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CONTENTS

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Electric Double Layer Supercapacitor (EDLS)

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Abstract

Various energy storage technologies have been developed in the market for various applications. Batteries are much common being used in several countries than fuel cells and research is also carrying on these technologies to make much better them. The electrochemical double – layer supercapacitor (EDLS) is an emerging technology, which really plays a key part for present and future in fulfilling the demands of electronic devices and systems. This paper describes the development of history, mathematical background and process of charge storage theories of the EDLCs technology.

Introduction

On account of their high capacitance values, they are called as Electrochemical Supercapacitors (ESs). ES are of two types depending on electrochemical process at the electrode, which are electric double layer supercapacitor (EDLS) and Faradaic Supercapacitor or Electrochemical Pseudocapacitor [1]. EDLS stores electrical energy in the interface between an electrolyte and a solid electrode [2]. EDLSs, therefore present a new breed of technology, which occupies the previously vacant position amongst the other energy storage technologies. They are capable to store large amount of energy than that of traditional capacitors, and are capable to deliver more power than that of batteries [3].

There are a number of desirable qualities that make them advantageous option as energy storage devices, as they have reversible storing and releasing charge capabilities (stability or long life) that make them to withstand a large number of charge/discharge cycles and are also able to charge/discharge quickly (power) than that of batteries [4].

This paper describes the development of history, mathematical background and process of charge storage theories of the EDLCs technology.

Theory and mathematics

EDLS store energy electrostatically by ion adsorption in the electric double layer formed at electrode/electrolyte interfaces without any chemical reactions, hence EDLS also called as electrostatic supercapacitors. The charging/discharging process is highly reversible due to nonchemical electrostatic process of without degradation of electrode material. Hence the life cycle of EDLSs exceeds 100,000 cycles. This is most important key factor for electric energy storage, energy harvesting and energy regeneration applications [5, 6].

Therefore the most important contribution to the capacitance of EDLS is due to double layer formation at electrode/electrolyte interface. Hence it is necessary to study the mechanism of electrode/electrolyte interface.

In 1853 Helmholtz proposed the concept of charge separation at electrode/electrolyte interface to behave as capacitor by storing charge [7 - 9] as depicted in Fig. 1. He suggested that a charged electrode immersed in electrolyte solution attracts the ions of opposite charge and repel ions of same charge due to a charge density arising from the excess or deficiency of electrons at the electrode surface. The layer of electronic charge at the electrode surface of electrode/electrolyte interface and the layer of rigid counter-ions in the electrolyte of electrode/electrolyte interface forms is known as electric double layer. The charge on the electrode is exactly balanced by equal but oppositely charged amounts of ions in the solution. The presence of monolayer of solvent molecules between the charges on electrode surface and ions of electrolyte limits the distance between charged layers. The line drowns between the centre of ions and surface of electrode/electrolyte forms the outer Helmholtz plane (OHP). The region between this line and charged layer at electrode is called as double layer by Helmholtz. An electric potential difference is produced to cause an electric field gradient across the charge separated layer. According to Helmholtz, the double layer capacitance per unit area is given by

$$C_H = \frac{\varepsilon_r \varepsilon_0}{d} \ (1.1)$$

where, ε_r is relative dielectric constant of solution of electrolyte, ε_0 is the dielectric constant of vacuum or free space and d is the thickness of the double layer.
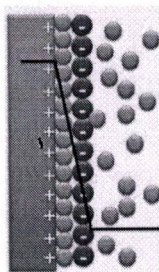

Fig. 1 Helmholtz double layer

This model accounts only for the different electrolytes with varying ionic radius of the ions, but it fail to account for the potential and electrolyte concentration dependence of the capacitance. This model seems to be applicable for higher concentration of electrolyte (> 1M) but fail for lower concentration.

The diffusion double layer model was proposed by Gouy [10] and Chapman [11] which relates the dependence of capacity on potential as well as electrolyte concentration, with the consideration that the distribution of ions should be continuous in the solution of electrolyte, which obeys the Boltzmann distribution. The model accounts for the fact that the ions in the solution of electrolyte are mobile due to combined effects of migration of ions towards interface of electrode/electrolyte driven by electric potential gradient and migration of ions away from interface driven by diffusion due to concentration gradient as well as dispersion due to thermal motion of ions to form 'diffusion layer' as depicted in Fig. 2. The charge density decreases with distance from the interface of the

electrode/electrolyte in the diffusion layer. In this model the electric double layer capacitance is overestimated because ions are treated as point charges resulting in unrealistically large ion concentration at the electrode interface [12, 13]. The Gouy-Chapman model unable to account experimentally found capacity - potential curve for all concentrations except at very lower concentrations (< 0.001M) and experimentally calculated capacitance is much lower than calculated by Gouy-Chapman equation.
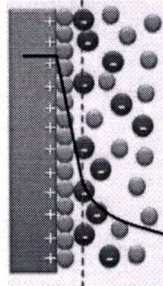

Fig. 2 Gouy- Chapman diffusion double layer model

Stern in 1924 proposed a model of EDL to account for finite size of ions [14]. Stern united the Helmholtz model and Gouy-Chapman model precisely and clearly to describes two distinct regions as (1) inner region termed as Stern layer (same as Helmholtz layer) and (2) the outer region as diffusion layer. Stern assumed the charge q_s on the solution side distributed in a compact layer/region q_H and remaining q_d in the diffusion layer/region, i.e. $q_s = q_H + q_d$. The interface is assumed to be neutral under all conditions i.e. charge on electrode surface is equal to the sum of charge in above mentioned two regions. Therefore, the total differential capacitance C of the interface is equal to the sum of capacitance due to Helmholtz layer C_H and diffusion layer C_d. i.e.

$$\frac{1}{C} = \frac{1}{C_H} + \frac{1}{C_d} \quad (1.2)$$

These adjacent two regions act like capacitors in series, to indicate that the smaller one of two capacitances determines the overall capacitance of double layer interface.

By applying Boltzmann distribution to the ionic concentration $C_{i(x)}$ of electrolyte in the diffusion layer at a distance x from interface, we have

$$C_{i(x)} = C_0 \exp\left(-\frac{z_i F V_x}{RT}\right) \quad (1.3)$$

where, C_0 is the bulk concentration of ions i, F is Faraday's constant, z_i is the valence number with sign, V_x is the electric potential at point x, R is real gas constant and T is the temperature of electrolyte solution.

The net charge in the unit volume of electrolyte solution in diffusion layer is

$$\rho = \sum z_i F C_{i(x)} = \sum z_i F C_0 \exp\left(-\frac{z_i F V_x}{RT}\right) \quad (1.4)$$

The relation between volumetric charge (charge per unit volume) and electric potential is given by Poisson equation as

$$\frac{d^2 V_x}{dx^2} = -\frac{\rho}{\varepsilon_r \varepsilon_0} = -\frac{1}{\varepsilon_r \varepsilon_0} \sum z_i F C_0 \exp\left(-\frac{z_i F V_x}{RT}\right) \quad (1.5)$$

But,

$$\frac{d^2 V_x}{dx^2} = \frac{1}{2}\frac{d}{dV_x}\left(\frac{dV_x}{dx}\right)^2 \quad (1.6)$$

Hence, from above two equations

$$d\left(\frac{dV_x}{dx}\right)^2 = -\frac{2}{\varepsilon_r \varepsilon_0}\sum z_i F C_0 \exp\left(-\frac{z_i F V_x}{RT}\right) dV_x \quad (1.7)$$

Integrating above equation

$$\left(\frac{dV_x}{dx}\right)^2 = -\frac{2RT}{\varepsilon_r \varepsilon_0}\sum C_0 \left\{\exp\left(-\frac{z_i F V_x}{RT}\right) - 1\right\} \quad (1.8)$$

$$\left(\frac{dV_x}{dx}\right)^2 = -\frac{2RT C_0}{\varepsilon_r \varepsilon_0}\left\{\exp\left(\frac{z_i F V_x}{RT}\right) - \exp\left(-\frac{z_i F V_x}{RT}\right)\right\} \quad (1.9)$$

The net charge within the diffusion layer is

$$\frac{dV_x}{dx} = \frac{1}{\varepsilon_r \varepsilon_0}\int_{x=x_1}^{x=\infty} \rho\, dx = -\frac{q}{\varepsilon_r \varepsilon_0}$$

$$\left(\frac{dV_x}{dx}\right)^2 = \left(\frac{q}{\varepsilon_r \varepsilon_0}\right)^2 = \frac{2RT C_0}{\varepsilon_r \varepsilon_0}\left\{\exp\left(\frac{z_i F V_x}{RT}\right) - \exp\left(-\frac{z_i F V_x}{RT}\right)\right\}$$

$$q = \sqrt{2\varepsilon_r \varepsilon_0 RT C_0}\left\{\exp\left(\frac{z_i F V_x}{2RT}\right) - \exp\left(-\frac{z_i F V_x}{2RT}\right)\right\} \quad (1.10)$$

$$q = \sqrt{8\varepsilon_r \varepsilon_0 RT C_0}\,\sinh\left(\frac{z_i F V_x}{2RT}\right) \quad (1.11)$$

The differential capacitance of the diffusion layer is

$$C_d = \frac{dq}{dV_x} = \left(\frac{z_i F}{2RT}\right)\sqrt{8\varepsilon_r \varepsilon_0 RT C_0}\,\cosh\left(\frac{z_i F V_x}{2RT}\right)$$

$$C_d = \frac{dq}{dV_x} = \sqrt{\frac{2\varepsilon_r \varepsilon_0 z_i^2 F^2 C_0}{RT}}\,\cosh\left(\frac{z_i F V_x}{2RT}\right) \quad (1.12)$$

$$\frac{1}{C} = \frac{1}{C_H} + \frac{1}{C_d} = \frac{C_d + C_H}{C_H C_d}$$

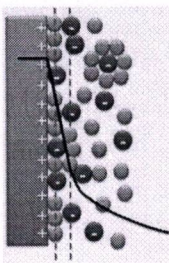$$C = \frac{C_H C_d}{C_H + C_d} \quad (1.13)$$

Fig. 3 Grahame double layer model

Grahame in 1947 proposed the possibility for some ionic or neutral species to penetrate into the region of solvent molecules monolayer in contact with the electrode surface could be possible due to absence of solvation shell of ions or loss of solvation shell when ions migrate towards electrode surface. These ions in direct contact with electrode surface were viewed as 'specifically adsorbed' ions. Therefore, this model proposed the existence of three regions or layer for electrode/electrolyte interface as, (1) inner Helmholtz plane (IHP) prolonged from electrode surface to a plane going through the centres of the specifically adsorbed ions, (2) the outer Helmholtz plane (OHP) passing through the centres of closest approached hydrated or solvated ions to the electrode surface and (3) the layer or region beyond the OHP as diffusion layer as shown in Fig. 3. The potential varies linearly with distance up to OHP and then exponentially through the diffusion region or layer. The width of diffusion layer decreases with increasing solution concentration.

Brockris, Devanathan and Muller in 1963 proposed a model which included the action of the solvent [15]. They suggested that a layer of water was present within the inner Helmholtz plane at the surface of the electrode. The dipoles of these molecules would have a fixed alignment because of the charge in the electrode. Some of the water molecules would be displaced by specifically adsorbed ions. Other layers of water would follow the first, but the dipoles in these layers would not be as fixed as those in the first layer.

Conclusion

The layer of electronic charge at the electrode surface of electrode/electrolyte interface and the layer of rigid counter-ions in the electrolyte of electrode/electrolyte interface forms is known as electric double layer. An electric potential difference is produced to cause an electric field gradient across the charge separated layer. The charge density decreases with distance from the interface of the electrode/electrolyte in the diffusion layer. Double layer describes two distinct regions as (1) inner region termed as Stern layer (same as Helmholtz layer) and (2) the outer region as diffusion layer. The interface is assumed to be neutral under all conditions i.e. charge on electrode surface is equal to the sum of charge in above mentioned two regions. Therefore, the total differential capacitance C of the interface is equal to the sum of capacitance due to Helmholtz layer C_H and diffusion layer C_d. These adjacent two regions act like capacitors in series, to indicate that the smaller one of two capacitances determines the overall capacitance of double layer interface.

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