1188*. Philadelphia: American Society for Testing and Materials; pp. 37–53.

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