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Influence of designed electrode surfaces on double layer capacitance in aqueous electrolyte: Insights from standard models

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ABSTRACT

Standard models, Helmholtz, Gouy-Chapman, Stern and Grahame models have been validated on the electrical double layers (EDLs) formed from three different electrode surfaces, i.e., plain, semi-sphere and cylindrical pore in aqueous electrolyte. The double layer potential (ϕ) and areal capacitance (C_{dl}) were estimated in the three models using MATLAB Simulink. It was found that the areal capacitance of the double layer strongly influenced by the nature/ type of the electrode surface in contact with the electrolyte. The cylindrical-type pore surface exhibited the large areal capacitance. The charge-discharge and impedance characteristics of the EDLs were also analyzed.

1. Introduction

Batteries and supercapacitors are typical electrochemical energy storage devices. Among them, the batteries have the capability to deliver energy over a long time at a relatively lower rate of current (low power). The batteries fail to deliver high power because, at high power discharge, the lifetime of the battery reduces drastically due to degradation of electrode material and diffusion limitation of ions involved in the electrochemical reactions. Thus, current trends in the electrochemical energy storage technology focus on the development of storage device that can deliver high power as well as high energy. In this regard, supercapacitors seem attractive storage device that can deliver high power for the large cycle of as high as 10^5 cycles. In fact, the supercapacitors can bridge the power gap between the batteries and conventional capacitors, especially for hybrid electric vehicles and electrical tools. Unfortunately, the supercapacitors have severe issues such as low energy density, high cost and high self-discharge. By addressing these issues, the market demand for the supercapacitors can be realized. Electrical double layer capacitor (EDLC) is based on mere charge separation at electrode/electrolyte interface. The electrodes for the EDLCs are typically made of high surface area carbon-based materials because of their porous nature. Aqueous electrolytes are generally employed as an electrolyte in EDLC, where water dipole acts as a dielectric material to provide high relative permittivity. The presence of water dipole in the electrolyte significantly reduces the distance between the two electrodes, to the order of angstrom (Å). Because of aforesaid aspects, the EDLC having high capacity is different from the conventional parallel plate capacitor whose capacity is directly proportional to relative permittivity (ε) and surface area (A), but inversely proportional to the distance between the two electrodes [1]. Modeling and simulations provide insights about designing novel materials for developing efficient device by reducing manufacturing cost as well as technical losses. Recently, Bang et al., has studied optical pore development of carbon models [2]. Similarly, Lu et al., has reported the porous carbon as high ion transport channel for electrode materials in supercapacitor [3]. Thus, to develop highly performing EDLC electrode for energy storage device, a proper understanding of electrical double layer (EDL) formed by different electrode surface in an electrolyte is indispensable.

Wang et al., presented scaling law for the estimation of the integral capacitance of EDLC supported by rigorous analysis and

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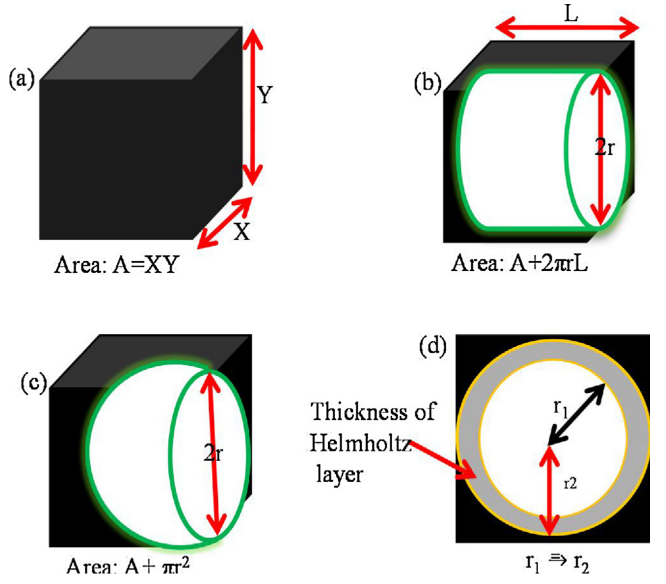

Fig. 1. Schematics of cross section of (a) Planar Surface, (b) Cylindrical pore surface, (c) Semi-sphere pore surface and (d) Front view of pore surfaces.

experimental data on porous carbon-based electrodes [4]. Gavish et al., examined the influence of relative permittivity on the EDLC properties by changing electrolyte concentration [5]. It was reported that higher concentration having less number of dipoles in the solution resulted in low capacitance, whereas lower concentration reduced the capacitance because ions extend to a longer distance from electrode surface due to thermal motion [6–9]. Ohshima et al., described a simple algorithm for the potential distribution in EDLC cylindrical pore surface [10]. He considered Poisson-Boltzman equation to describe potential distribution in a charged cylindrical pore filled with an aqueous electrolyte solution. Martin et al., estimated capacitance of EDLC based on carbon nanotube (CNT) using classical theory [11]. The curvature effect on Gouy-Chapman limit has been established. Shuai Bana et al., worked on the electrochemical equivalent circuit (Randle circuit) to analyze the charging-discharging properties of the EDLC [12].

To the best of our knowledge, the influence of different types of electrode surfaces on the capacitance of EDLC has not been well examined. Thus, in this work, we re-visited the EDLC characteristics of electrode surfaces having different types/ shapes of pores (plain, semi-sphere and cylindrical) as shown in Fig. 1 by applying Helmholtz, Gouy-Chapman, Stern and Grahame models in aqueous electrolyte. Alongside, we have also studied electrochemical charging/discharging and impedance features of the aforesaid model surfaces in aqueous electrolyte.

2. Various models for electrical double layer

A metal in contact with an aqueous solution generates solvated charged ions on its surface, where positive and negative ions are equally distributed throughout the surface. The free electrons will move away from or towards the interface depending on the direction of the electric (E) field. Thus, a net charge is induced on the metal, which will be equal in magnitude and opposite in sign to that on the solution side of the phase boundary. Therefore, charge separation occurs in the electrode surface/ solution interface known as an interfacial potential difference (ϕ). The properties of such electrified interface have been explained by Helmholtz (compact layer), Gouy-Chapman (diffuse layer), Stern and Grahame models.

As per Helmholtz model, two compact layers of charges are formed at the electrode/ electrolyte interface as a result of electrostatic interaction between the electrode surfaces and counter ions of the solution [13,14]. A uniform dipole distribution is present at the interface where potential varies linearly from the electrode surface to the bulk solution as schematically shown in Fig. 2(a). However, Helmholtz model did not account for the influence of thermal motion and ion absorption on the resultant double layer capacitance (C_{dl}). Gouy-Chapman described the EDL by considering the thermal motion of ions near the charged surface and is driven by diffusion and electrostatic forces, in particular at low concentration of electrolyte [15,16]. However, this model did not account for the influence of ion absorption on the electrode/ electrolyte interface. According to the Gouy-Chapman model, the double layer is not rigid at the electrode/ electrolyte interface; rather there is ion concentration gradient from electrode surface to the bulk solution due to thermal motion of ions as schematically shown as in Fig. 2(b).

The Stern model recommends a combination of the concepts of the Helmholtz and Gouy-Chapman models [17]. According to the Stern model, the electrical potential varies linearly with the distance from electrode surface up to Gouy-Chapman layer (rigid layer) and after that decreases exponentially (i.e., diffused layer) as schematically shown in Fig. 2(c). So, as per the Stern model, the capacitance is regarded as two series connected capacitors as given in (Eq. 1):

$$\frac{1}{\boldsymbol{C_{dl}}} = \frac{1}{\boldsymbol{C_{H}}} + \frac{1}{\boldsymbol{C_{GC}}} \qquad (1)$$

where, C_{dl}, C_H, and C_{GC} are double layer, Helmholtz and Gouy-Chapman capacitances, respectively [14].

The currently accepted Grahame model represents the real situation of an EDL. Grahame introduced concepts of inner Helmholtz plane (IHP) where ion absorption occurs on the electrode surface and outer Helmholtz plane (OHP). As shown in the Fig. 2(d), the anions are tightly attached to the electrode surface and partially desolated. This fact causes a reversal of electrostatic potential in the region between the IHP and OHP. The capacitance as per the Grahame model is shown below [14]:

$$\frac{1}{C_{dl}} = \frac{1}{C_{IHP}} + (\frac{1}{C_{OHP}} + \frac{1}{C_{GC}})(1 - \frac{dq_a}{dq_M}) \qquad (2)$$

where q_a and q_M are absorption charge and metal surface charge, respectively.

3. Analysis

In this work, we have modeled EDLC for three different electrode surfaces namely plain layer, semi-sphere and cylindrical in the aqueous electrolyte. The schematic of three different surfaces and the cross-section of the semi-sphere/ cylindrical surface are shown in Fig. 1. The areal capacitances of the EDL resulted on the three electrode surfaces were estimated based on Helmholtz, Gouy-Chapman, Stern and Grahame models. We have assumed the surface potential of 0.5 V and uniform dipole distribution. To calculate the potential change, in the parallel plane layer, linear Gauss law equation has been applied and similarly in the bulk solution, Poisson-Boltzmann equation has been applied. In addition, charging/ discharging and impedance characteristics of the EDLC have been also examined.

3.1. Helmholtz capacitance of model surfaces

According to Helmholtz, the electric double layer is the alignment of charge on the electrode and electrolyte interface similar to parallel plate capacitor. Gauss law states that the surface integral of

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