Journal of Power Sources 196 (2011) 865–867

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Short communication

Matrix circuit model for an electric double layer capacitor

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ARTICLE INFO

Article history:
Received 14 May 2010
Received in revised form 7 June 2010
Accepted 9 June 2010
Available online 17 June 2010

Keywords:
Energy storage
Electric double layer capacitors
Supercapacitors
Capacitance matrix
Capacitance coefficients

ABSTRACT

A mathematical model of an electric double layer capacitor is developed treating the capacitance as a matrix instead of a scalar. Model explicitly demonstrates that when two electrodes are immersed an electrolyte and a potential difference applied, a stable double layer that store energy is created. It is suggested that supercapacitors could be modeled on the basis of capacitance matrices whose elements parameterize the geometry of the porous electrode.

1. Introduction

Electric double layer capacitors (EDLCs) continue to receive much attention as energy storage components in a wide variety of applications ranging from consumer electronic gadgetry to transport and military electrical systems [1–9]. Many studies have been conducted to optimize the energy storage capacity of EDLCs (supercapacitors) and reduce the loss. Typically EDLC is constituted of two porous electrodes (generally made of carbon) separated by an ion permeable thin membrane and the whole unit is impregnated with an electrolyte. When the electrodes are connected to a DC power supply of voltage V, below the threshold of electrolytic decomposition, positive and negative ions move towards the porous electrodes forming ionic double layers over surface of the porous electrodes. The large surface area of the porous electrode and the thinness of the double layer (comparable to the Debye length) generate an enormous capacitance $C/2$ (C for each electrode connected in series). When the power supply is disconnected after reaching the equilibrium, separated negative and positive charges remain locked in the double layer interface of the porous electrodes. EDLCs are generally modeled on the basis of the equivalent circuits; for example the circuit shown in Fig. 1(a), for a symmetric EDLC, where two leaky capacitors (capacity C and leak resistance R_l) are connected in series with a resistance R_s in between and an external resistance R_e and symmetry assumed for simplicity. In reality, each capacitor C is a complex unit showing responses dissimilar to dielectric capacitors and many attempts have been made to model EDLCs adopting more intricate equivalent circuits and/or transport equations [10–15]. Yet another peculiarity of EDLC is that unlike simple dielectric capacitors, the 'plates' (double layer interfaces) generally carry 4 different charges Q_1, Q_2, Q_3, Q_4 maintained at potentials V_1, V_2, V_3, V_4 [Fig. 1(b)]. In this situation C cannot be treated as a scalar but a matrix. Here we present a matrix model of a symmetric EDLC. The model explicitly demonstrates that when two electrodes are inserted to an electrolyte and potential difference applied, stable energy storing double layer structure could be formed.

2. Model

To facilitate the analysis of the problems of electrostatics with conductors and interfaces Clerk Maxwell developed an elegant scheme based on coefficients of capacitance c_{ij} and potential p_{ij} to relate the charge and the corresponding potential distribution [16]. According to this scheme charges and potentials of N separated conductors are defined by column vectors $\mathbf{Q} = [Q_1\ Q_2\ \ldots\ Q_N]^T$ and $\mathbf{V} = [V_1\ V_2\ \ldots\ V_N]^T$, where T denote the transpose and the charges and potentials related by the equations [17]:

$$\mathbf{Q} = \mathbf{C}\mathbf{V} \tag{1}$$

and

$$\mathbf{V} = \mathbf{P}\mathbf{Q} \tag{2}$$

where $\mathbf{C}$ and $\mathbf{P}$ are $N \times N$ matrices with elements c_{ij} and p_{ij}. The matrix $\mathbf{P}$ is inverse of $\mathbf{C}$ and both matrices are symmetric ($c_{ij} = c_{ji}$,

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doi:10.1016/j.jpowsour.2010.06.024

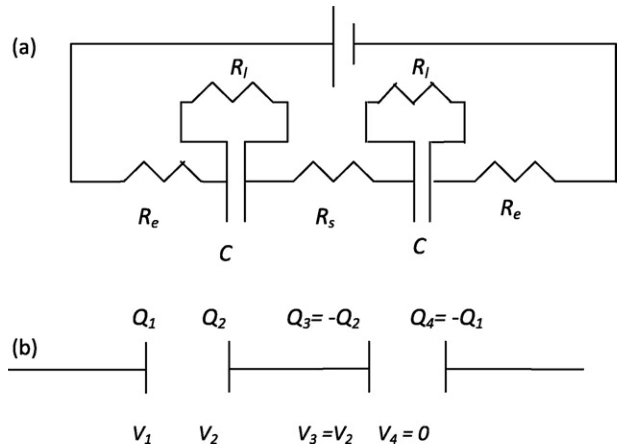

Fig. 1. (a) Equivalent circuit for a double layer capacitor and (b) schematic diagram showing the charges and the potentials of the interfaces.

$p_{ij} = p_{ji}$). The coefficients $c_{ii} > 0$ c_{ij} $(i \neq j) < 0$ and satisfy the condition:

$$\sum_{ij} \left| c_{ij} \right| < c_{ii} \tag{3}$$

The energy W of the capacitor is given by the quadratic form:

$$W = \frac{1}{2} \sum_{ij} c_{ij} V_i V_j = \frac{1}{2} \mathbf{V}^T \mathbf{C} \mathbf{V} \tag{4}$$

The capacitance coefficients c_{ij} attributed to a set of fixed conductors depend only on the geometry of the system and not on their charges or potentials.

Consider a EDLC with interface charges Q_1, Q_2, Q_3, Q_4 held at potentials V_1, V_2, V_3, V_4 (Fig. 2) described by Eq. (1) with:

$$\mathbf{Q} = \begin{bmatrix} Q_1 & Q_2 & Q_3 & Q_4 \end{bmatrix}^T \tag{5}$$

$$\mathbf{V} = \begin{bmatrix} V_1 & V_2 & V_3 & V_4 \end{bmatrix}^T \tag{6}$$

$$\mathbf{C} = \begin{pmatrix} c_{11} & c_{12} & c_{13} & c_{14} \\ c_{12} & c_{22} & c_{23} & c_{24} \\ c_{13} & c_{23} & c_{33} & c_{34} \\ c_{14} & c_{24} & c_{34} & c_{44} \end{pmatrix} \tag{7}$$

When the charged EDLC is in open-circuit condition, electrolyte remains in the equipotential region and no drift current passes through it. This condition is ensured if $V_3 = V_2$, also as there is freedom to choose the base of the potential of one electrode, we set $V_4 = 0$, so that,

$$\boldsymbol{V} = \begin{bmatrix} V_1 & V_2 & V_2 & 0 \end{bmatrix}^T \tag{8}$$

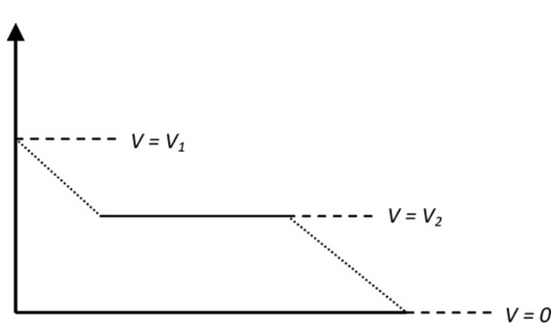

Fig. 2. Schematic diagram showing the potential gradients in a charged electrolytic double layer capacitor at open-circuit.

Figs. 1(b) and 2 indicate the potentials at different positions. In the absence of ionic discharge, electronic and ionic charges are separately conserved, i.e.,

$$Q_1 + Q_4 = 0 \tag{9}$$

$$Q_2 + Q_3 = 0 \tag{10}$$

Using (1) and (5)–(8) the conditions (9) and (10) can be expressed as,

$$(c_{11} + c_{14})V_1 + (c_{12} + c_{13} + c_{24} + c_{34})V_2 = 0 \tag{11}$$

$$(c_{12} + c_{13})V_1 + (c_{22} + c_{23} + c_{23} + c_{33})V_2 = 0 \tag{12}$$

The matrix (7) is written to satisfy the requirement of the symmetry of capacitance matrix. It can be further simplified assuming identical similarity of the two capacitor units, the condition for this being,

$$c_{44} = c_{11}, c_{33} = c_{22}, c_{34} = c_{12}, c_{24} = c_{13} \tag{13}$$

With the assumption (13), the capacitance matrix for a symmetric supercapacitor $\mathbf{C_S}$ can be written as,

$$\mathbf{C_S} = \begin{pmatrix} c_{11} & c_{12} & c_{13} & c_{14} \\ c_{12} & c_{22} & c_{23} & c_{13} \\ c_{13} & c_{23} & c_{22} & c_{12} \\ c_{14} & c_{13} & c_{12} & c_{11} \end{pmatrix} \tag{14}$$

Eqs. (11)–(13) impose the following additional constraint on the elements of the matrix:

$$(c_{11} + c_{14})(c_{22} + c_{23}) = (c_{12} + c_{13})^2 \quad \text{or} \quad c_{23} = (c_{12} + c_{13})^2 (c_{11} + c_{14})^{-1} - c_{22} \tag{15}$$

Thus $\mathbf{C_S}$ is a function only of five independent variables of the matrix elements $c_{11}, c_{22}, c_{12}, c_{13}, c_{14}$.

Using (4), the energy W of the capacitor system described by the matrix $\mathbf{C}$ is,

$$W = \frac{1}{2}[c_{11}V_1^2 + (c_{22} + c_{33} + 2c_{23})V_2^2 + 2(c_{12} + c_{13})V_1 V_2] \tag{16}$$

and W become minimum when

$$V_2 = -\frac{c_{12} + c_{13}}{c_{22} + c_{33} + 2c_{23}} V_1 \tag{17}$$

giving,

$$[W]_{\min} = \frac{1}{2}[c_{11} - (c_{12} + c_{13})^2 (c_{22} + c_{33} + 2c_{23})^{-1}]V_1^2 \tag{18}$$

As all non-diagonal elements of a capacitance matrix are negative and diagonal elements positive, $V_2 > 0$. Also the Eqs. (12) and (18) are identical, indicating that the condition for stability of the system (i.e., minimum energy) is the same as the condition for conservation of ionic charge. Thus the model explicitly demonstrates that when two electrodes are inserted to an electrolyte and a potential applied, energy storing double layer structure could be formed.

When the EDLC is symmetric [i.e., subject to the condition (13)], $W_{\min}$, Q_1 and Q_2 can be expressed in the form:

$$W_{\min} = \frac{1}{4}(c_{11} - c_{14})V_1^2 \tag{19}$$

$$Q_1 = \frac{1}{2}(c_{11} - c_{14})V_1 \tag{20}$$

$$Q_2 = \frac{1}{2}(c_{12} - c_{13})V_1 \tag{21}$$

Eqs. (19) and (20) suggest that energy stored in the symmetric EDLC is similar to sum of energies of two capacitors each of capacitance $C_s = 1/2(c_{11} - c_{14})$.

One of the most important issues related to EDLCs is self-discharge under open-circuit conditions. The above analysis can also be adopted to describe the self-discharge without a drift current in the electrolyte as the model assumes that the electrolyte is an equipotential region (i.e., the condition $V_2 = V_3$). Leakage currents across the symmetrically placed double layers and/or diffusion current in the electrolyte are dissipative processes that maintain the symmetry assumed in the model. In the case where the self-discharge occurs entirely via leakage through the double layer and using Ohm's law to express the current through the resister R_l, we obtain the relation:

$$R_l \frac{d}{dt}(Q_1 + Q_2) = V_1 - V_2 \tag{22}$$

Inserting (17), (20) and (21) in (22) and using (15):

$$\frac{dV_1}{dt} = -\frac{V_1}{\tau} \tag{23}$$

where

$$\tau = -R_l(c_{12} + c_{13})(c_{11} + c_{12} - c_{13} - c_{14})(c_{11} + c_{12} + c_{13} + c_{14})^{-1} \tag{24}$$

Properties of capacitance coefficients ensure that the term in the first bracket of (15) is negative other two brackets positive (and non-zero) making τ a positive quantity. Eq. (24) shows that, unlike a simple dielectric capacitor, the self-discharge time depends not only on capacitance (determining energy storage capacity) but several other parameters defining the potential distribution. The properties of capacitance coefficients imply $C \le c_{11}$, $\tau \le R_l c_{11}$. Thus in general self-discharge time of a symmetric EDLC is less than that of a dielectric capacitor of equivalent capacitance and leakage resistance.

3. Conclusion

If an EDLC is considered as it is constituted of double layer structures at two plane electrodes, then there is no electric field in the region between the two electrodes provided, (1) charges in each double layer are equal and opposite (2) electrode separation and linear dimensions are 'infinitely' large compared to the distance between the interfacial double layers. When this ideal situation is not realized, the response of the system to an applied potential needs to be described by a capacitance matrix [17], whose coefficients are determined to ensure that the conducting regions remain equipotential.

An apparently intriguing issue of supercapacitors is the question why the separated charges do not recombine despite the fact that they are separated by a conducting medium (electrolyte) unlike a conventional dielectric capacitor. The model explicitly demonstrates, how an energy storing stable double layer structure could be formed, when a potential difference is applied to two electrodes placed in an electrolytic medium. The model also shows that even the symmetrical EDLC cannot be defined by an equivalent capacitance of two identical units and resistances, the electrostatics of the problem invoke other parameters. Obviously, the model in the present form will not explain the charging and discharging characteristics of an EDLC. In reality, EDLCs are non-linear systems, capacitance coefficients depend on the applied potential. Again perfect symmetry of the anodic and cathodic double layers is never realized owing to the intrinsic differences of the anions and cations of same charge. Supercapacitors are complex systems and equivalent circuits and other physically meaningful methods are used for evaluation and interpretation of experimental data [18]. Capacitance coefficients are geometrical quantities, porous electrodes in a supercapacitor can be parameterized with these coefficients.

Acknowledgement

This work is supported by the US NSF Grant DMR 0805127.

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