Review of Newman’s Analytical Series on Disk Electrodes

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Abstract

Dr. John S. Newman, an expert and pioneer in electrochemical engineering, studied the electrical characteristics of disk electrodes extensively since the 1960s. Newman and his colleagues published the results in a series of articles in the Journal of the Electrochemical Society. This seminal series is consistent and well-written, and has been cited by many in electrochemistry and closely related fields. However, the articles, especially the later ones in the series, enjoined less familiarity in other fields, including biomedical engineering in which electrodes became widely used in neural stimulation. The purpose of this review is therefore to summarize Newman’s work on disk electrodes together and provide a comprehensive understanding of the original articles. The review mainly focuses on the behaviors of interest to neural stimulation, namely the primary distribution, frequency dispersion, and the current step and voltage step responses. More mathematical details are supplemented to the original calculation to help the readers follow the derivation more easily. Several adjustments are made to Newman’s original analyses. First, the equation sets are summarized into matrix form, which demonstrates the underlying structure of the electrode-electrolyte system. This formulation is helpful in showing the similarity and differences between different inputs discussed. Also, the normalization factors to give dimensionless variables have been slightly scaled by π/4 compared to the original articles, which endows them the representation of physical quantities. A consistent symbol naming system is used to refer to the results from different articles. Finally, some preliminary analyses are presented on the numeric accuracy of the solutions. The review will provide a
comprehensive understanding of the original articles, especially in the context of neuroengineering applications..

Acknowledgments

The first version of this review was completed in early 2012 at the University of Southern California (USC). In 2013, a shortened version only containing the primary distribution and current step response was planned as supplementary materials for the article by Wang et al., (2014); it was ultimately not submitted due to the revision of the manuscript shortening the length and reducing significant amount of discussion on the analytical framework by Nisancioğlu and Newman (1973a), and also due to the journal’s policy of not allowing online supplementary material. The review was further revised in 2015 and subsequently included as Chapter 6—Supplementary Materials in B. Wang’s dissertation, Investigation of the Electrode-Tissue Interface of Retinal Prostheses, Department of Biomedical Engineering, USC, Los Angeles, CA, USA, May 2016, ProQuest Dissertation No. 10124439. The authors acknowledge support from USC under a Viterbi Fellowship, the Biomimetic MicroElectronic Systems Engineering Research Center (BMES ERC) of the National Science Foundation (NSF) under Grant EEC-0310723, and the National Institutes of Health (NIH) under Grant U01 GM104604.

This current version includes an expanded introduction, reorganization of contents and additional analysis, correction of mathematical terminology and further supplementation of details, and editing of the text and remaking of figures. Critical comments on the contents and suggestions on improvement are most welcome!
**Introduction**

Dr. John S. Newman, an expert and pioneer in electrochemical engineering, studied the electrical characteristics of disk electrodes extensively since the 1960s. By applying his ability to reduce complex problems to their essential core elements and mastery of mathematical analysis (Newman and Battaglia, 2018, 2019), the system of equations describing the disk electrodes was solved analytically with ease and elegance. The results were published by Newman and his colleagues in the *Journal of the Electrochemical Society* and the articles formed a seminal series on this topic, which was well-written, consistent, and cited by many in electrochemistry, electrochemical engineering, and closely related fields. In the field of biomedical engineering, electrodes have become widely used in neural engineering applications. While the first article in Newman’s series on the electrolyte’s access resistance of the disk electrode [1] is well known, the series as a whole, and especially the later articles, enjoued less familiarity in the biomedical fields. Not only were many recent studies not placed into the context of these later publications by Newman et al., the wheels were sometimes completely reinvented with modern numeric and analytical methods.

The purpose of this review is therefore to summarize Newman’s work on disk electrodes together and provide a comprehensive understanding of the original articles, which are listed and introduced in the next section. The review mainly focuses on the behaviors of interest to neural stimulation, namely the Primary Distribution [1], Frequency Dispersion [3] and the Current Step [4] and Voltage Step [5] responses. The primary distribution is determined by ohmic resistance of the electrolyte; it occurs at the very beginning of a pulse when a voltage or current input is applied to the electrode and serves as the basis for other types of responses. The frequency dispersion is relevant for alternating current (AC) stimulation, such as transcranial AC stimulation (tACS) and kHz stimulation for nerve block. The step responses are relevant for transcranial direct current stimulation (tDCS) and the most commonly used form of stimulation using current- or voltage-controlled rectangular pulses, which are superposition of step inputs with various delays and amplitudes; responses to arbitrarily-shaped pulse waveforms can also be obtained from the step response (Wang et al., 2014).

Disk electrodes are used differently in electrochemistry and neuroengineering applications, such as having specific geometric configurations, being fabricated with distinct materials, and interfacing with electrolyte of different properties. As the titles of many articles in the series state, disk electrodes are often rotated in electrochemical engineering studies, which establishes a steady field of convection in the electrolyte to support relatively fast electrochemical reactions that would otherwise be limited by diffusion alone. Electrodes in neuroengineering, however, emphasize foremost safety and biocompatibility, and thus avoid movements and electrochemical reactions as much as possible. The inert materials, small amplitudes of electrode polarization, and short pulse widths or low pulse rates of many stimulation paradigms, however, prove ideal for placing neuroengineering electrodes into Newman’s framework in which the diffusion layer is neglected and the interface is linearized for deriving analytical solutions, as is further discussed below in
the comments on [2] and when the electrode-electrolyte model is introduced and solved. The implanted microelectrodes also interface with limited electrolyte space and thus the environment is quite different compared to electrochemical cells. However, the behavior of the interface is dominated by the electrolyte in the vicinity of the electrode surface, and due the contrast between the less conductive surrounding tissue and the conductive fluids with which the electrodes typically directly interfaces, such as the perilymph, vitreous humor, and cerebral spinal fluid, many of the ideal geometric assumptions in the analytical framework can be translated to realistic situations with fairly good accuracy.

Several adjustments and additions are made to Newman’s original analysis. First, the equation sets are summarized into matrix form, which demonstrates the underlying structure of the electrode-electrolyte system, placing the problem in the context of spectral analysis. This formulation is also helpful in showing the similarity and differences between the three different inputs analyzed in this review, i.e., sinusoidal voltage input, current step input, and voltage step input, and also provides easier implementation with the help of nowadays computer programs, e.g. MATLAB. Further, the Normalization Factors to give dimensionless variables are defined based on quantities of the primary distribution and therefore have been slightly scaled by $\pi/4 \approx 0.785$ compared to the original articles. This scaling endows the factors the representation of physical quantities, instead of mere normalization purpose. Typical values of the electrode parameters and the normalization factors are given as well, which are presented and discussed following the results in the Primary Distribution section where they are first introduced. Further, a consistent variable and symbol naming system is used to refer to the results across different articles, as given in the Symbol Naming section. Finally, some preliminary analyses are presented on the Numeric Accuracy of the solutions in the broader context of spectral analysis, which include the eigenvalue problem and the spatial distributions of the current density.

This review is suitable for anyone interested in the electrode–electrolyte interface, especially in the context of neuroengineering applications. Dr. Newman’s original derivation was quite concise and omitted many details. We supplemented a significant amount of mathematical calculation to help the readers follow the step-by-step derivation more easily and a mathematical appendix on Legendre functions is provided, thus making this review accessible even to undergraduate students with only intermediate level knowledge in partial differential equations and the relevant physics and chemistry. A numeric appendix containing the solutions to the system of equations is provided. Whereas the presented solutions are specific to the disk electrode in an ideal situation, the principles, such as the decomposition of the spatial components of the solution using orthonormal basis functions and separation of the temporal component into steady state response and transient response, are generalizable to many situations, such as electrodes of other geometry, with protrusion from or recession into the substrate, limited and irregular electrolyte space, and/or nonlinear interface parameters. These principles can be applied to or utilized in solving and optimizing electrode interfaces, before falling back on computational methods to perform brute force or “intelligent” searches to
obtain numeric solutions. After all, “computation is temptation that should be resisted as long as possible” (Boyd, 2001).

**List of Articles in the Series**

Whereas other articles on disk electrodes by Newman and colleagues exists, only those published in the *Journal of the Electrochemical Society* are included here. This is not meant to be an exhaustive list, as some articles on the convective flow or other topics not so closely related to this review are not included. The articles directly covered by this review are numbered, whereas other articles are listed by bullet points.

1. *Resistance for Flow of Current to a Disk*, vol. 113, no. 5, pp. 501–502, 1966a. This is the 1st article on this topic and gives the steady state solution to an ideal disk electrode without considering overpotentials on the electrode surface related to the double layer capacitance, Faradaic reactions, or diffusion. The solution is the primary current density distribution of the current/voltage step input. The voltage-current relationship gives the resistance of the electrolyte that can be obtained experimentally using the interrupter technique, and also provides the normalization factors for the following problems. The rotational elliptic coordinates are introduced to solve the Laplace equation, however due to the simplicity of the primary distribution, few details are given on how to solve the partial differential equations. This article’s steady rate of citation and high citation volume (800 as of July 2019) was discussed by Newman’s colleagues Orazem and Tribollet (2009).

2. *Current Distribution on a Rotating Disk below the Limiting Current*, vol. 113, no. 12, pp. 1235–1241, 1966b. The article addresses how the diffusion layer may shape the current density profile, when the charge transfer reaction but not the double layer charging is considered. Two limiting situations are discussed, namely the current density on the disk when the potential just outside the diffusion layer of the disk surface is uniform, i.e., the primary current distribution determined by ohmic resistance only, and, vice versa, the potential distribution when the current density is uniform. If the current density on the electrode is small compared to the limiting current density determined by mass transport, the concentration overpotential can be neglected and both the ohmic and kinetic resistances determine the secondary current distribution. Further including the mass transport resistance results in the tertiary distribution. Assuming the current density doesn’t become limited by the diffusion layer, its effect is not studied in many later articles in the series, especially those of interest for this review. This article gives more detail on how to solve the Laplace equation in rotational elliptic coordinates, including crucial steps for understanding calculations in later articles.

- *The Diffusion Layer on a Rotating Disk Electrode*, vol. 114, no. 3, p. 239, 1967. A brief follow-up discussion on numeric methods for solutions of the diffusion layer in [2].

- *Current Distribution on a Rotating Disk*, with V. Marathe, vol. 116, no. 12, pp. 1704–1707, 1969. Summary and experimental verification of [2].

3. *Frequency Dispersion in Capacity Measurements at a Disk Electrode*, vol. 117, no. 2, pp. 198–203, 1970a. This article studies sinusoidal voltage input to the disk electrode and it includes the double
layer capacitance and a linearized Faradaic reaction. The effective series resistance and electrode capacitance are calculated as a function of frequency, and include the influence of the charge transfer resistance, which is not modeled explicitly. More details on numeric solution of the Laplace equation are given, which, compared with the following two situations, will show consistency in the solutions when presented in a matrix format.

- **Ohmic Potential Measured by Interrupter Techniques**, vol. 117, no. 4, pp. 507–508, 1970b. The ohmic potential measured by current interruption, i.e., current steps, correspond to the primary current distribution. A discussion on the time constants involved in the discharging of the double layers capacitance is provided.

- **Limiting Current on a Rotating Disk with Radial Diffusion**, with W. H. Smyrl, vol. 118, no. 7, pp. 1079–1081, 1971. Discussion on the effect if diffusion in the radial direction is considered.

- **Detection of Nonuniform Current Distribution on a Disk Electrode**, with W. H. Smyrl, vol. 119, no. 2, pp. 208–212, 1972. Discussion on the implication of the nonuniform current distribution and its detection and measurement.

- **The Error in Measurements of Electrode Kinetics Caused by Nonuniform Ohmic-Potential Drop to a Disk Electrode**, with W. H. Tiedemann and D. N. Bennion, vol. 120, no. 2, pp. 256–258, 1973. Discussion on the consequence the nonuniform potential distribution in the electrolyte above the electrode surface has on the measurements of electrode parameters.

[4] **The Transient Response of a Disk Electrode**, with K. Nisancioğlu, vol. 120, no. 10, pp. 1339–1346, 1973a. This article describes the response to a current step input, and includes the double layer capacitance and a linearized Faradaic reaction. The method decomposes the response into a steady state response and a transient response, the latter being an eigenvalue problem consisting of eigensolutions associated with the different time constants.

[5] **The Transient Response of a Disk Electrode with Controlled Potential**, with K. Nisancioğlu, vol. 120, no. 10, pp. 1356–1358, 1973b. This article describes the response to a voltage step input, using similar technique as described in [4]. The study discusses the different time constant associated with the transient response, especially the zeroth time constant that is unique to the voltage step input.

- **Corrosion of an Iron Rotating Disk**, with N. Vahdat, vol. 120, no. 12, pp. 1682–1686, 1973. Application of the disk electrode model to calculate corrosion rate on iron disk electrodes.

- **An Asymptotic Solution for the Warburg Impedance of a Rotating Disk Electrode**, with R. V. Homsy, vol. 121, no. 4, pp. 521–523, 1974a. Analytical approximation of the Warburg impedance that models the diffusion at the interfaces at high frequencies. Related to [2].

- **The Short-Time Response of a Disk Electrode**, with K. Nisancioğlu, vol. 121, no. 14, pp. 523–527, 1974. Since the transient responses in [4] and [5] involve an infinite set of eigenfunctions, each being
a combination of the infinite set of basis functions, the numeric solution can be very laborious to solve. This article provides an efficient asymptotic solution for the short-time transients.

- **Current Distribution on a Plane below a Rotating Disk**, with R. V. Homsy, vol. 121, no. 11, pp. 1448–1451, 1974b. A stationary disk electrode is placed below the rotating disk. The solution of Laplace equation in rotational elliptic coordinates appears in the electrolyte layer immediately above the electrode.

- **Current Distribution on a Disk Electrode for Redox Reactions**, with P. Pierini and P. Appel, vol. 123, no. 3, pp. 366–369, 1976. Development of the models for the overpotential and diffusion layer. The solution of Laplace equation in rotational elliptic coordinates appears in the electrolyte layer immediately above the electrode.

- **Potential Distribution for Disk Electrodes in Axisymmetric Cylindrical Cells**, with P. Pierini, vol. 126, no. 8, pp. 1348–1352, 1979. Solution for disk electrode with limited electrolyte space.

- **Analytic Expression of the Warburg Impedance for a Rotating Disk Electrode**, with B. Tribollet, vol. 130, no. 4, pp. 822–824, 1983. Analytical expression of the Warburg impedance. Related to (Homsy and Newman, 1974a).

- **Corrosion of a Rotating Iron Disk in Laminar, Transition, and Fully Developed Turbulent Flow**, with C. G. Law, vol. 133, no. 1, pp. 37–42, 1986. The calculation of the potential distribution utilizes the techniques and results of earlier work in the series.

- **The Kramers-Kronig Relations and Evaluation of Impedance for a Disk Electrode**, with M. M. Jakšić, vol. 133, no. 6, pp. 1097–1101, 1986. The impedance spectroscopy of electrodes obey the Kramers-Kronig relation. Based on this relation, the capacitance as a function of frequency [3] can be calculated from the effective electrode resistance, and vice versa.

- **Current Distribution at Electrode Edges at High Current Densities**, with W. H. Smyrl, vol. 136, no. 1, pp. 132–139, 1989. Calculation of the large current density at the electrode’s edge for Tafel kinetics. Related to (Nisancioğlu and Newman, 1974).

- **Corrections to Kinetic Measurements Taken on a Disk Electrode**, with A. C. West, vol. 136, no. 1, pp. 139–143, 1989. Correcting the errors due to the nonuniform current distribution of the electrode and showing the condition under which the errors can be neglected. Related to (Tiedemann, Newman, and Bennion, 1973)

- **Current Distribution near an Electrode Edge as a Primary Distribution Is Approached**, with A. C. West, vol. 136, no. 10, pp. 2935–2939, 1989. Current density at the electrode’s edge when the insulator and electrode have arbitrary angle of intersection, of which the disk electrode is a special case. Related to (Nisancioğlu and Newman, 1974) and (Smyrl, and Newman, 1989).

- **Cathodic Protection for Disks of Various Diameters**, with S. X.-Z. Li, vol. 148, no. 4, pp. B157–B162, 2001. Applying the disk electrode model to cathodic protection.
Model of the Disk Electrode

System of Equations

A disk electrode of radius $a$ is embedded in an infinite large insulating substrate interfacing with a semi-infinite large space of electrolyte of isotropic conductivity $\kappa$. Voltage or current is applied to the metal part of the electrode, which is equipotential, and the ground is located at infinity. A cylindrical coordinate system $(r, \phi, z)$ is established with the origin at the disk center and the $z$ axis pointing perpendicular into the electrolyte space (Figure 1).

As the bulk electrolyte space contains no sources or sinks and no concentration gradients of the solvents, current continuity yields

$$\nabla \cdot J = 0 , \quad r, z \geq 0 ,$$

for the current density $J$. Together with Ohm’s law

$$\vec{J} = -\kappa \nabla \phi = -\kappa \left( r \frac{\partial \phi}{\partial r} \hat{r} + \frac{1}{r} \frac{\partial \phi}{\partial \phi} \hat{\phi} + \frac{\partial \phi}{\partial z} \hat{z} \right) ,$$

where $\hat{r}$, $\hat{\phi}$, and $\hat{z}$ are unit vectors of the coordinate system, Laplace equation holds for the electric potential $\phi(r, \phi, z, t)$

$$\nabla^2 \phi = \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \phi}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 \phi}{\partial \phi^2} + \frac{\partial^2 \phi}{\partial z^2} = 0 , \quad r, z \geq 0 .$$

The second term is always zero as the system is axisymmetric, and the azimuth $\phi$ is omitted in all further analysis. The time variable $t$ is only specifically shown when its inclusion is necessary for disambiguation.

General boundary conditions for the voltage and current that apply to all the situations studied include

$$\begin{cases} \left| \phi(r, z) \right| < +\infty , & r \geq 0, z \geq 0 , \\ \phi(r, z) = 0 , & r, z \to +\infty , \\ J_z(r, z) = J_0(r) , & z = 0^+, r \leq a , \\ J_z(r, z) = 0 , & z = 0, r > a , \end{cases}$$

where $J_0(r)$ and $J_z(r, 0^+)$ denote the normal current density through the electrode surface and axial current density immediately outside the diffusion layer in the bulk electrolyte (Figure 2). These conditions
state that, the potential within the electrolyte is finite, the ground is at infinity, the current density on the electrode surface is continuous with that in the electrolyte, and the substrate is insulating, respectively.

Figure 2. The current density components within the microscopic interface of the electrode consists of capacitive and Faradaic components. The diffusion layer has negligible thickness compared to the dimension of the bulk electrolyte and the current density within this layer is typically considered to be normal to the electrode surface and contains no tangential components. The concentration gradients within the diffusion layer can be represented either as a concentration overpotential or as an impedance (dashed outline). In the Randles circuit, the Warburg element associated with the concentration polarization is typically connected in series with the charge transfer resistance, and the interface’s double layer is connected in parallel with these two elements (dashed line) and often replaced with a constant phase element. The current density is continuous through the interface and diffusion layer and with the normal current density of the bulk electrolyte at the outer border of the diffusion layer.

The above boundary conditions do not directly connect the potential \( \phi(r, z) \) and current \( J(r, z) \) in the bulk electrolyte with the voltage \( V \) or current \( I \) input applied to the electrode. To complete the description of the disk electrode, the electrode voltage \( V \) is related to the bulk electrolyte potential right outside the diffusion layer \( \phi_0(r) = \phi(r, 0^+) \). The difference between the two is defined as the overpotential

\[
V_{OP}(r) = V - \phi_0(r) , \quad r \leq a .
\]  

The overpotential can be considered to consist of two components (Figure 2). A surface/activation overpotential spans across the microscopic interface, within which the double layer charging and Faradaic charge transfer occur. Between the outer boundary of the interface and the inner boundary of the bulk electrolyte, concentration gradients may exist in a thin diffusion layer due to mass transport not being able to replenish or diffuse reactants fast enough to and away from the electrode surface. Due to the thinness of this layer, diffusion and the associated current density is assumed to be only in the normal direction of the electrode surface. Depending on the formalism of the interface model, the influence of the concentration on the potentials can be either described as a concentration overpotential or an equivalent circuit element,
such as the Warburg element associated with charge transfer or as a constant phase element to combine its effect with the double layer (Newman, 2004; Orazem and Tribollet, 2008). Assuming that the current densities across the electrode are small and not limited by mass transport, the concentration gradients are ignored and so is the associated overpotential in the diffusion layer.

The current density due to the charging or discharging of the double layer is described by a differential capacitance

\[ J_{DL}(r) = \gamma \frac{\partial (V_{OP}(r))}{\partial t} , \quad r \leq a , \]

with \( \gamma \) being the double layer capacitance per unit area. The double layer capacitance is voltage dependent and non-linear, deserving a dedicated book chapter to fully discuss its behavior (Newman, 2004), but for simplicity is considered constant in the subsequent analysis.

Under small surface overpotential \( V_{OP} \) (defined with regard to an equilibrium potential), the current density of the charge transfer reaction can be given by a linear approximation

\[ J_{CT}(r) = g_{CT} V_{OP}(r) , \quad r \leq a , \]

where the charge transfer conductance

\[ g_{CT} = (\alpha_a + \alpha_c) j_0 \frac{ZF}{RT} \]

relates to the kinetics of a single Faradaic reaction described by the Butler–Volmer equation. Here, the parameters \( \alpha_a \) and \( \alpha_c \) are the anodic and cathodic charge transfer coefficients, respectively, \( j_0 \) is the exchange current density, \( Z \) is the number of electrons involved in the reaction, \( T \) is the absolute temperature, \( F \) is the Faraday constant, and \( R \) is the universal gas constant. Again, this approximation is a significant oversimplification of the complex behavior of the charge transfer process (Newman, 2004), however, is often sufficient for the chemically-inert electrodes in biomedical applications.

Together, the current densities of the double layer and charge transfer components are part of the boundary condition of current continuity

\[ J_0(r) = J_{DL}(r) + J_{CT}(r) = J_z(r, z) , \quad z = 0^+, r \leq a , \]

Combining (6)–(8) into Eq. (10), the electrode voltage \( V \) and the electrolyte potential \( \varphi_0(r) \) are therefore related by

\[ \gamma \frac{\partial (V - \varphi_0(r))}{\partial t} + g_{EF}(V - \varphi_0(r)) = -\kappa \frac{\partial \varphi(r, z)}{\partial z} , \quad z = 0^+, r \leq a . \]

The total current passing through the electrode \( I \), whether directly applied to the electrode or as a response to an applied voltage input, is given by

\[ I(t) = \int_0^a J_0(r, t) \cdot 2\pi rdr . \]

Thus, the disk electrode system becomes solvable given (3)–(5), (11) and (12).
Rotational Elliptic Coordinates

Given the complexity of the set of equations, it is natural to use Fourier series methods for solving differential equations and expressing the solution based on basis functions. In the cylindrical coordinates, Bessel functions can be used as the basis for the radial coordinates to solve for the primary distribution (Wiley and Webster, 1982), whereas an incorrect choice of the spherical coordinates with spherical harmonics as basis functions will lead to a dead end (Newman and Battaglia, 2018).

The ideal coordinate system for the disk electrode is the rotational elliptic coordinates \((\xi, \eta, \phi)\) as shown in Figure 3, which results from rotating a two-dimensional elliptic coordinate system about the non-focal axis of the ellipse, i.e., the symmetry axis that separates the foci. Particularly, the foci are chosen to be at the edges of the electrode, so that the cylindrical coordinates \((r, \phi, z)\) are related by

\[
\begin{align*}
    r &= a \cdot \sqrt{(1 + \xi^2)(1 - \eta^2)} \\
    z &= a \cdot \xi \cdot \eta \\
    \phi &= \phi
\end{align*}
\]

with \(\eta \in [0,1]\), \(\xi \in [0, +\infty)\), and \(\phi \in [0, +2\pi)\).

Figure 3. The disk electrode and electrolyte space in rotational elliptic coordinates. \(\xi\) is a normalized distance from the “center” of the coordinate system, i.e., the disk electrode, and \(\eta\) is the cosine of the “latitude”, with the electrode and insulator residing on the “equatorial plane”. Reprinted and adapted with permission from Newman (1966a), J. Electrochem. Soc., 113(5), 501. Copyright 1966, The Electrochemical Society.
The rotational elliptic coordinates are an alternative definition of oblate spheroidal coordinates \((\mu, \nu, \phi)\) with \(\xi = \sinh \mu\) and \(\eta = \cos \nu\) (Newman, 1966a; Myland and Oldham, 2005): \(\xi\) is analogous to the radial coordinate in a spherical coordinate system, \(\eta\) is the cosine of the latitude \(\nu\), \(\phi\) is the longitude, the electrode and insulator are on the “equatorial plane”, and the “center” of the coordinate system is not a point as but the entire disk. The inverse relationships of the coordinates is

\[
\begin{align*}
    \xi &= \frac{\sqrt{((\hat{r} + 1)^2 + \hat{z}^2)((\hat{r} - 1)^2 + \hat{z}^2) + (\hat{r}^2 + \hat{z}^2 - 1)}}{2}, \\
    \eta &= \frac{\sqrt{((\hat{r} + 1)^2 + \hat{z}^2)((\hat{r} - 1)^2 + \hat{z}^2) - (\hat{r}^2 + \hat{z}^2 - 1)}}{2},
\end{align*}
\]

with \(\hat{r} = r/a\) and \(\hat{z} = z/a\) as normalized cylindrical coordinates, and the boundaries and axis of symmetry are related to their original definitions by

\[
\begin{align*}
    \begin{cases}
        z = 0^+, r \leq a \\
        z = 0, r > a \\
        r, z \to +\infty \\
        r = 0, z \geq 0
    \end{cases} \Rightarrow \begin{cases}
        \xi = 0^+, \eta \in [0,1] \\
        \eta = 0, \xi \in (0, +\infty) \\
        \xi \to +\infty, \eta \in [0,1] \\
        \eta = 1, \xi \in [0, +\infty)
    \end{cases} \quad (15)
\end{align*}
\]

These lines and other equal-\(\xi\) lines and equal-\(\eta\) lines are also shown in Figure 3.

Laplace equation in rotational elliptic coordinates with axial symmetry becomes

\[
\nabla^2 \varphi(\xi, \eta) = \frac{\partial}{\partial \xi} \left[ (1 + \xi^2) \frac{\partial \varphi(\xi, \eta)}{\partial \xi} \right] + \frac{\partial}{\partial \eta} \left[ (1 - \eta^2) \frac{\partial \varphi(\xi, \eta)}{\partial \eta} \right] = 0 \quad (16)
\]

The current density right above the electrode is given by

\[
I_0(r) = -\kappa \frac{\partial \varphi(r,z)}{\partial z} \bigg|_{z=0^+} = -\frac{\kappa}{a\eta} \frac{\partial \varphi(\xi, \eta)}{\partial \xi} \bigg|_{\xi=0^+} = J_\xi(0^+, \eta), \quad r \leq a \text{ or } \eta \in [0,1] \quad (17)
\]

with \(\eta|_{z=0^+} = \sqrt{1 - (r/a)^2}, \ r \in [0, a]\). On the other hand, on the insulation boundary condition becomes

\[
I_\xi(r, 0) = -\kappa \frac{\partial \varphi(r,z)}{\partial z} \bigg|_{z=0} = -\frac{\kappa}{a\xi} \frac{\partial \varphi(\xi, \eta)}{\partial \eta} \bigg|_{\eta=0} = J_\eta(\xi, 0) = 0, \quad r > a \text{ or } \xi \geq 0 \quad (18)
\]

with \(\xi|_{z=0} = \sqrt{(r/a)^2 - 1}, \ r \in [a, +\infty)\).

Integration of any function \(f\) on the disk surface is given by

\[
\int_0^a f(r, 0) \cdot 2\pi r \, dr \quad \Rightarrow \quad 2\pi a^2 \int_0^1 f(0, \eta) \cdot \eta \, d\eta \quad ,
\]

which is used to calculate the total current or charge on the electrode–electrolyte interface.

**Basis Functions and General Form of Solution**

Using separation of variables, the potential in the electrolyte space is set to
\[ \varphi(\xi, \eta) = N(\eta)M(\xi) \quad , \]  

and Laplace equation (16) then becomes two ordinary second order differential equations

\[
\begin{align*}
&\frac{d}{d\eta}\left[(1-\eta^2)\frac{dN(\eta)}{d\eta}\right] + \lambda N(\eta) = 0 \quad , \\
&\frac{d}{d\xi}\left[(1+\xi^2)\frac{dM(\xi)}{d\xi}\right] - \lambda M(\xi) = 0 \quad .
\end{align*}
\]

Despite the ordering of the rotational elliptic coordinates having \( \xi \) appear first, from here on, the equations and functions involving \( \eta \) are typically placed first as they concern the system’s behavior on the electrode surface and are more important. They are also relatively simpler and easier to handle.

The solutions are Legendre functions for (21) and Legendre functions with imaginary argument for (22). Let \( \lambda = l(l+1) \), then

\[
\begin{align*}
N_l(\eta) &= c_l^{\text{NP}} P_l(\eta) + c_l^{\text{NQ}} Q_l(\eta) \\
M_l(\xi) &= c_l^{\text{MP}} P_l(\xi/i) + c_l^{\text{MQ}} Q_l(\xi/i)
\end{align*}
\]

with \( P_l(\eta) \) and \( Q_l(\eta) \) being the \( l \)th order Legendre functions of the first and second kind, respectively. The boundary conditions (4) and (5) in the new coordinate system yields the following conditions

\[
\begin{align*}
|\varphi(\xi, \eta)| < +\infty \quad &\Rightarrow |N_l(\eta)||M_l(\xi)| < +\infty \quad \forall \eta \in \mathbb{N}^0, \quad c_l^{\text{NQ}} = 0 \\
-\frac{\kappa}{a^2} \frac{\partial \varphi(\xi, \eta)}{\partial \eta}\bigg|_{\eta=0} = 0 \quad &\Rightarrow \frac{dP_l(\eta)}{d\eta}\bigg|_{\eta=0} = 0 \quad \forall \eta \in \mathbb{N}^0 \quad , \\
\lim_{\xi \to +\infty} \varphi(\xi, \eta) = 0 \quad &\Rightarrow \lim_{\xi \to +\infty} M_{2n}(\xi) = 0
\end{align*}
\]

which apply to all situations. For \( M_l(\xi) \), the Legendre functions are evaluated on the imaginary axis. The complex coefficients \( c_{2n}^{\text{MP}} \) and \( c_{2n}^{\text{MQ}} \) are chosen so that \( M_{2n}(\xi) \) is a real function on \( \xi \in [0, +\infty) \) with the first condition in (24) satisfied and normalized so that \( M_{2n}(0) = 1 \). See Appendix A for details on the Legendre functions and a derivation for \( M_{2n}(\xi) \) and \( M_{2n}'(0) \) and their properties, which were omitted in Newman’s original work for brevity (Newman, 1966b, equations [14]–[15] and [19]).

Combining and renaming the coefficients, the general solution can be written in a form of summation

\[
\varphi(\xi, \eta) = \sum_{n=0}^{+\infty} B_n P_{2n}(\eta) M_{2n}(\xi) \quad .
\]

Here, \( P_{2n}(\eta)M_{2n}(\xi) \) are dimensionless and normalized basis functions of the disk electrode system. The coefficients \( B_n \), typically in units of Volts, will be determined for each specific input voltage/current applied to the disk electrode by the equivalent form of boundary condition (11) in rotational elliptic coordinates.

The potential fields in the electrolyte are given for a few basis functions in Figure 4, which are displayed in the original cylindrical coordinates due to the distortion of geometry in rotational elliptic coordinates.
The disk electrode is shown in black in the panels with the flanking insulator substrate in white. The influence in the electrolyte is determined by $M_{2n}(\xi)$ of each basis function. Almost all non-trivial behaviors of the solutions will be limited within very close proximity—less than one times the radius—of the electrode surface, except for the zeroth solution which decays slower and extends its influence to about one order of magnitude further into the solution.

![Figure 4](image)

**Figure 4.** The dimensionless and normalized potential field distribution of some base functions ($n = 0, 1, 4,$ and $9$) in the electrolyte space. The black bar on the bottom of each graph represents the disk electrode. The field of the zeroth basis function is non-negative, non-oscillatory, and penetrates deep into the electrolyte space, while higher order basis function are oscillatory and limited to the proximity of the electrode surface.

Besides penetrating its field into the electrolyte, the zeroth basis function is critical in delivering the current. Notice that $P_0(\eta) \equiv 1$ and

$$\int_0^1 P_{2n}(\eta) d\eta = \int_0^1 P_0(\eta) P_{2n}(\eta) d\eta = \frac{\delta_{0n}}{4n+1} = \delta_{0n}, \quad (26)$$

Therefore, the total current through the electrode is only determined by the zeroth term

$$I = 2\pi a^2 \int_0^1 \left( -\frac{\kappa}{a\eta} \frac{\partial \varphi(\eta, \xi)}{\partial \xi} \right) \eta d\eta$$

$$= -2\pi a \kappa \left( \sum_{n=0}^{+\infty} B_n M'_{2n}(0) \int_0^1 P_{2n}(\eta) d\eta \right) = 4\pi a B_0. \quad (27)$$

The normalized surface potential and current density distributions of the first 11 basis functions are
shown in Figure 5. The zeroth term indicates a steady state of uniform electrolyte potential distribution above the electrode surface, i.e., primary distribution. All the other higher order terms will determine how much the actual distribution will deviate from this distribution without altering the total current. Interestingly, the current distribution of higher order solutions have higher magnitude at both the center and the periphery of the disk, while the lower order ones mainly have high current density at the periphery.

![Figure 5. The potential and current density distribution in the electrolyte on the surface of the electrode of the first 11 basis functions. The current density has a singularity at the edge for each basis function.](image)

**Symbol Naming**

In the upcoming sections, the following convention has been adopted for variable naming, superscripts and subscripts, which also applies to the analysis above.

Table 1 List of symbols, subscripts, and their meaning

| Symbol | Description                                                                 |
|--------|------------------------------------------------------------------------------|
| \( \varphi(r,z) \) | Potential in the electrolyte space                                           |
| \( \varphi_0(r) \) | Potential in the electrolyte immediately outside the diffusion layer: \( \varphi_0(r) = \varphi(r,0^+) \) |
| \( J(r,z) \) | Current density in the electrolyte space: \( J(r,z) = \hat{z} \cdot J_z(r,z) + \hat{r} \cdot J_r(r,z) \) |
| \( J_0(r) \) | Current density through the interface of the electrode: \( J_0(r) = J_z(r,0^+) \) |
| \( V \) | Voltage of the electrode of the interface, general case                       |
| \( V_0 \) | Amplitude of voltage step input, or primary voltage response to current step input |
| \( I \) | Total current flowing across electrode-electrolyte interface, general case |
| \( I_0 \) | Amplitude of current step input, or primary current response to voltage step input |
Table 2 List of superscripts and their meaning

| Superscript | Meaning |
|-------------|---------|
| None        | General situation, e.g., \( \varphi(r, z) \) |
| P           | Primary distribution, e.g., \( \varphi^P(r, z) \) |
| H           | Harmonic oscillation\(^\#\), e.g., \( J_z(r, z, t) = J_z^H(r, z) e^{i\omega t} \) |
| SS          | Steady state response, e.g., \( J_0^{SS}(r) \) |
| TZ          | Transient response, e.g., \( V^{TZ}(t) \) |
| (i)         | The \( i \)th\(^\#\) eigenfunction of the transient response, e.g., \( B_{n}^{(i)} \) |

\(^\#\) The imaginary unit, \( i = \sqrt{-1} \), is given in roman font to distinguish it from the index \( i \), given in italic font.
Primary Distribution (Newman, 1966a)

Current Distribution and Electrode Resistance

This is the solution for the disk electrode without considering the surface overpotential related to the double layer and reaction currents (or infinite large double layer capacitance or reaction conductance depending on type of input). The potential and current distribution is completely determined by the ohmic resistance of the electrolyte. It is the primary distribution at \( t = 0^+ \) for a disk electrode applied with step input of current or voltage. The potential on the electrode is held constant at \( V_0 \), and the boundary condition of the electrolyte potential immediately next to the electrode is

\[
\phi_0^P(\eta) = V_0, \quad \eta \in [0,1],
\]

indicating that

\[
B_n^P = \begin{cases} V_0, & n = 0 \\ 0, & n \neq 0 \end{cases},
\]

which is also obvious from discussion on (27). The solution is the zeroth order basis function

\[
\phi^P(\eta, \xi) = V_0 M_0(\xi),
\]

which can be written in several equivalent forms:

\[
\frac{\phi^P(\xi, \eta)}{V_0} = \frac{2}{\pi} \arctan\left(\frac{1}{\xi}\right) = 1 - \frac{2}{\pi} \arctan(\xi) = \frac{2}{\pi} \arcsin\left(\frac{1}{\sqrt{1 + \xi^2}}\right). \tag{31}
\]

The current density on the disk and total current are therefore

\[
J_0^P(\eta) = J_{0^+}(0^+, \eta) = \frac{2 \kappa V_0}{\pi a \eta}, \tag{32}
\]

\[
I_0 = 4 \kappa a V_0. \tag{33}
\]

The effective series resistance of the electrolyte, also termed access resistance, is

\[
R_S = \frac{V_0}{I_0} = \frac{1}{4 \kappa a}. \tag{34}
\]

The surface current density, as shown in Figure 6, can also be given in the cylindrical coordinates as

\[
J_0^P(r) = \frac{2 \kappa V_0}{\pi \sqrt{a^2 - r^2}} = \frac{\bar{J}_0}{2\sqrt{1 - (r/a)^2}}, \tag{35}
\]

with the average current density given as

\[
\bar{J}_0 = \frac{I_0}{\pi a^2} = \frac{4 \kappa V_0}{\pi a}. \tag{36}
\]
Normalization Factors and Dimensionless Variables

Besides the obvious choice of electrode radius for length normalization, two characteristic quantities are used for normalization in the later calculations of this review. The average electrolyte conductance from the electrode surface ($\xi = 0^+$) to ground ($\xi \to +\infty$) of the primary distribution is

$$\bar{g}_S = \frac{\bar{G}_S}{\pi a^2} = \frac{1}{\pi a^2 R_S} = \frac{4 \kappa}{\pi a}.$$ (37)

The characteristic time constant is

$$\tau = R_S C_{DL} = \frac{\pi \gamma a}{4 \kappa},$$ (38)

with the total double layer capacitance at steady state given as

$$C_{DL} = \gamma \pi a^2.$$ (39)

The characteristic time constant would have typical numbers in the range of microseconds to milliseconds depending on the size and material of the electrode, as well as the electrolyte. Typically values of the double layer capacitance $\gamma$ of metal electrodes are in the range between 10 and 40 $\mu$F/cm$^2$, physiological salines have conductivity $\kappa$ on the order of 0.1~1 S·m$^{-1}$, and electrode size $a$ is in the range between tens of micrometers and several millimeters. As will be seen in the next section, strictly speaking the time constant is frequency dependent as both the resistance and capacitance are. Also local charging and discharging rates differ from the global process, giving rise to local time constants. The validity of the overall time constant is discussed by Oldham (2004) and $\tau$ represents the average local time constant weighted by both area and current density.
With these normalization quantities, several dimensionless quantities are introduced. The dimensionless frequency and time are

\[ \Omega = \tau \omega = \frac{\pi y a}{4 \kappa \omega}, \]  
\[ \theta = \frac{t}{\tau} = \frac{4\kappa}{\pi ay} t, \]

and the dimensionless charge transfer conductance is

\[ G = \frac{g_{CT}}{\bar{g}_S} = (\alpha_a + \alpha_c) \frac{\pi a j_0 n F}{4\kappa RT}, \]

which is similar to \( J \), the dimensionless exchange current density defined by Newman (1996b, 1970b) and Nisancioğlu (1973a,b).

In practice, typical biomedical electrodes have much smaller Faradaic reactions conductance compared to the electrolyte conductance. In the Randles model, the parallel resistance of the Faradaic reactions extracted from impedance spectroscopy is typically in the megaohm to gigaohm range, compared to kilohm values of the series resistance of the electrolyte. This gives several orders of magnitudes difference between the two quantities and hence \( G \) is typically very small, i.e., \( G < 10^{-3} \ll 1 \). Or in terms of conductance per unit surface area, platinum, for example, has \( g_{CT}^{Pt} \approx 34 \mu S \cdot cm^{-2} \) (Richardot and McAdams, 2002), whereas \( \bar{g}_S \approx 0.01 \sim 1 \) S \cdot cm^{-2} with the typical electrode and electrolyte parameters given above. However calculations for \( G = 1 \) and larger values are also performed to identify the general trend.
**Frequency Dispersion (Newman 1970a)**

With AC input on the electrode, the current can pass from the electrode to the electrolyte by either capacitive charging of the double layer or charge transfer via Faradaic reactions. The overall equivalent circuit can be modeled by a capacitive interface, which is often characterized as a constant phase element in spectroscopy, and the electrolyte resistor in series. In this model, there is no explicit model element for the Faradaic conductance, but its effect is accounted for in the frequency dispersion of the double layer capacitance and series resistance of the electrolyte.

The electrode potential is given as

\[ V(t) = V_H e^{i\omega t}, \]  

(43)

and the potential in the electrolyte is normalized with respect to the electrode potential

\[ \varphi(r, z, t) = \varphi_H(r, z)e^{i\omega t} = V_H U_H(r, z)e^{i\omega t}. \]  

(44)

With these quantities, the boundary condition (11) on the electrode therefore becomes

\[ \frac{\partial U_H(\xi, \eta)}{\partial \xi} \bigg|_{\xi=0^+} = -\frac{4(i\Omega + G)}{\pi} \eta \left( 1 - U_H^H(\eta) \right). \]  

(45)

Obviously, the normalized potential distribution \( U_H^H(\eta, \xi) \) also satisfy the Laplace equation and the same boundary conditions (4) as \( \varphi(\eta, \xi) \). Therefore

\[ U_H^H(\xi, \eta) = \sum_{n=0}^{+\infty} B_n^H P_{2n}(\eta)M_{2n}(\xi), \]  

(46)

with the coefficients \( B_n^H(\Omega) \) being functions of the input frequency. Therefore, (45) is rewritten as

\[ \sum_{n=0}^{+\infty} B_n^HM'_{2n}(0)P_{2n}(\eta) = -\left( \frac{4(i\Omega + G)}{\pi} \eta \left( 1 - \sum_{n=0}^{+\infty} B_n^HP_{2n}(\eta) \right) \right). \]  

(47)

To determine their value, especially \( B_0^H \), (47) is multiplied by \( P_{2m}(\eta) \) and integrated with respect to \( \eta \) over 0 to 1. Utilizing the orthogonality of Legendre polynomials, this results in an infinite set of equations for \( B_n^H \)

\[ \sum_{n=0}^{+\infty} B_n^HM'_{2n}(0) \frac{\delta_{mn}}{4m+1} = -\left( \frac{4(i\Omega + G)}{\pi} \right) \int_0^1 \eta \left( 1 - \sum_{n=0}^{+\infty} B_n^HP_{2n}(\eta) \right) P_{2m}(\eta) d\eta, \]  

(48)

which can be written in matrix format

\[ \left( A^H - \frac{M^H}{G + i\Omega} \right) B^H = A_0^H, \]  

(49)

where \( B^H = [B_0^H, B_1^H, \ldots, B_n^H, \ldots]^T \), \( M^H \) is a diagonal matrix.
\[ M^H = \text{diag} \left( \frac{\pi M_{2m}^2(0)}{4(4m + 1)} \right), \quad m \in \mathbb{N}^0, \]  

and \( A^H \) and \( A_0^H \) are matrices and vector defined as

\[
\begin{align*}
A^H &= [A_{m,n}]_{+\infty \times +\infty}, \quad m, n \in \mathbb{N}^0, \\
A_0^H &= [A_{m,0}]_{+\infty \times 1}, \quad m \in \mathbb{N}^0,
\end{align*}
\]

with

\[
\begin{align*}
A_{m,n} &= A_{n,m} = \int_0^1 \eta P_{2m}(\eta)P_{2n}(\eta) d\eta, \quad m, n \in \mathbb{N}^0, \\
A_{0,n} &= A_{n,0} = -\frac{P_{2n}(0)}{2(2n - 1)(n + 1)}, \quad n \in \mathbb{N}^0.
\end{align*}
\]

See Tables B2 and B3 for the numeric values of these matrices.

Solving the coefficients of the basis functions gives

\[
B^H = \left( A^H - \frac{M^H}{(G + i\Omega)} \right)^{-1} A_0^H,
\]

which is practical only with the matrix indices truncated to a finite number \( n_{\text{max}} \) of rows and columns. See the Numeric Accuracy section for discussion on the accuracy of the solution.

With \( B_0^H \) calculated, the AC current through the electrode is given according to (27) as

\[
I^H = 4a\kappa B_0^HV^H.
\]

The complex impedance of the electrode-electrolyte system is therefore

\[
Z^H = \frac{V^H}{I^H} = \frac{1}{4a\kappa B_0^H} = R_s^H + \frac{1}{i\Omega C_{\text{DL}}^H},
\]

with

\[
\frac{R_s^H}{R_s} = \text{Re}(B_0^H) / |B_0^H|^2, \quad \frac{C_{\text{DL}}^H}{C_{\text{DL}}} = \text{Im}(B_0^H) / |B_0^H|^2,
\]

from comparing (55) with (34) and (39). Hence the frequency dispersion could be obtained.

Figure 7 shows the normalized impedance spectrum of the disk electrode for a few selected values of \( G \). The frequency dispersion of resistive and capacitive impedance are also shown in Figure 8. For low frequencies, the charge transfer resistance’s behavior significantly influences both the series resistance and capacitance and the system’s behavior would be better represented with the charge transfer resistance explicitly modeled. The capacitive impedance seem to peaks at \( \Omega = G \) and shows a constant phase element behavior that deviates from the −1 log-log slope for higher frequency (Huang et al., 2007a, b).

With all \( B_n^H \), the potential and current density distribution are calculated (Figure 9). For \( \Omega \to +\infty \), the distributions converge to the primary distributions regardless of \( G \), a trend which is already seen for \( \Omega = \)
10, and would be evident for larger $\Omega$. For $\Omega = 0$, the distributions are the same as the steady state response for voltage step input. For $G \to +\infty$, the distributions converge to the primary distributions regardless of $\Omega$.

![Impedance spectroscopy of disk electrode](image1)

Figure 7. Impedance spectrum of the disk electrode for different Faradaic conductance values.

![Equivalent resistive and capacitive impedance](image2)

Figure 8. Equivalent resistive and capacitive impedance of the disk electrode for different Faradaic conductance values.
Figure 9. The potential and current density distribution on the surface of the electrode for different normalized frequencies and charge transfer reaction conductance.
Transient Response to Current Step Input (Nisancioğlu and Newman, 1973a)

The transient response to current step input
\[ I(t) = I_0 \cdot u(t) \quad , \]
(57)
applied to the electrode has the same boundary condition (11) as in the sinusoidal situation. The dimensionless Faradaic conduction \( G \) (42) is again utilized to simplify the equation later.

Decomposition of the Solution

The solution can be given as a decomposition of a steady-state response and transient contribution,
\[ \varphi(r, z, t) = \varphi^{SS}(r, z) \cdot u(t) - \varphi^{TZ}(r, z, t) \quad , \]
(58)
in which the former includes the contribution of the entire input current which stays constant \( I(t) \equiv I_0 \equiv I^{SS} \), and the later represents the shift from the initial condition to the steady-state solution and doesn’t contribute to the current input on the electrode. The initial condition immediately after the input onset \( t = 0^+ \) is easily shown to be identical to the primary distribution, therefore the current and potential values \( I_0 \) and \( V_0 \) for the primary distribution are used as normalization factors for the solution afterwards. This gives the convenience to set the coefficient of the zeroth term in the steady-state solution
\[ \frac{\varphi^{SS}(\eta, \xi)}{V_0} = \sum_{n=0}^{+\infty} B_n^{SS} P_{2n}(\eta) M_{2n}(\xi) \quad (59) \]
to unity \( (B_0^{SS} = 1) \), as the total current input is always the same during the shift. The voltage on the electrode as well as other variables could also be decomposed in the same manner
\[ V(t) = V^{SS} \cdot u(t) - V^{TZ}(t) \quad . \]
(60)

Steady State Response

Analyzing the general boundary condition (11) for the steady state gives
\[ \left. \frac{\partial \varphi^{SS}(\eta, \xi)}{\partial \xi} \right|_{\xi=0+} = -\frac{4G}{\pi} \eta \left( V^{SS} - \varphi^{SS}_0(\eta) \right) \quad . \]
(61)

Utilizing the same method for the frequency dispersion problem, the equation is multiplied by \( P_{2m}(\eta) \) and integrated with respect to \( \eta \) over 0 to 1 after substituting (59) into (61):
\[ \frac{V^{SS}}{V_0} = \frac{1}{A_{m,0}} \left( \sum_{n=0}^{+\infty} A_{m,n} B_n^{SS} \right) - \frac{\pi M_{2m}(0) B_m^{SS}}{4G(4m + 1)} \quad , \quad m \in \mathbb{N}^0 \quad . \]
(62)

For \( m = 0 \), with \( B_0^{SS} = 1 \) and \( A_{0,0} = 1/2 \), the condition (62) becomes
\[
\frac{V^{SS}}{V_0} = \frac{1}{A_{0,0}} \left( \sum_{n=0}^{+\infty} B_n^{SS} A_{0,n} - \frac{\pi M'_0(0) B_0^{SS}}{4G} \right) = 1 + \frac{1}{G} + 2 \sum_{n=1}^{+\infty} A_{0,n} B_n^{SS} .
\]

(63)

For \( m \in \mathbb{N}^+ \), (63) is substituted into the left side of (62) and yields
\[
\sum_{n=1}^{+\infty} \left[ A_{m,n} - 2A_{m,0} \cdot A_{0,n} - \frac{\pi M'_{2m}(0) \delta_{mn}}{4G(4m + 1)} \right] B_n^{SS} = \frac{A_{m,0}}{G} .
\]

(64)

Let \( B^{SS} = [B_1^{SS}, B_2^{SS}, \ldots, B_n^{SS}, \ldots]^T \), the group of equations of (64) can be written in matrix form
\[
(G (A - 2A_0 A_0^T) - M) B^{SS} = A_0 ,
\]

(65)

where \( A, A_0, \) and \( M \) are matrices defined as
\[
A = A^T = [A_{m,n}]_{+\infty \times +\infty} , \quad m, n \in \mathbb{N}^+, \\
A_0 = [A_{m,0}]_{+\infty \times 1} , \quad m \in \mathbb{N}^+, \\
M = \text{diag} \left( \frac{\pi M'_{2m}(0)}{4(4m + 1)} \right) , \quad m \in \mathbb{N}^+ ,
\]

(66)

which are sub-matrices of \( A^H, A_0^H, \) and \( M^H, \) respectively. See Tables B2 and B3 for the numeric values of these matrices.

Solving the coefficient of the basis functions of the Laplace equation with the matrix indices truncated to a finite number \( n_{\text{max}} \) of rows and columns gives
\[
B^{SS} = (G (A - 2A_0 A_0^T) - M)^{-1} A_0 .
\]

(68)

and therefore the steady state solution of the electric field is obtained via (59). See Table B4 for the numeric values of \( B^{SS} \). The potential and current density distributions are shown in Figure 10. For \( G \rightarrow +\infty \), the steady-state distributions converge to the primary distributions, while for \( G = 0 \), the current density is uniform.

The steady state voltage is given according to (62) as
\[
\frac{V^{SS}}{V_0} = 1 + \frac{1}{G} + 2B^{SS} A_0 .
\]

(69)

The steady state voltage is shown in Figure 11 as a function of the Faradaic conductance, and the solution indicates that a steady state voltage could only be reached on the electrode if \( G > 0 \).

In the special case with an ideally polarizable electrode, with \( G = 0 \), the solution is unbounded. Intuitively, the current could only pass through the system by constantly charging the double layer capacitance. While the current density and potential distributions in the electrolyte will reach an asymptote, the electrode voltage and overpotential will continue to grow linearly. The current on the interface will shift from the primary distribution to a uniform one over time, and the boundary condition (11) becomes
Figure 10. The steady state potential and current density distribution on the surface of the electrode for different Faradaic reaction conductance.

Figure 11. The steady state voltage of the electrode for different Faradaic reaction conductance.

\[
- \frac{\kappa}{a \eta} \frac{\partial \Phi^{SS}(\eta, \xi)}{\partial \xi} \bigg|_{\xi=0^+} = J_0 = \frac{l_0}{\pi a^2} .
\]  

(70)

The coefficients could be calculated as

\[
B^{SS}_n = - \frac{4(4n + 1)}{\pi M'_{2n}(0)} A_{0,n}
\]  

(71)
or
\[ B^{SS} = -M^{-1}A_0 \quad , \] (72)

which could also be directly obtained from (68) with \( G \to 0 \). The potential on the electrode will continue to grow linearly as long as the step input is maintained, and its “steady-state” could be given as
\[ V^{SS}(t) = \frac{I_0 \cdot t}{C_{DL}} + \overline{\varphi^{SS}} \quad , \] (73)

where the average potential in the solution above the electrode is
\[
\overline{\varphi^{SS}}(V_0) = \left( 2\pi a^2 \int_0^\infty \sum_{n=0}^{+\infty} B_n^{SS} P_{2n}(\eta) \eta d\eta \right) \left( \pi a^2 \right) = 1 + 2 \sum_{n=1}^{+\infty} B_n^{SS} A_{n,0} = 1 - 2A_0^T M^{-1} A_0 = \sum_{n=0}^{+\infty} \frac{(4n + 1) P_{2n}^4(0)}{(2n - 1)^2(n + 1)^2} = \frac{32}{3\pi^2} .
\] (74)

Therefore, the “steady-state” voltage on an ideally polarizable electrode is given as
\[ \frac{V^{SS}(t)}{V_0} = \frac{t}{R_s C_{DL}} + \frac{32}{3\pi^2} = \theta + \frac{32}{3\pi^2} . \] (75)

**Eigenfunctions of the Transient Response**

The transient response doesn’t contribute to the current input, and only redistributes the potential and current density throughout the entire space from their initial state to the steady state. Because the boundary condition (11) is a first order differential equation in terms of time, the solution could be assumed to be exponential decays of certain spatial eigenfunctions using the method of variable separation
\[
\varphi^{TZ}(r, z, t) V_0 = \left[ \sum_{i=1}^{+\infty} C^{(i)} e^{\frac{-t}{\tau^{(i)}} U^{(i)}(r, z)} \right] \cdot u(t) ,
\] (76)

where \( \tau^{(i)} \) is the time constant of the decay, \( C^{(i)} \) is the coefficient for the decay, and \( U^{(i)}(r, z) \) is the spatial distribution of the field associated with the \( i \)th decay. Switching to rotational elliptical coordination and introducing the dimensionless eigenvalue
\[
\Lambda^{(i)} = \frac{\tau}{\tau^{(i)}} - G \quad \Leftrightarrow \quad \tau^{(i)} = \frac{\tau}{\Lambda^{(i)} + G} ,
\] (77)

the solution to the potential in the electrolyte is

---

1 This number with \( \pi^2 \) was given in the original article by [Nisancioğlu and Newman (1973a, eq. 39)]. I remember being able to deduce it in the last step of the series summation during the initial writing of this review in 2012, however, it eluded me in later years. I’d appreciate any tips and comments on the calculation of this series. —B. Wang.
\[
\frac{\varphi^{TZ}(\eta, \xi, \theta)}{V_0} = \left[ \sum_{i=1}^{\infty} C^{(i)} e^{-\theta(\Lambda^{(i)} + g)} U^{(i)}(\eta, \xi) \right] \cdot u(\theta),
\]

with \( U^{(i)}(\eta, \xi) \) given as

\[
U^{(i)}(\eta, \xi) = \sum_{n=1}^{\infty} B^{(i)}_n P_{2n}(\eta) M_{2n}(\xi).
\]

The transient part of the voltage on the electrode can be given as

\[
\frac{V^{TZ}(\theta)}{V_0} = \left[ C^{(0)} e^{-\theta g} + \sum_{i=1}^{\infty} C^{(i)} e^{-\theta(\Lambda^{(i)} + g)} \right] \cdot u(\theta),
\]

with equal coefficients \( C^{(i)} \) for \( i > 0 \). This is possible as the spatial distributions \( U^{(i)}(\eta, \xi) \) could be scaled by their coefficients \( B^{(i)}_n \). These terms correspond to the charge redistribution of the double layer capacitance through the electrolyte (Figure 12). The zeroth term is unique to the electrode voltage, and represents the local charge redistribution via Faradaic reaction with time constant \( \tau^{(0)} = \tau/G \) (equivalent eigenvalue \( \Lambda^{(0)} = 0 \), with the eigenfunction for potential and current density in the electrolyte equal zero). If there is no Faradaic reaction \( (G = 0) \), then \( C^{(0)} = 0 \).

![Figure 12](image-url)

Figure 12. Charge redistribution of the double layer via different pathways during the transient. The zeroth eigenfunction distribute charge through local Faradaic reaction, while higher order eigenfunction distribute charge through currents in the electrolyte.

For each transient decay, the general boundary condition (11) becomes

\[
\frac{\partial U^{(i)}(\eta, \xi)}{\partial \xi} \bigg|_{\xi=0^+} = \frac{4\eta}{\pi} \Lambda^{(i)} \left( 1 - U^{(i)}_0(\eta) \right),
\]

(81)
with \( B_0^{(i)} = 0 \) from the analysis. The specific boundary condition (81) then becomes

\[
\sum_{n=1}^{+\infty} B_n^{(i)} P_{2n}(\eta) M'_{2n}(0) = \frac{4\eta}{\pi} \Lambda^{(i)} \left( 1 - \sum_{n=1}^{+\infty} B_n^{(i)} P_{2n}(\eta) \right). \tag{82}
\]

Again, the equation is multiplied by \( P_{2m}(\eta) \) and integrated with respect to \( \eta \) over 0 to 1, yielding

\[
\sum_{n=1}^{+\infty} A_{0,n} B_n^{(i)} = A_{0,0} = \frac{1}{2}, \quad m = 0 \tag{83}
\]

and

\[
\sum_{n=1}^{+\infty} \left[ A_{m,n} + \frac{\pi M'_{2m}(0) \delta_{m,n}}{4\Lambda^{(i)}(4m + 1)} \right] B_n^{(i)} = A_{m,0}, \quad m \in \mathbb{N}^+. \tag{84}
\]

Let \( \mathbf{B}^{(i)} = [B_1^{(i)}, B_2^{(i)}, \ldots, B_n^{(i)}, \ldots]^T \), and (84) can be written in matrix format

\[
\left( \mathbf{A} + \frac{\mathbf{M}}{\Lambda^{(i)}} \right) \mathbf{B}^{(i)} = \mathbf{A}_0, \tag{85}
\]

with \( \mathbf{A}, \mathbf{A}_0, \) and \( \mathbf{M} \) already defined in (66)–(67). And the coefficients could be expressed as

\[
\mathbf{B}^{(i)} = \left( \mathbf{A} + \frac{\mathbf{M}}{\Lambda^{(i)}} \right)^{-1} \mathbf{A}_0. \tag{86}
\]

Substituting (86) into (83) gives

\[
\mathbf{A}_0^T \left( \mathbf{A} + \frac{\mathbf{M}}{\Lambda^{(i)}} \right)^{-1} \mathbf{A}_0 = \frac{1}{2}, \quad i \in \mathbb{N}^+. \tag{87}
\]

Due to the inverse operation of the matrix, (87) is a polynomial equation of \( \Lambda^{(i)} \) with infinite order. For numeric calculation, all matrixes are truncated to \( n_{\text{max}} \) of rows and columns, and (87) becomes a polynomial equation of order \( n_{\text{max}} \). Hence the first \( n_{\text{max}} \) eigenvalues could be obtained with ascending value (descending value for \( \tau^{(i)} \)), and the corresponding coefficients \( \mathbf{B}^{(i)} \) can then be obtained from (86).

See Table B5 for the numeric values of \( \Lambda^{(i)} \) and \( \mathbf{B}^{(i)} \) obtained with \( n_{\text{max}} = 200 \).

As can be observed from (81)–(87), the eigenvalues and spatial distribution of the transient response’s eigenfunctions are independent of the presence or magnitude of the Faradaic reaction. The normalized potential and current density distributions of the eigenfunctions are shown in Figure 13.

The current density on the electrode is proportional to \( VTZ(\theta) - \varphi_0^{TZ}(\eta, \theta) \) or \( 1 - U_0^{(i)}(\eta) \) according to (81). The current density of one eigenfunction is orthogonal to the potential of another:
\[
\int_0^1 U_0^{(i)}(\eta) \left( 1 - U_0^{(j)}(\eta) \right) \eta d\eta = \frac{\delta_{ij}}{\Lambda^{(i)}} \sum_{n=1}^{+\infty} \frac{\pi M'_{2n}(0)}{4(4n + 1)} \left( B_n^{(i)} \right)^2 = \frac{\delta_{ij}}{\Lambda^{(i)}} \left( B^{(i)} \right)^T M B^{(i)},
\]

which is utilized to obtain the coefficient \( C^{(i)} \) for the exponential decay.

Figure 13. The normalized and dimensionless “potential” and “current density” distribution on the surface of the electrode of the eigenfunctions of the transient response to current step input.

**Transient Response**

The initial condition after input onset \( (t = 0^+) \) is the primary distribution. For the potential, (58) could be evaluated at \( t = 0^+ \) on the electrode surface \( (z = \xi = 0) \) giving

\[
\frac{\varphi(r, 0, 0^+)}{V_0} = 1 = \left[ \frac{\varphi^{SS}(r, 0)}{V_0} - \frac{\varphi^{TZ}(r, 0, 0^+)}{V_0} \right] \cdot u(0^+)
\]

\[
= \frac{\varphi^{SS}(\eta)}{V_0} - \sum_{i=1}^{+\infty} C^{(i)} U_0^{(i)}(\eta),
\]

Multiplying by \( 1 - U_0^{(j)}(\eta) \) for \( j \in \mathbb{N}^+ \) and utilizing the relationship (89) yields
Although the eigenfunctions of the transient components are independent of the Faradaic reaction, the decay time constants \( \tau^{(i)} \) and the corresponding coefficients \( C^{(j)} \) are not, as \( B^{SS} \) is dependent on \( G \). With all the coefficients \( C^{(j)} \) given for \( i > 0 \) (Table B6), the spatial distribution of the transient response is solved and the potential and current density distributions on the electrode surface at \( t = 0^+ \) are shown in Figure 14. The transient response constructed from eigenfunctions shows ripples due to the Gibbs effect (see Numeric Accuracy section), and therefore, the current distribution was spatially filtered.

\[
C^{(j)} = \frac{\int_0^1 \sum_{n=1}^{+\infty} B^{SS}_n P_{2n}(\eta) \left(1 - U^{(j)}_0(\eta)\right) \eta \, d\eta}{\int_0^1 U^{(i)}_0(\eta) \left(1 - U^{(j)}_0(\eta)\right) \eta \, d\eta} \]
\[
= \frac{1}{A^{(j)}} \sum_{n=1}^{+\infty} \frac{\pi M'_n(0)}{4(4n + 1)} \frac{b^{(j)}_n B^{SS}_n}{\sum_{i=1}^{+\infty} \delta_{ij} \sum_{n=1}^{+\infty} \frac{\pi M'_n(0)}{4(4n + 1)} \left(B^{(i)}_n\right)^2} \]
\[
\sum_{i=1}^{+\infty} \frac{1}{A^{(j)}} \sum_{n=1}^{+\infty} \frac{\pi M'_n(0)}{4(4n + 1)} \left(B^{(i)}_n\right)^2 \]
\[
= \frac{(B^{SS})^T MB^{(j)}}{(B^{(j)})^T MB^{(j)}}.
\]

For the electrode voltage, however, \( C^{(0)} \) remains to be solved, and could be obtained by evaluating (60) and (80) at \( \theta = 0 \)

\[
C^{(0)} = \begin{cases} 
\frac{V^{SS}}{V_0} - 1 - \sum_{j=1}^{+\infty} C^{(j)}, & G \neq 0 \\
0, & G = 0 
\end{cases}
\]

\[
(91)
\]

Figure 14. The potential and current density distribution of the transient response to current step input on the surface of the electrode at \( t = 0^+ \) for different Faradaic reaction conductance.
However an easier way is through analysis of the current density components on the electrode-electrolyte interface. The steady state solution only contains Faradaic current as the double layer is charged to its asymptotic value. On the other hand, the transient response contains both Faradaic current and capacitive current component that are not equal in magnitude at any location. The initial condition is the primary distribution in the electrolyte at $t = 0^+$, and as the overpotential is zero, there is only capacitive current. Thus the initial capacitive current of the transient response equals the primary current distribution on the electrode

$$\gamma \left. \frac{\partial}{\partial t} \left( V^{TZ}(t) - \phi^{TZ}(r, z, t) \right) \right|_{z=0, t=0^+} = -j^0_B(r, 0) \ , \quad (92)$$

which is

$$-\frac{\gamma}{\tau} V_0 \left( C^{(0)} G + \sum_{i=1}^{+\infty} C^{(i)} \left( \Lambda^{(i)} + G \right) \left( 1 - U_0^{(i)}(\eta) \right) \right) = -\frac{2 \kappa V_0}{\pi a \eta} \ . \quad (93)$$

Multiplying both side by $\eta$ and integrating over $[0,1]$, the summation equals zero for $i \neq 0$ utilizing (88), therefore yielding

$$C^{(0)} G = 1 \iff C^{(0)} = \frac{1}{G} \ . \quad (94)$$

The transient response is dominated by the eigenfunctions of lower order components of $\Lambda^{(i)}$, $i \geq 1$. See Table B6 for the numeric values of $C^{(i)}$. As the Faradaic reaction rate increases, the coefficients of $C^{(i)}$, $i \geq 1$ decreases. This indicates that more transient current runs through local Faradaic charge transfer versus through the electrolyte.
Transient Response to Voltage Step Input ([Nisancioglu and Newman, 1973b](#))

The transient response to a voltage step input

\[ V(t) = V_0 \cdot u(t) \]  \hspace{1cm} (95)

applied to the electrode is similarly decomposed to a steady state solution and a transient solution.

\[ \varphi(r, z, t) = \varphi^{SS}(r, z) \cdot u(t) - \varphi^{TZ}(r, z, t) \]  \hspace{1cm} (96)

**Steady State Response**

The steady state solution for the voltage step input has a different current compared to the initial primary response \( I^{SS} \neq I_0 \), and the transient response contributes a net current \( I^{TZ}(t) \) that results in the difference between the primary current value and the steady state value. Nevertheless the steady state solution of this system could be easily given by scaling the results of the previous calculation for the current step input. Since the voltage is forced to stay at its initial value \( t \equiv V_0 = V^{SS} \), all the other steady state values \( (\varphi^{SS}(r, z), J_0^{SS}(r), \text{etc.}) \) will be scaled by a factor

\[ F = \left( 1 + \frac{1}{G} + 2A_0^\top (G (A - 2A_0A_0^\top) + M)^{-1} A_0 \right)^{-1}, \]  \hspace{1cm} (97)

which is the inverse of the right side of (69). The scaling factor is plotted in Figure 15 as a function of the Faradaic reaction \( G \). If \( G = 0 \), then this scaling factor becomes zero, and all the steady state values except for the overpotential are also zero as well. This is intuitive as the steady state without Faradaic reaction to discharge the double layer capacitance results in fully charged capacitance with no current following in the electrolyte. The steady state potential and current density distributions on the electrode surface is shown in Figure 16.

![Figure 15. Scaling factor the steady state response of the voltage step input compared to that of the current step input as a function of Faradaic reaction conductance.](image)
Figure 16. The steady state potential and current density distribution on the surface of the electrode for different Faradaic reaction conductance.

**Eigenfunctions of the Transient Response**

In the voltage step input situation, the transient response will follow a different course to connect the primary distribution to the steady state, and is the focus of the analysis. Using the same notation in (77), the transience is given as

\[
\frac{\phi^{TZ}(\eta, \xi, \theta)}{V_0} = \sum_{i=0}^{+\infty} C^{(i)} e^{-\theta (A^{(i)}+G)} U^{(i)}(\eta, \xi) \cdot u(\theta),
\]

with the summation starting from 0, indicating the net current. Obviously \( V^{TZ} = 0 \), and the boundary condition (11) is

\[
\frac{\partial U^{(i)}(\eta, \xi)}{\partial \xi} \bigg|_{\xi=0^+} + \frac{4\eta}{\pi} A^{(i)} U^{(i)}_0(\eta) = 0.
\]

Again, setting

\[
U^{(i)}(\eta, \xi) = \sum_{n=0}^{+\infty} B^{(i)}_n(\eta) P_{2n}(\eta) M_{2n}(\xi)
\]

yields

\[
\sum_{n=0}^{+\infty} \left[ A_{m,n} + \frac{\pi M_{2m}(0) \delta_{mn}}{4A^{(i)}(4m+1)} \right] B^{(i)}_n = 0, \quad m \in \mathbb{N}^0.
\]
To solve the set of equations, the first coefficient of $U^{(i)}(\eta, \xi)$ is set to $B_0^{(i)} = 1$ for normalization, and the eigenfunctions are scaled by the coefficients $C^{(i)}$. Then applying the same technique as in $(83)$–$(86)$ yields the equations for all the eigenvalues $\Lambda^{(i)}$

$$A_0^T \left( A + \frac{M}{\Lambda^{(i)}} \right)^{-1} A_0 = \frac{1}{2} \left( 1 - \frac{1}{\Lambda^{(i)}} \right), \quad i \in \mathbb{N}^0,$$

and for the corresponding coefficient $B_n^{(i)}$

$$B^{(i)} = -\left( A + \frac{M}{\Lambda^{(i)}} \right)^{-1} A_0.$$

All eigenvalues, except for $\Lambda^{(0)}$, have a counterpart similar in value for the current step and voltage step input problem. The zeroth eigenvalue that is distinctively different from the other eigenvalues is due to the difference on the right-hand-side of the equations $(102)$ and $(87)$. See Table B7 for the numeric values of $\Lambda^{(i)}$ and $B^{(i)}$ obtained with $n_{\text{max}} = 200$.

The potential and current density distributions of the eigenfunctions are shown in Figure 17.

![Figure 17. The "potential" and "current density" distribution on the surface of the electrode of the eigensolution of the transient response to current step input.](image)

The current density on the electrode is proportional to $\phi_0^{(i)}(\eta, \theta)$ or $U_0^{(i)}(\eta)$ as seen from $(99)$. The eigenfunctions therefore satisfy an orthogonality described as

$$\int_0^1 U_0^{(i)}(\eta) U_0^{(j)}(\eta) \eta d\eta = -\frac{\delta_{ij}}{\Lambda^{(i)}} \sum_{n=0}^{+\infty} \frac{\pi M_{2n}^2(0)}{4(4n + 1)} \left( B_n^{(i)} \right)^2 \delta_{ij},$$

$$= \frac{\delta_{ij}}{\Lambda^{(i)}} \left[ \frac{1}{2} - \left( B^{(i)} \right)^T M B^{(i)} \right].$$

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Transient Response

Similar to (90), the coefficients $C^{(i)}$ could be determined by the initial condition of the potential. Now that the steady state solution is scaled ($B_0^{SS} = F$), the coefficients are given by

$$C^{(i)} = \frac{F - 2(B^{SS})^T MB^{(i)} - 1}{1 - 2(B^{(i)})^T MB^{(i)}}. \quad (105)$$

Or utilizing the same analysis of the current density components, the same conclusion holds for the potential step input, i.e. the initial capacitive current of the transient solution equals the primary current distribution on the electrode:

$$\gamma \frac{\partial \left(0 - \varphi^{TZ}(r, z, t)\right)}{\partial t} \bigg|_{z=0, t=0^+} = -J_0^P(r, 0) \quad , \quad (106)$$

which is

$$-\frac{\gamma}{\tau} V_0 \sum_{i=0}^{+\infty} C^{(i)} (\Lambda^{(i)} + G) U_0^{(i)}(\eta) = -\frac{2 \kappa V_0}{\pi a \eta} \quad . \quad (107)$$

Using (104) yields an alternative expression

$$C^{(i)} = \frac{\Lambda^{(i)}}{2(\Lambda^{(i)} + G) \sum_{n=0}^{+\infty} \frac{\pi M_{2n}^r(0)}{4(4n + 1)} \left(B_n^{(i)}\right)^2} \quad (108)$$

$$= \frac{\Lambda^{(i)}}{(\Lambda^{(i)} + G)(2(B^{(i)})^T MB^{(i)} - 1)} \quad .$$

See Table B8 for the numeric values of $C^{(i)}$. The transient response is thus solved, and the potential and current density distributions on the electrode surface at $t = 0^+$ are shown in Figure 18.

With $B_0^{(i)} = 1$, the electrode current is given as

$$\frac{l(\theta)}{I_0} = \frac{l^{SS}}{I_0} - \sum_{n=0}^{+\infty} C^{(i)} e^{-\theta (\Lambda^{(i)} + G)} \quad . \quad (109)$$
Figure 18. The potential and current density distribution of the transient response to voltage step input on the surface of the electrode at $t = 0^+$ for different Faradaic reaction conductance. The traces were filtered after the construction from the eigenfunction.
Numeric Accuracy

Numeric solution for the frequency dispersion, current step response and voltage step response all involve an infinite set of equations, summarized in the form of matrices. The matrices need to be truncated for the solution to be possible, and therefore the accuracy of the solutions should be evaluated.

To solve the coefficients $B^H$ for the frequency dispersion, (53) involves inverse operation of a matrix. However, as the terms of $A^H_0$ on the right hand side of the equation decrease with increasing $n$, the accuracy of the calculated terms $B^H_0$ could be guaranteed by setting $n_{\text{max}}$ so that the $n$th term of $A^H_0$, i.e. $A_{0,n}$ is small enough. For the calculation, $n_{\text{max}}$ was set to 200, which has an accuracy of $10^{-10}$ (relative difference when increasing $n_{\text{max}}$ by 1). Also, the coefficients $B^H_n$ decay fast in amplitude, allowing accurate calculation of the potential and current density distribution with only a few basis functions.

For the current step response and voltage step response, however, the truncation of (87) and (102) reduces the order of the polynomial equation for the eigenvalues. A truncation of $n_{\text{max}}$ gives $n_{\text{max}}$ eigenvalues, and therefore the accuracy of the solution is reduces. This is further complicated by the complexities and difficulties in solving symbolic inversion of large matrix. To investigate which of the eigenvalues are accurate, the eigenvalues are plotted from solutions obtained with several $n_{\text{max}}$ (10, 20, 30, 40, 50, 80, etc.), showing high linearity ($R^2 > 0.999999$) (Figure 19).

![Figure 19. The eigenvalues of the transient response of the current step input, solved with different size of matrix truncation. Horizontal axis is the order. Markers in blue show eigenvalues considered accurate after comparing the values solved from different sizes of matrix truncation. Markers in red show eigenvalues considered inaccurate when comparing with those solved by matrix truncated to larger size. The dotted line connect the eigenvalues solved from the same matrix truncation size. The dashed line is a linear regression of the accurate eigenvalues, showing highly linear behavior.](image-url)
The accuracy could be checked by comparing the same order eigenvalues calculated with different $n_{\text{max}}$, with a relative difference less than 0.001% is considered accurate. Apparently, as $n_{\text{max}}$ increases, more eigenvalues become accurate enough to be included for later calculations and the corresponding coefficients belong to the “believable scales” (Boyd, 2001, p. 427). Approximately 50%–60% of the eigenvalues and coefficients can be considered accurate, which is an empirical rule for “spectral blocking” (Boyd, 2001, pp. 132, 207, 427). Similar results could be obtained for the voltage step response.

Another aspect of accuracy arises when assembling the current density distribution on the electrode surface from the basis functions due to its behavior at the disk’s edge. Figure 20 shows Gibbs ripple towards the edge of the electrode, as often seen in the reconstruction of Fourier series. For small $n_{\text{max}}$, the ripples could be somewhat reduced with increased $n_{\text{max}}$ (Antoni and Scherson, 2006), but these “spectral ringing” are inherent due to the discontinuity and independent of $n_{\text{max}}$ and therefore should be carefully treated (Boyd, 2001, p. 419). The current density distribution presented in the previous sections were spatially filtered to get rid of the oscillation with frequencies higher than 10 cycles per unit length, while keeping in mind that ideally there is a singularity at the very edge. An alternative way to obtain the current density without such ripples is to utilize the reconstructed potential distribution, which is continuous and should not suffer from Gibbs phenomenon.

Figure 20. The unprocessed current density distribution of the transient response to current step input on the surface of the electrode at $t = 0^+$ for different charge transfer conductance, corresponding to the right panel of Figure 14. The Gibbs ripples demonstrate the spectral ringing at the electrode’s edge due to the current density reaching infinity.
Appendix A—Legendre Functions and their Extension on the Imaginary Axis

To solve (22), the Legendre functions need to be extended to the imaginary axis. The Legendre function are first introduced, with background knowledge only related to this review given. For further details on the Legendre function, any mathematical textbook can be consulted. The detailed derivation of the solution to (22) that Newman (1966b) omitted is then discussed to complete the analysis on the Basis Functions.

Legendre Functions

Legendre functions are solution to the Legendre equation, a second order differential equation derived from Laplace equation in a spherical coordinate system \((r, \phi, \theta)\). Using separation of variables, the equation for \(\theta = \arccos x\) under axial symmetric condition is the Legendre equation

\[
\frac{d}{dx} \left[ (1 - x^2) \frac{df(x)}{dx} \right] + l(l + 1)f(x) = 0 , \quad |x| \leq 1 .
\]  

(A1)

The solution to the Legendre equation is

\[
f(x) = c_1 P_l(x) + c_2 Q_l(x) ,
\]

(A2)

with \(P_l(x)\) and \(Q_l(x)\) being the Legendre function of the first and second kind, respectively. Generally speaking \(l\) could be complex, and usually \(P_l(x)\) and \(Q_l(x)\) are complex and not bounded at the points \(x = \pm 1\). If \(l \in \mathbb{N}^0\), then \(P_l(x)\) becomes a polynomial and with normalization \(P_l(1) = 1\):

\[
P_l(x) = \sum_{m=0}^{[l/2]} \frac{(-1)^m (2l - 2m)!}{2^l \cdot m! (l - m)! (l - 2m)!} x^{l-2m} .
\]

(A3)

\(Q_l(x)\) is obtained from \(P_l(x)\) by the method of reduction of order:

\[
Q_l(x) = u_l(x) P_l(x) ,
\]

(A4)

with

\[
u_l(x) = \int_x^1 \frac{d\tilde{x}}{(1 - \tilde{x}^2) P_l^2 (\tilde{x})} .
\]

(A5)

\(Q_l(x)\) is unbounded at \(x = \pm 1\) and could also be written as

\[
Q_l(x) = P_l(x) Q_0(x) - W_l(x) ,
\]

(A6)

where \(W_l(x)\) denotes a polynomial of order \(l - 1\).

Legendre functions have several characteristics, with the following two being important for the disk electrode analysis:

- Orthogonality: Legendre functions are orthogonal polynomials over the interval \([-1,1]\):

\[
\int_{-1}^1 P_n(x) P_m(x) \, dx = \frac{2}{2l + 1} \delta_{nm} .
\]

(A7)
Recurrent generation: Higher order Legendre functions could be generated by lower order ones (also applies to \( Q_l(x) \) and \( W_l(x) \)):

\[
(l + 1)P_{l+1}(x) = (2l + 1)xP_l(x) - lP_{l-1}(x) .
\] (A8)

Starting functions for recurrent generation are given as follows:

\[
\begin{align*}
P_0(x) &= 1, \\
P_1(x) &= x, \\
P_2(x) &= \frac{3x^2 - 1}{2},
\end{align*}
\]

\[
\begin{align*}
Q_0(x) &= \frac{1}{2}\ln\left(\frac{1 + x}{1 - x}\right), \\
Q_1(x) &= \frac{x}{2}\ln\left(\frac{1 + x}{1 - x}\right) - 1, \\
Q_2(x) &= \frac{(3x^2 - 1)}{4}\ln\left(\frac{1 + x}{1 - x}\right) - \frac{3x}{2},
\end{align*}
\]

\[
\begin{align*}
W_0(x) &= 0, \\
W_1(x) &= 1, \\
W_2(x) &= \frac{3x}{2}.
\end{align*}
\]

The lower order functions are given in Figure A1 for even and odd number of \( l \).

**Evaluating Legendre Functions on the Imaginary Axis**

Substituting the variable \( \xi \) by a purely imaginary one

\[
\xi = f(\hat{\xi}) = i\hat{\xi} ,
\] (A10)

the function \( M(\xi) \) satisfies

\[
\begin{align*}
d\hat{M}(\hat{\xi}) &= M(f(\hat{\xi})) = \hat{M}(\hat{\xi}) \\
\frac{d\hat{M}(\hat{\xi})}{d\hat{\xi}} &= \frac{dM(\xi)}{d\xi} \frac{d\xi}{d\hat{\xi}} = i \frac{dM(\xi)}{d\xi} .
\end{align*}
\] (A11)

Therefore for each \( \lambda = l(l + 1) \), substituting (A11) into (32) gives

\[
\frac{d}{d\hat{\xi}}\left[(1 - \xi^2)\frac{d\hat{M}(\hat{\xi})}{d\hat{\xi}}\right] + l(l + 1)\hat{M}(\hat{\xi}) = 0 .
\] (A12)

Equation (A12) indicates that \( \hat{M}(\hat{\xi}) \) is a Legendre function, hence

\[
\hat{M}_l(\hat{\xi}) = c_l^{MP}P_l(\xi) + c_l^{MQ}Q_l(\xi) ,
\] (A13)

and

\[
M_l(\xi) = \hat{M}_l(\xi/i) = c_l^{MP}P_l(\xi/i) + c_l^{MQ}Q_l(\xi/i) .
\] (A14)

Before the Legendre functions are evaluated on the imaginary axis, the variable is first extended to the complex plane \( z = x + iy \in \mathbb{C} \), and \( P_l(z) \) and \( Q_l(z) \) become complex. With \( l \in \mathbb{N}_0 \), \( P_l(z) \) is a polynomial, and \( Q_l(z) \) could also be obtained by (A4)–(A6). The corresponding regions of convergence (ROC) are \( z \in \mathbb{C}\{z = \infty\} \) for \( P_l(z) \), and \( z \in \mathbb{C}\{z = \pm 1, \infty\} \) for \( Q_l(z) \), respectively. The latter could be inferred from the recurrent generation of \( Q_l(z) \) and the expression of the first term \( Q_0(z) \)

\[
Q_0(z) = \frac{1}{4}\ln\left[\frac{(1 + x)^2 + y^2}{(1 - x)^2 + y^2}\right] + i\frac{1}{2}\arctan\left(\frac{2y}{1 - x^2 - y^2}\right) .
\] (A15)
Figure A1. Legendre functions of the first and second kind, plotted separately for even and odd orders. For $P_l(x)$, the oscillations have amplitude of $O(n^{-1/2})$ over most of the interval, with the narrow boundary layers near the endpoints where the polynomial rises to $\pm 1$ (Boyd, 2001, p53).

Modifying the equations (A4)–(A6) gives

$$\frac{Q_l(\xi/i)}{P_l(\xi/i)} = u_l(\xi/i) = \int^{\xi/i} \frac{d\tilde{x}}{(1 - \tilde{x}^2)P^2_l(\tilde{x})} = -i \int^{\xi} \frac{d\tilde{x}}{(1 + \tilde{x}^2)P^2_l(\tilde{x}/i)} , \tag{A16}$$

and

$$Q_l(\xi/i) = P_l(\xi/i)Q_0(\xi/i) - W_l(\xi/i) . \tag{A17}$$

The functions $P_l(\xi/i)$ and $Q_l(\xi/i)$ are bounded on $\xi \in [0, +\infty)$, and unbounded at $+\infty$. $l = 0$ is the only exception where both functions converge for $\xi \to +\infty$.  

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The first few functions are given as
\[
\begin{align*}
P_0(\xi/i) &= 1 \\
P_1(\xi/i) &= \xi/i \\
P_2(\xi/i) &= -\frac{3\xi^2 + 1}{2}
\end{align*}
\]
\[
\begin{align*}
Q_0(\xi/i) &= -i\tan(\xi) \\
Q_1(\xi/i) &= -(\xi \tan(\xi) + 1) \\
Q_2(\xi/i) &= \frac{i}{2}[(3\xi^2 + 1)\tan(\xi) + 3\xi]
\end{align*}
\]
\[
\begin{align*}
W_0(\xi/i) &= 0 \\
W_1(\xi/i) &= 1 \\
W_2(\xi/i) &= -\frac{3\xi}{2}
\end{align*}
\]  \hspace{1cm} (A18)

With \( l = 2n \), \( P_{2n}(\xi/i) \) is real and \( Q_{2n}(\xi/i) \) and \( W_{2n}(\xi/i) \) are imaginary.

For \( M_{2n}(\xi) \) to be real, \( c_{2n}^{MQ} \) is imaginary. To satisfy the conditions relevant to \( M_{2n}(\xi) \)
\[
\begin{align*}
|M_{2n}(\xi)| &< +\infty \\
\lim_{\xi \to +\infty} M_{2n}(\xi) &= 0 \\
M_{2n}(0) &= 1
\end{align*}
\]  \hspace{1cm} (A19)

the following must be true:
\[
\begin{align*}
M_{2n}(0) &= c_{2n}^{MP}P_{2n}(0) = 1 \\
\lim_{\xi \to +\infty} c_{2n}^{MP}P_{2n}(\xi/i) + c_{2n}^{MQ}Q_{2n}(\xi/i) &= 0 \\
\Rightarrow \quad c_{2n}^{MP} &= \frac{1}{P_{2n}(0)} \\
c_{2n}^{MQ} &= -c_{2n}^{MP} \lim_{\xi \to +\infty} \left( \frac{P_{2n}(\xi/i)}{Q_{2n}(\xi/i)} \right)
\end{align*}
\]  \hspace{1cm} (A20)

The coefficient \( c_{2n}^{MP} \) (Table B1) could be easily calculated as the reciprocal of \( P_{2n}(0) \):
\[
c_{2n}^{MP} = \frac{1}{P_{2n}(0)} = \frac{(-1)^n(2^n \cdot n!)^2}{(2n)!}.
\]  \hspace{1cm} (A21)

The limit for the coefficient \( c_{2n}^{MQ} \) could be calculated from (A16) as
\[
\lim_{\xi \to +\infty} \left( \frac{P_{2n}(\xi/i)}{Q_{2n}(\xi/i)} \right) = \left[ \lim_{\xi \to +\infty} \left( \frac{Q_{0}(\xi/i) + W_{2n}(\xi/i)}{P_{2n}(\xi/i)} \right) \right]^{-1} = \frac{2i}{\pi}.
\]  \hspace{1cm} (A22)

Therefore
\[
c_{2n}^{MQ} = -\frac{2i}{\pi} c_{2n}^{MP} = -\frac{2i}{\pi} \left( \frac{(-1)^n(2^n \cdot n!)^2}{(2n)!} \right).
\]  \hspace{1cm} (A23)

The functions \( M_{2n}(\xi) \) are shown in logarithmic scale in Figure A2. It should be noticed that the decay to zero is very fast even for small \( n \). For example when \( n \geq 1 \) the function decays to less than \( 10^{-2} \) within \( \xi \leq 3 \). Hence the zeroth order of the solution will dominate the middle to far field in the conductive medium, and the electrode would be perceived as a point source from far away. Higher order functions are decaying extremely fast and any contribution would be very limited to the origin of the \( \xi \) axis, i.e. very close to the electrode-electrolyte interface.

The derivative of \( M_{2n}(\xi) \) at the origin is used several times such as for calculating the current density on the electrode surface (27) and the matrix \( M^H \) (50). Utilizing the relationship (A16) and \( P'_{2n}(0) = 0 \), \( M'_{2n}(0) \) is represented by the first term in the series expansion of \( Q_{2n}(\xi/i) \)
Figure A2. The “radial” component of the solution $M_{2n}(ξ)$ on log-log scale, obtained from evaluating the Legendre function on the imaginary axis. The high order function decay very quickly, indicating that they don’t influence the field distribution in the electrolyte very much. Only the zeros order solution extends far into the electrolyte space.

$$M_{2n}'(0) = c_{2n}^M \frac{dQ_{2n}(\xi/i)}{d\xi}\bigg|_{\xi=0}$$

$$= \frac{-i \cdot c_{2n}^MQ_{2n}(0)}{(1 + \xi^2)p_{2n}^2(\xi/i)}\bigg|_{\xi=0}$$

$$= - \frac{2}{\pi p_{2n}^2(0)} = \frac{-2}{\pi} \frac{(2^n \cdot n!)^4}{[(2n)!]^2}$$

(A24)

For the matrices $M^H$ and $M$, the diagonal elements have an asymptote that could be given by using the Stirling’s approximation for large $n$

$$n! \approx \sqrt{2\pi n} \left(\frac{n}{e}\right)^n$$

(A25)

as

$$\lim_{n \to +\infty} \frac{\pi M_{2n}'(0)}{4(4n + 1)} = \lim_{n \to +\infty} \frac{\pi}{4(4n + 1)} \left(\frac{-2}{\pi} \frac{(2^n \cdot n!)^4}{[(2n)!]^2}\right)$$

$$= \lim_{n \to +\infty} \frac{-2^{4n} \cdot 4\pi^2 n^2 \left(\frac{n}{e}\right)^{4n}}{2(4n + 1) \cdot 2\pi \cdot 2n \left(\frac{2n}{e}\right)^{4n}}$$

$$= -\pi/8$$

(A26)
Appendix B—Tables and Figures of Numerical Calculations

Legendre functions related results

Table B1: Coefficient for constructing the Legendre functions on the imaginary axis. The first 50 of \( c_{2n}^{MP} \) are given, where as \( c_{2n}^{MQ} \) and \( M_{2n}'(0) \) could be easily calculated from \( c_{2n}^{MP} \) by using (A23) and (A24).

| \( n \) | \( c_{2n}^{MP} \) | \( c_{2n}^{MP} \) | \( n \) | \( c_{2n}^{MP} \) |
|---|---|---|---|---|
| 0  | 1.00000 | 17 | -7.36194 | 34 | 10.37316 |
| 1  | -2.00000 | 18 | 7.57228  | 35 | -10.52349 |
| 2  | 2.66667  | 19 | -7.77694 | 36 | 10.67171  |
| 3  | -3.20000 | 20 | 7.97635  | 37 | -10.81790 |
| 4  | 3.65714  | 21 | -8.17089 | 38 | 10.96214  |
| 5  | -4.06349 | 22 | 8.36091  | 39 | -11.10450 |
| 6  | 4.43290  | 23 | -8.54671 | 40 | 11.24507  |
| 7  | -4.77389 | 24 | 8.72855  | 41 | -11.38390 |
| 8  | 5.09215  | 25 | -8.90669 | 42 | 11.52105  |
| 9  | -5.39169 | 26 | 9.08133  | 43 | -11.65659 |
| 10 | 5.67546  | 27 | -9.25268 | 44 | 11.79058  |
| 11 | -5.94572 | 28 | 9.42091  | 45 | -11.92305 |
| 12 | 6.20423  | 29 | -9.58618 | 46 | 12.05408  |
| 13 | -6.45240 | 30 | 9.74866  | 47 | -12.18369 |
| 14 | 6.69138  | 31 | -9.90848 | 48 | 12.31194  |
| 15 | -6.92212 | 32 | 10.06575 | 49 | -12.43887 |
| 16 | 7.14541  | 33 | -10.22061|   |   |
Numeric matrices

Table B2: $A^H$ and $A_{0,0}$, $A_0$ and $A$, in the form of $A^H = \begin{bmatrix} A_{0,0} & A_0^T \\ A_0 & A \end{bmatrix}$.

|       | 0   | 1    | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 9   | ...
|-------|-----|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 0     | 0.5000 | 0.1250 | -0.0208 | 0.0078 | -0.0039 | 0.0023 | -0.0015 | 0.0010 | -0.0007 | 0.0005 | ...
| 1     | 0.1250 | 0.1250 | 0.0339 | -0.0063 | 0.0025 | -0.0013 | 0.0008 | -0.0005 | 0.0004 | -0.0003 | ...
| 2     | -0.0208 | 0.0339 | 0.0703 | 0.0202 | -0.0037 | 0.0015 | -0.0008 | 0.0005 | -0.0003 | 0.0002 | ...
| 3     | 0.0078 | -0.0063 | 0.0202 | 0.0488 | 0.0145 | -0.0027 | 0.0011 | -0.0006 | 0.0004 | -0.0002 | ...
| 4     | -0.0039 | 0.0025 | -0.0037 | 0.0145 | 0.0374 | 0.0113 | -0.0021 | 0.0009 | -0.0005 | 0.0003 | ...
| 5     | 0.0023 | -0.0013 | 0.0015 | -0.0027 | 0.0113 | 0.0303 | 0.0093 | -0.0018 | 0.0007 | -0.0004 | ...
| 6     | -0.0015 | 0.0008 | -0.0008 | 0.0011 | -0.0021 | 0.0093 | 0.0254 | 0.0079 | -0.0015 | 0.0006 | ...
| 7     | 0.0010 | -0.0005 | 0.0005 | -0.0006 | 0.0009 | -0.0018 | 0.0079 | 0.0219 | 0.0069 | -0.0013 | ...
| 8     | -0.0007 | 0.0004 | -0.0003 | 0.0004 | -0.0005 | 0.0007 | -0.0015 | 0.0069 | 0.0193 | 0.0061 | ...
| 9     | 0.0005 | -0.0003 | 0.0002 | -0.0002 | 0.0003 | -0.0004 | 0.0006 | -0.0013 | 0.0061 | 0.0172 | ...
| ⋮     | ⋮    | ⋮    | ⋮    | ⋮    | ⋮    | ⋮    | ⋮    | ⋮    | ⋮    | ⋮    |

Table B3: $M^H$ and $M$ are both diagonal matrixes, with $M^H = \begin{bmatrix} -1/2 & 0 \\ 0 & M \end{bmatrix}$.

|   n   | $M^H_{n,n}$ |   n   | $M^H_{n,n}$ |   n   | $M^H_{n,n}$ |
|-------|-------------|-------|-------------|-------|-------------|
| 0     | -0.5000     | 11    | -0.39280    | 22    | -0.39272    |
| 1     | -0.4000     | 12    | -0.39278    | 23    | -0.39272    |
| 2     | -0.39506    | 13    | -0.39277    | 24    | -0.39272    |
| 3     | -0.39385    | 14    | -0.39276    | 25    | -0.39272    |
| 4     | -0.39337    | 15    | -0.39275    | 26    | -0.39272    |
| 5     | -0.39314    | 16    | -0.39275    | 27    | -0.39272    |
| 6     | -0.39301    | 17    | -0.39274    | 28    | -0.39271    |
| 7     | -0.39293    | 18    | -0.39274    | 29    | -0.39271    |
| 8     | -0.39288    | 19    | -0.39273    | 30    | -0.39271    |
| 9     | -0.39284    | 20    | -0.39273    | :     | :           |
| 10    | -0.39282    | 21    | -0.39273    | +∞    | -π/8        |
### Current Step Response

Table B4: Coefficients $B_{n}^{SS}$ for constructing the steady state solution of the current step input.

|        | $G = 0$          | $G = 0.1$        | $G = 1$          | $G = 10$         |
|--------|------------------|------------------|------------------|------------------|
| $B_1^{SS}$ | 1.00000          | 1.00000          | 1.00000          | 1.00000          |
| $B_2^{SS}$ | 0.31250          | 0.30592          | 0.25912          | 0.11754          |
| $B_3^{SS}$ | -0.05273         | -0.05491         | -0.06795         | -0.07024         |
| $B_4^{SS}$ | 0.01984          | 0.02055          | 0.02610          | 0.04093          |
| $B_5^{SS}$ | -0.00993         | -0.01026         | -0.01291         | -0.02454         |
| $B_6^{SS}$ | 0.00580          | 0.00598          | 0.00746          | 0.01542          |
| $B_7^{SS}$ | -0.00373         | -0.00384         | -0.00476         | -0.01018         |
| $B_8^{SS}$ | 0.00256          | 0.00264          | 0.00325          | 0.00704          |
| $B_9^{SS}$ | -0.00185         | -0.00190         | -0.00234         | -0.00507         |
| $B_{10}^{SS}$ | 0.00139         | 0.00143          | 0.00175          | 0.00378          |
| $B_{11}^{SS}$ | -0.00107       | -0.00110         | -0.00135         | -0.00290         |
| $B_{12}^{SS}$ | 0.00085         | 0.00087          | 0.00107          | 0.00228          |
| $B_{13}^{SS}$ | -0.00069       | -0.00071         | -0.00086         | -0.00183         |
| $B_{14}^{SS}$ | 0.00056         | 0.00058          | 0.00071          | 0.00149          |
| $B_{15}^{SS}$ | -0.00047       | -0.00048         | -0.00059         | -0.00124         |
| $B_{16}^{SS}$ | 0.00040         | 0.00041          | 0.00050          | 0.00104          |

| $V_{SS}/V_0$ | \_ | 11.07922 | 2.06818 | 1.13327 |
Table B5: Eigenvalues $\Lambda^{(i)}$ and coefficients $B^{(i)}_{n}$ for constructing the eigenfunctions of the transient response of current step input.

| $i$ | 1       | 2       | 3       | 4       | 5       | 6       | 7       | 8       | 9       | 10      | ... |
|-----|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|------|
| $\Lambda^{(i)}$| 3.23686 | 5.76645 | 8.26009 | 10.74212 | 13.21888 | 15.69280 | 18.16501 | 20.63610 | 23.10643 | 25.57620 | ... |
| $B^{(i)}_{1}$| 4.56973 | 3.77405 | 3.44403 | 3.25860 | 3.13835 | 3.05343 | 2.98996 | 2.94056 | 2.90091 | 2.86832 | ... |
| $B^{(i)}_{2}$| 3.58511 | -3.70788 | -4.65165 | -4.79056 | -4.75592 | -4.67961 | -4.59717 | -4.44807 | -4.38846 | -4.36383 | ... |
| $B^{(i)}_{3}$| 0.51738 | -7.51661 | -0.26793 | 2.76529 | 4.12700 | 4.79007 | 5.12852 | 5.30285 | 5.38877 | 5.42520 | ... |
| $B^{(i)}_{4}$| 0.10883 | -2.89555 | 9.61985 | -5.38646 | 1.50528 | -1.06637 | -2.72102 | -3.80111 | -4.52140 | -5.01134 | ... |
| $B^{(i)}_{5}$| -0.03142 | -0.67827 | 6.80910 | -8.19370 | -8.96686 | -6.36996 | -3.57332 | -1.25152 | 0.55192 | 1.92822 | ... |
| $B^{(i)}_{6}$| 0.02274 | 4.56973 | 9733.77405 | 3.44403 | 3.25860 | 3.13835 | 3.05343 | 2.98996 | 2.94056 | 2.90091 | ... |
| $B^{(i)}_{7}$| 0.10883 | -2.89555 | 9.61985 | -5.38646 | 1.50528 | -1.06637 | -2.72102 | -3.80111 | -4.52140 | -5.01134 | ... |
| $B^{(i)}_{8}$| -0.03142 | -0.67827 | 6.80910 | -8.19370 | -8.96686 | -6.36996 | -3.57332 | -1.25152 | 0.55192 | 1.92822 | ... |
| $B^{(i)}_{9}$| 0.02274 | 4.56973 | 9733.77405 | 3.44403 | 3.25860 | 3.13835 | 3.05343 | 2.98996 | 2.94056 | 2.90091 | ... |
| $B^{(i)}_{10}$| 0.00684 | 0.01470 | 0.02444 | -0.02855 | 1.34838 | -8.32077 | 15.72582 | 2.78725 | -9.11201 | -12.08159 | ... |
| $B^{(i)}_{11}$| -0.00544 | -0.01174 | -0.01900 | -0.03497 | 0.25080 | -3.31803 | 12.97479 | -13.5525 | -10.4004 | 1.88896 | ... |
| $B^{(i)}_{12}$| 0.00441 | 0.00955 | 0.01553 | 0.02140 | 0.07855 | -0.89858 | 6.63451 | -16.8432 | 7.28305 | 14.42925 | ... |
| $B^{(i)}_{13}$| -0.00364 | -0.00789 | -0.01285 | -0.01847 | -0.01763 | -0.23866 | 2.34433 | -11.13101 | 18.13177 | 1.66850 | ... |
| $B^{(i)}_{14}$| 0.00304 | 0.00660 | 0.01078 | 0.01545 | 0.02133 | -0.01123 | 0.69463 | -4.95840 | 15.96042 | -15.44917 | ... |
| $B^{(i)}_{15}$| -0.00257 | -0.00591 | -0.00914 | -0.01313 | -0.01740 | -0.02767 | 0.12123 | -1.73843 | 8.88252 | -19.64680 | ... |
Table B6: Coefficients $C^{(i)}$ of the eigenfunctions of the transient response of current step input.

| $n$ | $G = 0$ | $G = 0.1$ | $G = 1$ | $G = 10$ |
|-----|---------|-----------|---------|----------|
| $C^{(0)}$ | - | 10 | 1 | 0.1 |
| $C^{(1)}$ | 0.03692 | 0.03582 | 0.02821 | 0.00903 |
| $C^{(2)}$ | 0.01356 | 0.01333 | 0.01156 | 0.00496 |
| $C^{(3)}$ | 0.00710 | 0.00702 | 0.00634 | 0.00321 |
| $C^{(4)}$ | 0.00438 | 0.00434 | 0.00401 | 0.00227 |
| $C^{(5)}$ | 0.00298 | 0.00296 | 0.00277 | 0.00170 |
| $C^{(6)}$ | 0.00216 | 0.00215 | 0.00203 | 0.00132 |
| $C^{(7)}$ | 0.00164 | 0.00163 | 0.00155 | 0.00106 |
| $C^{(8)}$ | 0.00129 | 0.00128 | 0.00123 | 0.00087 |
| $C^{(9)}$ | 0.00104 | 0.00103 | 0.00099 | 0.00072 |
| $C^{(10)}$ | 0.00085 | 0.00085 | 0.00082 | 0.00061 |
| ... | ... | ... | ... | ... |
Voltage Step Response

Table B7: Eigenvalues $\Lambda^{(i)}$ and coefficients $B_n^{(i)}$ for constructing the eigenfunctions of the transient response of voltage step input.

| $i$ | 0    | 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 9   | ... |
|-----|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| $\Lambda^{(i)}$ | 0.90931 | 3.39041 | 5.85921 | 8.32702 | 10.79460 | 13.26209 | 15.72954 | 18.19698 | 20.66440 | 23.13182 | ...
| $B_0^{(i)}$ | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | ... |
| $B_1^{(i)}$ | 0.39451 | -3.30704 | -3.20144 | -3.08673 | -3.00260 | -2.94030 | -2.89258 | -2.85489 | -2.82433 | -2.79903 | ...
| $B_2^{(i)}$ | -0.01974 | -3.09446 | 2.69232 | 3.87544 | 4.20749 | 4.29990 | 4.30959 | 4.28807 | 4.25489 | 4.21818 | ...
| $B_3^{(i)}$ | 0.01259 | -0.52802 | 6.45944 | 0.65745 | -2.15584 | -3.53763 | -4.26428 | -4.66685 | -4.89691 | -5.02954 | ...
| $B_4^{(i)}$ | -0.00657 | -0.10223 | 2.64610 | -8.32546 | -5.09803 | -1.69133 | 0.70001 | 2.29885 | 3.37463 | 4.11142 | ...
| $B_5^{(i)}$ | 0.00393 | 0.02410 | 0.63787 | -6.16120 | 7.06425 | 8.21140 | 6.07128 | 3.56954 | 1.41585 | -0.29728 | ...
| $B_6^{(i)}$ | -0.00256 | -0.01843 | 0.03554 | -2.27050 | 9.75696 | -2.49614 | -8.00976 | -8.76740 | -7.55547 | -5.74426 | ...
| $B_7^{(i)}$ | 0.00178 | 0.01289 | 0.03502 | -0.43176 | 5.33232 | -11.52214 | -3.84585 | 3.99848 | 8.05051 | 9.27630 | ...
| $B_8^{(i)}$ | -0.00129 | -0.00946 | -0.02056 | -0.10618 | 1.62963 | -9.36729 | 9.90614 | 9.29270 | 2.43707 | -3.64253 | ...
| $B_9^{(i)}$ | 0.00097 | 0.00718 | 0.01605 | 0.01863 | 0.40730 | -4.07287 | 13.04355 | -4.63473 | -11.23179 | -8.54562 | ...
| $B_{10}^{(i)}$ | -0.00075 | -0.00559 | -0.01255 | -0.02158 | 0.02998 | -1.27762 | 7.80961 | -14.57467 | -2.80008 | 8.37870 | ...
| $B_{11}^{(i)}$ | 0.00060 | 0.00446 | 0.01003 | 0.01672 | 0.03202 | -0.24198 | 3.14134 | -12.18478 | 12.51967 | 9.96900 | ...
| $B_{12}^{(i)}$ | -0.00048 | -0.00362 | -0.00817 | -0.01368 | -0.01915 | -0.07429 | 0.85897 | -6.28195 | 15.82526 | -6.60770 | ...
| $B_{13}^{(i)}$ | 0.00040 | 0.00298 | 0.00675 | 0.01133 | 0.01661 | 0.01564 | 0.22817 | -2.23599 | 10.54522 | -17.02880 | ...
| $B_{14}^{(i)}$ | -0.00033 | -0.00250 | -0.00565 | -0.00951 | -0.01390 | -0.01951 | 0.01206 | -0.66515 | 4.72715 | -15.12894 | ...
| $B_{15}^{(i)}$ | 0.00028 | 0.00211 | 0.00479 | 0.00807 | 0.01181 | 0.01587 | 0.02580 | -0.11780 | 1.66486 | -8.47037 | ...
| $\vdots$ | $\vdots$ | $\vdots$ | $\vdots$ | $\vdots$ | $\vdots$ | $\vdots$ | $\vdots$ | $\vdots$ | $\vdots$ | $\vdots$ | $\vdots$ |
Table B8: Coefficients $C^{(i)}$ of the eigenfunctions of the transient response of voltage step input.

| $n$ | $G = 0$ | $G = 0.1$ | $G = 1$ | $G = 10$ |
|-----|---------|-----------|---------|----------|
| $C^{(0)}$ | −0.88889 | −0.80082 | −0.42334 | −0.07409 |
| $C^{(1)}$ | −0.05700 | −0.05537 | −0.04402 | −0.01443 |
| $C^{(2)}$ | −0.01865 | −0.01834 | −0.01593 | −0.00689 |
| $C^{(3)}$ | −0.00914 | −0.00903 | −0.00816 | −0.00415 |
| $C^{(4)}$ | −0.00541 | −0.00536 | −0.00495 | −0.00281 |
| $C^{(5)}$ | −0.00357 | −0.00354 | −0.00332 | −0.00203 |
| $C^{(6)}$ | −0.00253 | −0.00251 | −0.00238 | −0.00155 |
| $C^{(7)}$ | −0.00189 | −0.00188 | −0.00179 | −0.00122 |
| $C^{(8)}$ | −0.00146 | −0.00145 | −0.00139 | −0.00098 |
| $C^{(9)}$ | −0.00116 | −0.00116 | −0.00112 | −0.00081 |
| $C^{(10)}$ | −0.00095 | −0.00095 | −0.00091 | −0.00068 |
| $\vdots$ | $\vdots$ | $\vdots$ | $\vdots$ | $\vdots$ |
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