

## The Principle of Electro-Sorption Technology and Electrode Materials

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### ABSTRACT

In recent years, the electro-sorption technology (EST) has been increasingly applied in the field of water treatment. Firstly, this paper conducts a review on the development history of the EST theory from the classic models (Helmholtz-Perrin model, Gouy-Chapman (GC) model, and Gouy-Chapman-Stern (GCS) model) to the modern electrical double layer (EDL) models (Grahame, electrical triple-layer model, and composite model) as well as the recent status of the theoretical research. Besides, the future development direction and research focus of the EST theoretical model were given. Finally, the current research status of carbon electrodes, metal oxide electrodes and composite electrodes was summarized. This study shall provide theoretical supports for practical application of high-efficiency EST, and the direction for the future development of EST-based electrode materials.

**Keywords:** *electro-sorption, electrical double layer (EDL) theory, mathematical model, electrodes*

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## 1. INTRODUCTION

In recent years, the problems such as water shortage and poor drainage water quality etc. have hindered the sustainable development of China's industrial economy. Water conservation and wastewater reuse have become vital to the development of industrial enterprises. Nowadays, the Chinese government has regarded the environmental protection as the key to economic transformation. For this, it has promulgated a series of laws and regulations such as the Energy Conservation Law and the Environmental Protection Law, which specify the requirements for water use and drainage water quality in industrial enterprises. In particular, the State Council issued the Water Pollution Prevention and Control Action Plan [1], to solve various water pollution problems. Also, clear restrictions on the water consumption by industrial enterprises are proposed, and various measures are taken to improve the water use efficiency and to strictly prohibit the pollution discharge without permit or unlicensed discharge.

As an environment-friendly technology, EST has been widely used in the water treatment field with the advantages of energy saving, high efficiency, less fouling and no secondary pollution. Firstly, the main energy consumption in the electro-sorption process is made to promote ion migration, and the electrode itself does not produce obvious chemical reactions. Compared with distillation and reverse osmosis technologies, the EST separates the solute ions from the solution, but not the solvent from the raw water to be treated, which don't need high temperature or pressure, and then requires less energy. Secondly, the high water-yield is one of its important advantages, since the regenerated water can be reused; if using an optimized process combination, it is even possible to obtain a water yield of more than 90%, which is favored by enterprises with large wastewater production. Meanwhile, it only needs to release the electrical energy in the stored electrodes during the EST regeneration, with no additional chemicals. When compared with the ion exchange

method, the EST avoids the transportation, storage and use of concentrated acid and alkali, while no acid-base neutralization solution is produced; compared with the reverse osmosis method, it does not need to use reducing agents, scale inhibitors and other chemicals, and have no secondary pollutants. Besides, the electro-sorption device requires no membrane material, and uses the inert electrode material, which has low requirements for raw water pretreatment. The millimeter width water flow channel is used in the device, to ensure no clogging and good tolerance to particulate matter. The whole process adopts an automatic control system, with high automation and simple operation. Thanks to its wide adaptability and good practicality, the EST can be applied in the deep purification of drinking water, reuse of industrial wastewater, desalination of wastewater, and desalination etc. But the physicochemical properties of the electrode material are closely related to the desalination efficiency of the EST. So, it's necessary to regulate the physicochemical properties of the electrode material itself for a high capacitive deionization (CDI) and adsorption capacity. In view of the above, this paper analyzes the current research status of the EST, and studies the mechanism of electro-sorption based on the EST principle. Then, it gives a review of different electro-sorption electrode materials such as carbon electrodes, metal oxide electrodes, and composite electrodes when they are applied in desalination of seawater and adsorption treatment of pollutants in water bodies. Finally, the conclusions and prospects are made for the development of EST [2].

## 2. EST PRINCIPLE AND DEVELOPMENT HISTORY

Electro-Sorption Technology (EST), also known as Capacitive Deionization (CDI) [3], reduces the ion content in the main body of the solution for desalination through the use of the applied voltage to form an electrostatic field that attracts charged particles in water to the electrode surface for enrichment and storage in the double electric layer [4, 5]. With

a certain capacity limit, the EDL will reach a saturation state after a period of adsorption. At this point, the reuse of the electro-sorption device can be started by reversing the electrodes or removing the applied power supply. In the electrochemical system, when the solution passes between the electrodes composed of cathode and anode, the charged particles in the solution will move to the electrode with opposite polarity under the action of the applied voltage lower than the solution decomposition voltage, and will be adsorbed by the electrode and enriched in the double layer, thus realizing the separation of charged particles and solvent to achieve desalination. And the treated solution will be excluded by the outlet. As the applied voltage disappears or the polarity of the power supply is switched, the charged particles stored on the electrode are released and flow out with the water under

the joint action of water flow and electric field force, to achieve the regeneration of the electrode.

The EST was first proposed and studied back in the 1940s. As the first to discover the adsorption phenomenon of direct current, Grahame carried out several adsorption experiments using n-octanol, which all showed that electro-sorption materials have the ability to adsorb. But due to the lack of theoretical guidance, he believed that the adsorption behavior of materials in electric fields was formed by the materials themselves [6]. The breakthrough for the principle began in the 1960s, and then more studies focused on theoretical and experimental studies of electro-sorption for more than half a century. The whole research history is mainly divided into three stages: theoretical research, material optimization and engineering applications. The EST development history is shown in Figure 1 [7].

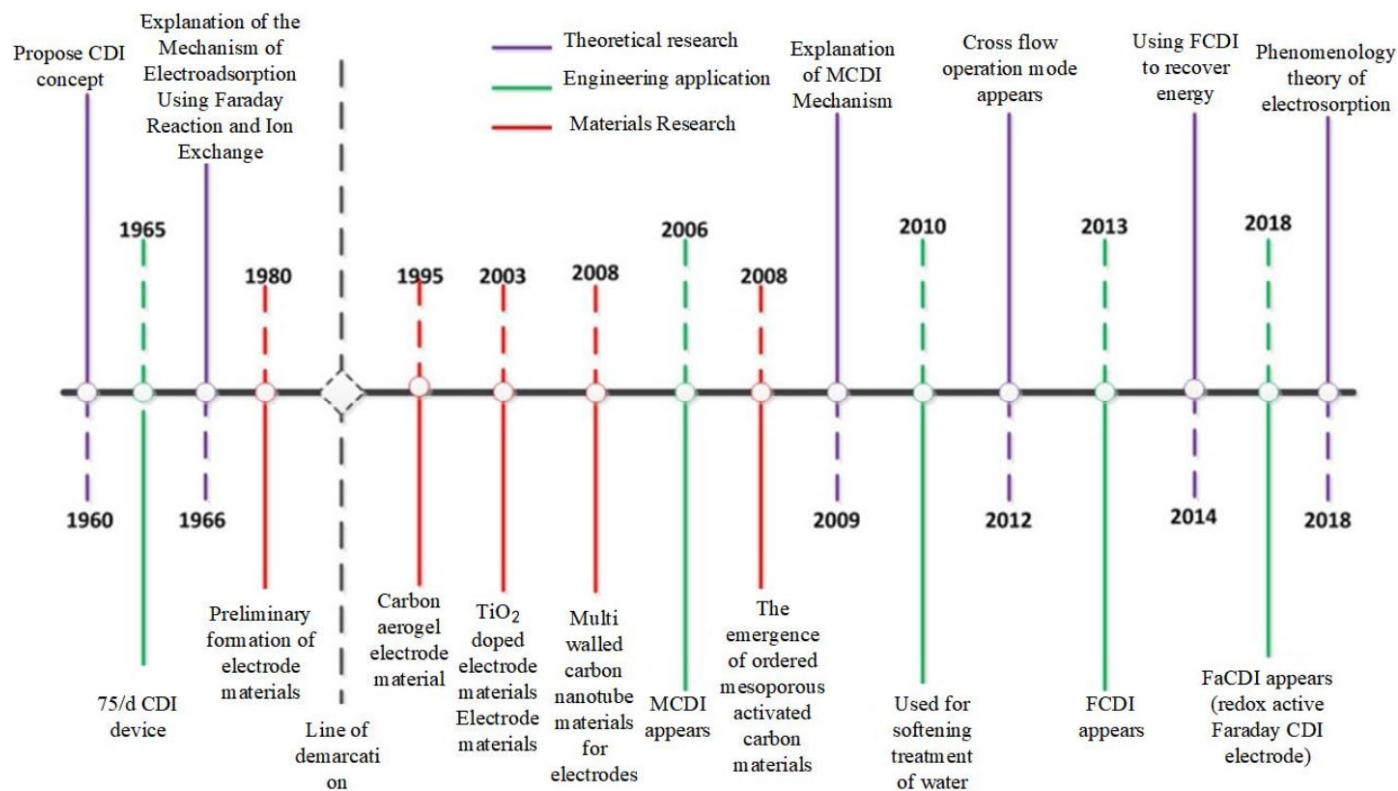


Figure 1. Development history of EST

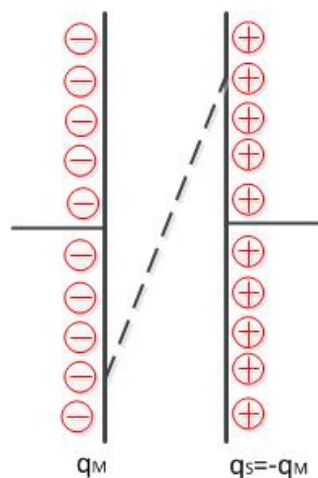


Figure 2. Schematic diagram of Helmholtz parallel-plate capacitor model

### 3. ELECTRICAL DOUBLE LAYER (EDL) THEORY

#### 3.1 Classic models

##### 3.1.1 Stern layer model (Helmholtz-Perrin model)

In the late 19th century, Helmholtz and Perrin first proposed a model for the charge distribution at the solid-liquid interface, i.e., the Helmholtz-Perrin model [8, 9]. This model treats the solid-liquid and phase interfaces as two parallel plates, respectively. If one plate has a surface charge of  $q$ , then the other has an inverse charge of  $-q$ . And the liquid-phase interface is located at the OHP/IHP (outer Helmholtz plane/inner Helmholtz plane) position, forming an EDL structure similar to a parallel-plate capacitor. The DEL structure can be viewed as a parallel-plate capacitor with the plate distance of  $d$  and a constant capacitance of  $C$ , as shown in Figure 2.

The potential drop between the two parallel plates is linear, indicating that the surface charge  $q$  is proportional to the

surface potential  $\phi$ . Combining the electrostatic theory of parallel-plate capacitors, we obtained:

$$C = \frac{\epsilon A}{d} \quad (1)$$

$$C_d = \frac{dq}{d\phi} \quad (2)$$

Combining the two equations above, it's given by:

$$q = C\phi \quad (3)$$

where,  $d$  is the distance between parallel-plates,  $\epsilon$  is the dielectric constant of the material between the two electrode surfaces, and  $A$  is the area of the electrodes.

The Helmholtz-Perrin model, serving as a theoretical basis for explaining early electrokinetic phenomena, only applies to EDL structures with small total surface charge  $q$  or large electrolyte concentration. Then the charge can be considered absent in the main body of the liquid phase, but is not satisfied in dilute solutions [10, 11]. The model does not consider the charge distribution at the interface during ionic adsorption and beyond the IHP/OHP interface. It's an idealized model, but does not correspond to the real situation and cannot fully explain the electrokinetic phenomenon [12].

### 3.1.2 Diffuse layer model (Gouy-Chapman model)

The simplified Helmholtz-Perrin model considers that the charge on the electrode is balanced and distributed by an equal but oppositely charged amount of ions on both sides of the solid-liquid interface, which does not match the actual charge distribution. Thus, the diffuse layer model (Gouy-Chapman model) was proposed in the early 20th century [13, 14]. In this model, the opposite charge in the liquid phase is dispersed around the solid-phase interface; due to the electrostatic attraction of positive and negative charges, the smaller the distance  $d$  from the solid-phase interface, the more the countercharge is; as the distance  $d$  increases, the less the opposite charge is [15]. As shown in Figure 3, it's assumed that the opposite charge on the liquid-phase side is distributed in the space around the solid-phase interface according to the Boltzmann relationship.

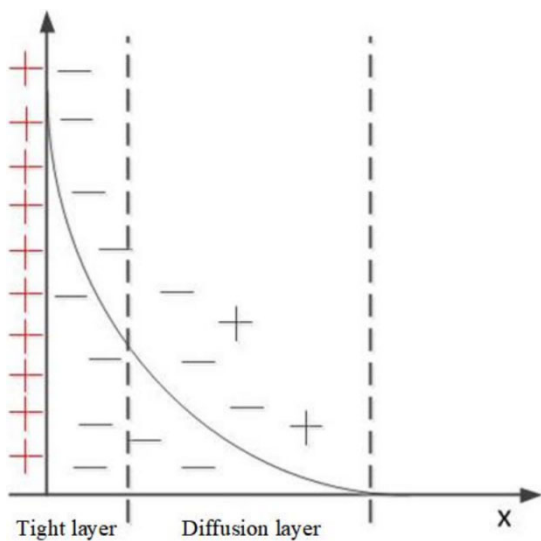


Figure 3. Schematic diagram of Gouy-Chapman diffuse double-layer model

The distribution of the opposite charge in the liquid phase follows the Boltzmann equation:

$$C_i(x) = C_i^0 \exp(-Z_i F \phi_x / (RT)) \quad (4)$$

Combining Gauss's law in electromagnetic field theory:

$$q = \epsilon \epsilon_0 d\phi/dx \quad (5)$$

The potential distribution in the entire liquid phase space is obtained by derivation and simplification:

$$\ln \phi_x = -(2C_0 Z^2 e_0^2 / (\epsilon \epsilon_0 kT))^{0.5} x + C \quad (6)$$

$$\ln \phi_x = -Kx + C \quad (7)$$

where,  $K$  is the Debye-Hueckel constant;  $k$  is the Boltzmann constant;  $C_0$  is the concentration of particles in the main body of the liquid phase;  $Z$  is the number of charges carried by the particles;  $\epsilon$  is the relative dielectric constant;  $\epsilon_0$  is the vacuum dielectric constant.

It can be further simplified to an exponential form:

$$\phi_x = \phi_0 e^{-Kx} \quad (8)$$

From the above, it can be seen clearly that the potential  $\phi_x$  in the diffuse layer varies exponentially with the distance  $x$  from the solid-phase electrode surface. The diffuse layer model explains the electrokinetic phenomenon, depicts the distribution of the opposite charge in the liquid phase attracted around the solid-phase interface, explains well the difference between the thermodynamic potential and the electric potential, and obtains the effect of the electrolyte nature on the capacitance of the diffuse layer. However, it cannot explain how the potential can change its sign etc. [16, 17].

### 3.1.3 GCS double layer model (Gouy-Chapman-Stern model)

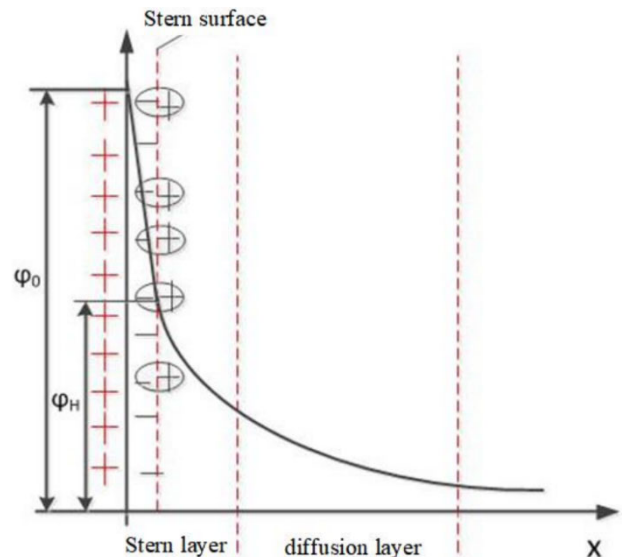


Figure 4. Schematic diagram of the Stern model

In 1924, an improved GCS model was proposed on the basis of the diffuse layer model [18, 19]. This model no longer treats the diffusing particles as point charges, but divides the liquid phase charge into two parts at the OHP/IHP position. One part of charge is distributed at the OHP/IHP position, and its

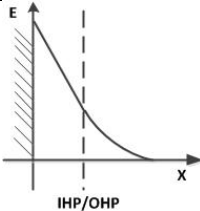
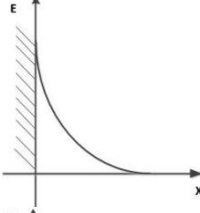
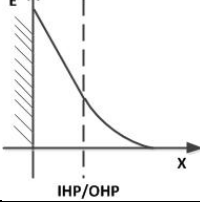
electricity quantity is set to  $q_H$ , which follows the laws and characteristic equations of the stern layer model (Helmholtz-Perrin model) described earlier; the other part is distributed in the liquid phase outside the OHP/IHP with the electricity  $q_G$ , following the diffuse layer model (Gouy-Chapman model) above. Also, the charge all satisfies the equilibrium equation  $q_l = q_H + q_G$ ,  $q_M = q_l$ ,  $q_M = q_H + q_G$  and the total voltage drop of the double layer is equal to the sum of the stern layer and the diffuse layer:  $\phi_{bulk} - \phi_M = (\phi_{bulk} - \phi_H) + (\phi_H - \phi_M)$ .

The charge distribution inside the Stern plane follows the Helmholtz-Perrin model, and the potential decreases linearly from  $\phi_0$  to  $\phi_H$ ; the charge distribution outside the Stern plane follows the laws and characteristic equations of the Gouy-Chapman model, and the potential decreases from  $\phi_H$  to 0 exponentially, as shown in Figure 4. The GCS model

illustrates the physical meaning of the electric potential in detail, and to a certain extent, it can reasonably explain the electrokinetic phenomenon, thus providing a more detailed and scientific understanding of the EDL microstructure.

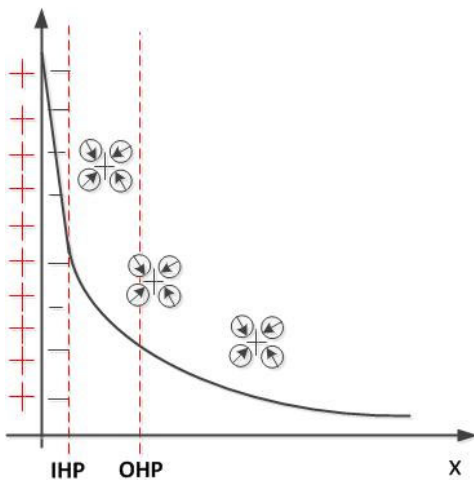
Subsequently Song [20] compared three types of double layer conductivity models for muddy sandstone. Jiang et al. [21] have proposed an novel electric triple layer(ETL) model as an improved model of electrical double layer(EDL) to predict electroosmosis flow rate on the electrode surface at low frequency. Charmas et al. [22] have presented an electrical tetra-layer model to distinguish the magnitude of cations and anions adsorbed on the surface of electrolyte solutions and oxides. This model considers that the anions and cations in the electrolyte are in different electrical layers. It can be seen that the EDL model tends to develop in a more complex and microscopic direction. Table 1 compares the structural features of the three classic models.

**Table 1.** Comparison of structural features between three classic models

Model	Equation	Model Legend	Application scope
Helmholtz-Perrin model	$q = C\phi$		The charge distribution outside the IHP/OHP plane is ignored; it's suitable for EDL structures with small total surface charge $q$ or large electrolyte concentration
Gouy-Chapman model	$\phi_x = \phi_0 e^{-kx}$		The parabolic relationship between phase interface capacitance and electrode potential is explained, and ions are viewed as point charges.
GCS model	$\phi_{bulk} - \phi_M = (\phi_{bulk} - \phi_H) + (\phi_H - \phi_M)$		Ions are affected by both electric field and thermal motion, and it's suitable for non-characteristic adsorption

### 3.2 Modern EDL Theory

#### 3.2.1 Grahame model



**Figure 5.** Schematic diagram of the Grahame model

In 1947, Grahame proposed a more refined EDL model based on the above classic models. This model laid the foundation for the continuous improvement of the modern EDL model [22, 23]. Stern divided the solution into a stern layer and a diffuse layer, and Grahame further classified the inner layer into two planes: an inner Helmholtz plane with a dielectric constant of only 6, which corresponds to the Stern layer in the GCS model and follows the Helmholtz-Perrin model; an outer Helmholtz plane containing hydrated ions that can move together. Grahame believes that the charge is not uniformly distributed at the solid-phase interface and the surface charge is rearranged when ion adsorption occurs in the Stern layer. The principle of Grahame's model is shown in Figure 5.

#### 3.2.2 Microporous region-based EDL model

In 2002, Ying et al. [24] investigated the electro-sorption behavior of carbon aerogels for ions in water solutions and developed a microporous region-based EDL model through the Grahame and Parsons theory and their own experimental studies. The study found that the overlap phenomenon of double layer is not negligible due to the specificity of the



carbon aerogel's pore structure. Therefore, this model takes into account the effects of double-layer overlap and ion-specific adsorption on the electro-sorption capacity, and obtains an EDL model around the microporous region that fits better with the experimental results. The EDL model considering the overlap effect is given as:

$$\eta_d = V/2 - \phi_{ecm} - \varepsilon_0/C_1 \quad (9)$$

where,  $\eta_d$  is the diffuse layer potential near the anode,  $V$  is the applied external voltage,  $\phi_{ecm}$  is the electrode potential corresponding to the maximum electric capillary, which is a function of the solution concentration  $C$  considering the specific adsorption of ions,  $\varepsilon_0$  is the charge surface density,  $C/m^2$ ;  $C_1$  is the inner capacitance, remaining constant in the low voltage range,  $F/m^2$ .

Considering the effect of ion-specific adsorption, it is necessary to determine the function relationship between  $\phi_{ecm}$  and solution concentration. Therefore, based on the relationship between the surface concentration ( $n$ ) of the specific adsorbed ion, the ion concentration ( $C$ ) in the bulk solution and the double-layer potential difference ( $\phi$ ) proposed by Grahame and Parsons [25], we assumed the relationship between the solution concentration ( $C$ ) and  $\phi_{ecm}$  as:

$$k_1/C = \exp(k_2\phi_{ecm}) \quad (10)$$

where,  $K_1$  and  $K_2$  are constants (determined by the anions in solution). Combining the Eqns. (9) and (10) above, the EDL model around the microporous region of the carbon aerogel is derived as:

$$\eta_d = V/2 - \ln^{K_1 C^{-1}} / (K_2 \ln e) - \varepsilon_0/C_1 \quad (11)$$

### 3.2.3 Nanomaterial intra-pore EDL model

In 2006, Hou et al. [26] conducted both the experimental and theoretical studies to explore the basic mechanism of the EDL formed inside the pores of nanostructured carbon-based materials. Through the characterization experiments of the pore size distribution and the specific capacitance of the EDL, it's concluded that the microporous region accounts for a large part of the total specific surface area and therefore the overlap effect of the EDL can have a significant effect on the electro-sorption capacitance. The diffuse layer inside the pore determines the magnitude of the EDL capacitance if the solution has low concentration and the materials approach the zero charge point. It can mitigate the influence of the overlap effect on the electro-sorption capacitance by increasing the pore size, solution concentration and applied voltage. Irrespective of specific adsorption, the inner capacitance  $C_1$  of this model can be assumed to remain constant in the low-pressure range [27]. To compare the potential distribution in different cases, the Gouy-Chapman-Grahame theory was applied to obtain an EDL model for nanomaterials:

$$Y = (\eta - \eta_d)/\eta_0 \quad (12)$$

$$Y_M = (\eta_M - \eta_d)/\eta_0 \quad (13)$$

where,  $Y$  is the potential drop at any point relative to the diffuse layer potential, dimensionless potential;  $\eta$  is the EDL electricity,  $\eta_d$  is the diffuse layer voltage,  $Y_M$  is the mid potential, dimensionless potential;  $\eta_0$  is the surface voltage,  $\eta_M$  is the mid voltage.

In 2007, Mo et al. [28] concluded that there is a discrepancy between the theoretical and actual adsorption amounts of electrodes through theoretical calculation. Then, by analyzing the related reasons, they proposed a "three-dimensional pore-channel double-layer model" based on the classic EDL models. Such model is mainly influenced by the factors such as the depth, radius, surface area, pore volume, electrode resistance and solution internal resistance of the pore channel, etc., so as to obtain the influence rule of various factors on the performance of electrode materials and the desalination effect of the whole device, which shall provide theoretical guidance and technical directions for selecting the optimal capacitive adsorption materials and improving the electrodes.

In 2018, by immobilizing charged groups onto porous electrodes, He et al. [29] obtained redox active FaCDI electrodes as a way to enhance the deionization performance of the EDL. A generalized EDL model was developed based on the fact that the charge on the electrode surface at different voltages can be regulated by Faraday reactions during capacitive deionization. Figure 6 shows the schematic diagram of the FaCDI model. The model can predict the performance of CDI cell enhancement and inversion, complying with the experimental observations. Experimental results demonstrated that FaCDI outperforms conventional CDI and ECDI systems in terms of deionization performance, with adsorption capacities 50%-100% higher than CDI systems, and it depends on the Faraday redox potential at smaller cell voltages.

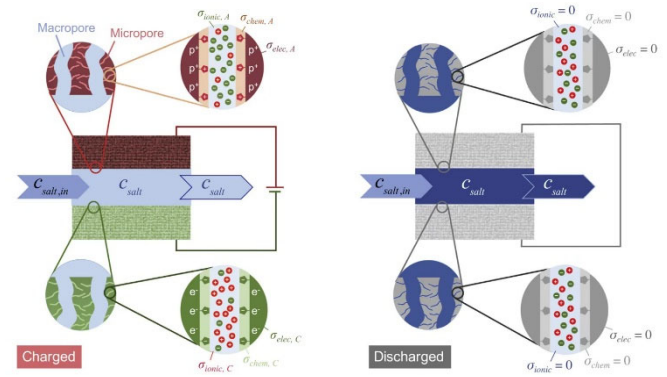


Figure 6. Schematic diagram of a FaCDI structure

Also, Attard [30] in 2018 presented a phenomenological theory of electro-sorption based on the concept of local charge and local electron polarization rate (Friedel oscillations). The UV absorption properties displayed by molecular entities in aqueous solutions are used to predict the extent and nature of ion and molecular adsorption on electrode surfaces. The model can predict the extent of ion adsorption at the potential of zero charge (PZC) in some cases, and also provide theoretical support for metal underpotential deposition (UPD) processes on single crystal electrodes. Future studies on the prediction of electrocatalytic trends and adsorption processes associated with neutral molecules will provide a theoretical basis for a large number of electro-sorption behaviors.

Although the EDL models have been studied more, there still exist some problems with them. For example, Helmholtz-Perrin is an interface model in an ideal case that cannot fully explain the causes of electrokinetic phenomena. Based on this model, the Gouy-Chapman model was proposed to explain these phenomena more rationally, and depict the distribution of the opposite charge around the solid-phase interface, but it still fails to explain the cause of the sign changes in the

electrical potential. For this, the GCS model emerged to fully summarize the previous models and reasonably explain the electrokinetic phenomena, laying the foundation for improving the EDL structure. Through the revision history of the EDL model, it clearly found that this model has been refined from simple to complex, and from phenomenon to essence. Also, with the use condition being simplified and the application scope being expanded, the model can reflect the microscopic principles of electro-sorption more realistically. In recent years, many studies have focused on the microscopic adsorption behavior of electro-sorption on specific materials and established material-specific EDL models, which is also the future direction of EDL research. It's of great significance to guide the future research of electrochemistry by reviewing the previous in-depth studies from different perspectives.

## 4. ELECTRODE MATERIALS FOR ELECTROSORPTION

### 4.1 Carbon electrodes

Generally characterized by large specific surface area, high electrical conductivity, and chemical stability, carbon electrodes are one of the commonly used materials for preparing adsorption electrode samples. They are chemically inert and have a long service life as adsorption electrodes in the complex water environment; meanwhile, they are easy for structure adjustment, widely available, simple to prepare and relatively inexpensive, so as to be often applied as adsorption electrodes in electro-sorption research experiments of seawater desalination, such as activated carbon, graphite, carbon aerogel and carbon nano etc.

#### 4.1.1 Activated carbon

Electrode materials made of activated carbon have been developed earlier, and widely used in industrial applications at present. In recent years, activated carbon is considered to be an ideal electrode material because of its large specific surface area, porous structure, strong adsorption, stable chemical properties and regeneration etc.

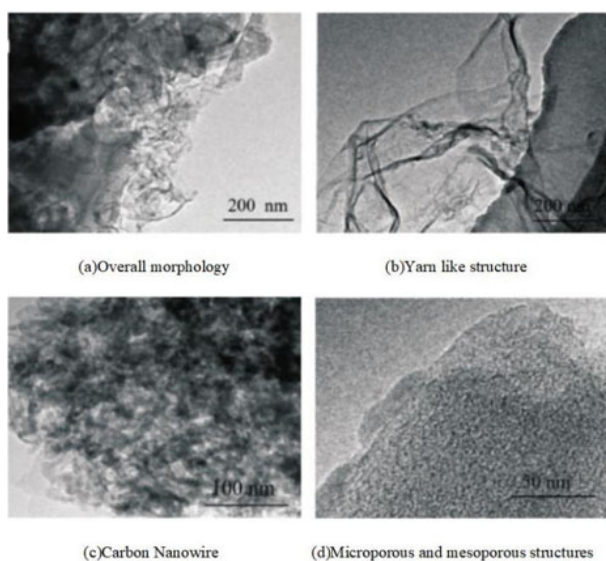


Figure 7. SEM image of the GAC

According to the previous studies, activated carbon materials are mostly microporous concentrated structure. Ajay

and Dinesh [31] used bamboo as precursor and KOH as activator to synthesize nano activated carbon under nitrogen atmosphere, and to increase the surface area and pore size performance of electrodes. Han et al. [32] prepared high specific surface area-based activated carbon from pepper straw using chemical activation method, and the GAC (granular activated carbon) made under certain conditions has a specific surface area of 743.429 m<sup>2</sup>/g and a specific capacitance of 262.595 F/g. Its SEM image is shown in Figure 7.

#### 4.1.2 Graphene electrodes

Graphene exhibits many excellent properties in the fields of optics, mechanics, and materials science. It's one of the most-preferred electrode materials. Using KMnO<sub>4</sub> as an etching agent, Xu et al. [33] prepared three-dimensional graphene materials with unique mesoporous morphology by a simple carbothermal reaction. This material can reach the electro-sorption performance of 6.38 mg/g in a solution with an applied voltage of 1.2 V and an initial NaCl concentration of 75 mg/L, i.e., 2.3 times that of two-dimensional graphene materials and 1.5 times that of three-dimensional graphene materials with macroporous structure, respectively, which is attributed to the short ion transport distance and low charge transfer resistance of the mesoporous structure. Yang et al. [34] made 3D graphene materials by immersing sponges in graphene oxide solution and changing the annealing temperature, which increased the specific surface area from 178 m<sup>2</sup>/g to 305 m<sup>2</sup>/g.

#### 4.1.3 Carbon aerogel electrodes

Carbon aerogel is a lightweight, porous, amorphous, bulk nanocarbon material with a continuous three-dimensional network structure that can be controlled and sheared at the nanoscale. Due to its unique nano-network structure, it also has ultra-low thermal conductivity, high specific surface area and controllable pore size distribution, with a great prospect in electrode materials.

Lv et al. [35] used graded carbon aerogels decorated with polypyrrole from liquefied wood to achieve high energy density and capacitance supercapacitors. Ji et al. [36] utilized the magnesium acetate and magnesium hydroxide as catalysts for the condensation reaction of resorcinol with formaldehyde; the resulting condensation products were dried at room temperature and carbonized at high temperature to form carbon aerogels. A comparative study between them revealed that the electrochemical performance of the carbon aerogel obtained with magnesium hydroxide as the catalyst was the best, with specific capacitance up to 123 F/g. The pore size distribution of the carbon aerogel is shown in Figure 8.

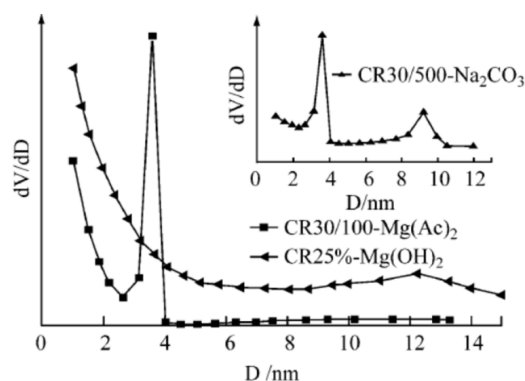


Figure 8. Pore size distribution of carbon aerogels

#### 4.1.4 Carbon nanomaterial electrodes

Carbon nanomaterials have at least one dimension of the dispersed phase less than 100 nm. They mainly include three types: carbon nanotubes, carbon nanofibers and carbon nanospheres. Due to their properties of high electrical conductivity, ultra-stability, high specific surface area, and low density, such materials are widely used in the EST.

Shi et al. [37] took thermosetting phenolic resin (PF) as the carbon source to synthesize new one-dimensional mesoporous carbon fibers by electrostatic spinning method and simple heat treatment. The mesoporous carbon nanomaterials were characterized by XRD, specific surface area, and pore size distribution. The results showed that a large number of mesoporous structures existed inside the carbon nanofibers incorporated with PluroF127. Among them, MCNFs-2 obtained a specific surface area of 1444.26 m<sup>2</sup>/g, thus providing more active sites and specific capacitance; in 6 mol/L KOH aqueous solution, the MCNFs-2 electrode acquired a high discharge specific capacity (13 F/g, current density of 0.05 A/g) and excellent multiplicity performance.

#### 4.1.5 Performance comparison between four types of carbon-based materials

Table 2 compares the performance of the four types of

carbon-based materials. It can be seen that activated carbon electrodes are more mature than the other three types, since it developed earlier and has been already applied in certain industries, but with poor electrical conductivity; graphene electrodes are characterized by good electrical conductivity and thermal conductivity, gradually moving toward industrialization, while they have the disadvantages of reduced specific area and easy agglomeration etc.; carbon aerogel electrodes have good regeneration performance and strong corrosion resistance, but expensive and complicated in preparation process; carbon nanomaterials boast unique pore structure, high specific surface area, good electrical conductivity, etc., but have the risk of environmental pollution, failing to realize large-scale industrial production.

In sum, although all the above four types of carbon-based electrode materials have broad application prospects, they also need additional activation, carbonization, loading and other treatments to modify them according to the practical application requirements, which greatly increases the production cost. Therefore, it shall be the focus and difficulty of future research on electro-sorbent materials to select suitable methods and dopants for modifying the electrode materials and then reducing the fabrication cost according to the industrial requirements.

**Table 2.** Performance comparison of four types of carbon materials [38]

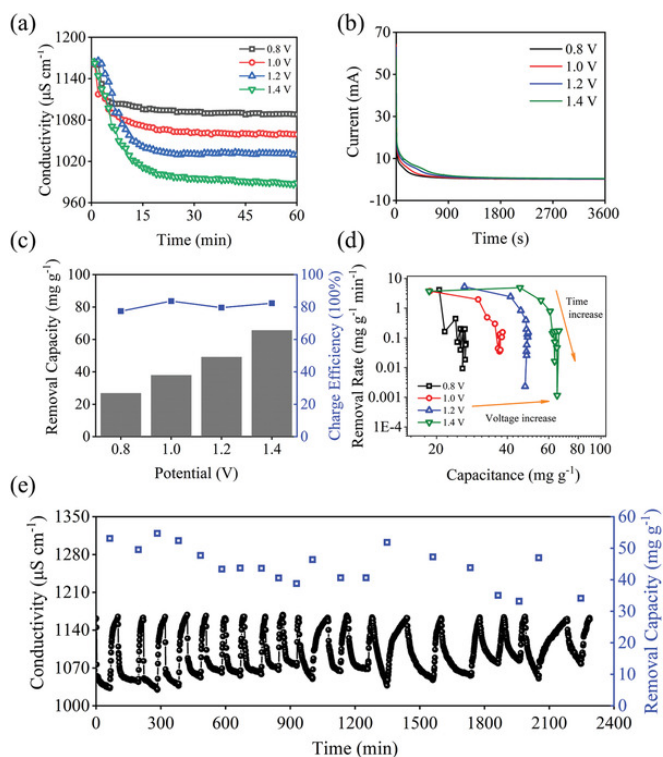
Performance	Activated Carbon electrodes	Graphene electrodes	Carbon aerogel electrodes	Carbon nanomaterial electrodes
Large specific surface area	√		√	
High porosity	√	√	√	
High specific capacitance	√	√		√
Controlled pore size			√	
High electrical conductivity		√		√
Advantages		√	√	√
Good thermal conductivity		√		√
Low density		√		√
Good chemical stability			√	√
Good regeneration	√		√	
Technology maturity	More mature, with some industrial applications	Gradually tend to be industrialized	In the phase of research	n the phase of research
Broad application prospect	√	√	√	√
Poor conductivity	√			
Easy clogging		√		
Complex process	√	√	√	√
Disadvantages		√	√	√
High cost		√	√	√
Difficulty in large-scale production			√	√
Risk of environmental pollution		√		√

#### 4.2 Metal oxide electrodes

The metal oxide electrode of electro-sorption, as a new type of electrocatalytic material, have the advantages of high efficiency, stability and regeneration. Metal oxide electrodes are involved in electrocatalytic reactions through surface active sites, charge transfer and reaction mechanism etc. to achieve efficient and stable electrocatalytic effects during the electro-sorption process. Their structural features such as porous structure, high specific surface area and good electrical conductivity can provide more active sites and increase the

surface area of the electrode, thus improving the reaction rate and efficiency, as well as greatly influencing their electrocatalytic performance. Metal oxide electrodes in electro-sorption are promising for a wide range of applications in fields such as energy conversion and environmental management. For example, Wang [39] synthesized NiCo<sub>4</sub>MnO<sub>8.5</sub> (Ni-Co-Mn-O) with a stepped porous structure using a simple hydrothermal method. Electrochemical tests showed that Ni-Co-Mn-O has low internal resistance and ion diffusion impedance, and the desalination capacity of the

electrode was increased from 26.84 mg/g to 65.61 mg/g by increasing the voltage from 0.8 to 1.4 V in a solution concentration of  $1.0 \times 10^{-2}$  mol/L NaCl solution, while the charging efficiency was stabilized at about 80%. The retention rate of desalination capacity remained 64.27% after cycling for 20 times (Figure 9). The ion species and concentration test results of the solution indicated that irreversible desalination of Ni, Co and Mn ions occurred during the charging and discharging process, which may lead to the decay of the desalination capacity in the Ni-Co-Mn-O electrode.



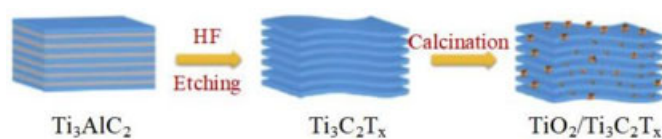
**Figure 9.** (a) Real-time conductivity of Ni-Co-Mn-O CDI; (b) Current change of Ni; (c) Desalination capacity and charge efficiency changing with voltages; (d) CDI Ragone plot; (e) Cycling performance

Using their "memory effect", Qiao [40] selected two layered metal oxides as electrode materials for the anode, and activated carbon with nitric acidification for the cathode to remove arsenic ions from water bodies and achieve the water purification. The study found that the layered metal oxides have good adsorption effect for heavy metal ions. Wang [41] tested the three thin film electrodes of NiAl-MMO, NiCoAl-MMO, and NiAl-MMO/Pd for salt removal performance, and found that the optimal adsorption conditions for NiAl-MMO were: initial salt concentration of 3 mmol/L, static voltage 1.0 V, and pH 8 of the solution, while the adsorption rate of Cr ions reached 58.17% and the adsorption capacity was  $0.51 \text{ mg/cm}^2$ .

### 4.3 Composite electrode

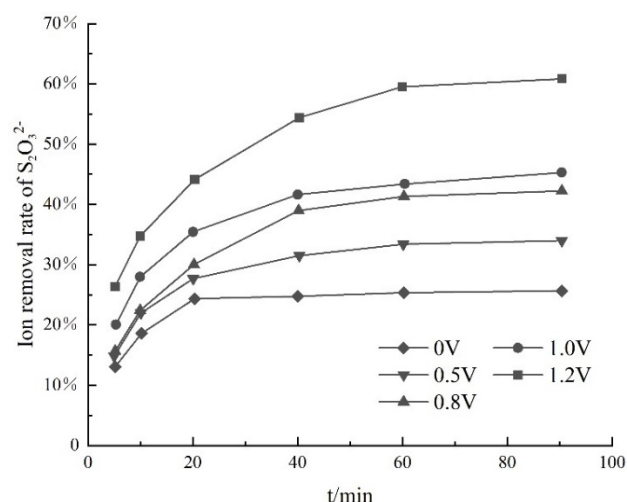
Composite electrodes are composed of two or more different materials, which can avoid the deficiencies of single electrode materials and thus achieve synergistic effects. They have not only the electro-sorption function but also degradation, deposition and ion selectivity, so as to be generally used for the adsorption and separation of specific targets. In a comprehensive view, carbonaceous materials are

the most commonly used substrate among the composite electrode materials due to the advantages of easily adjustable structure, wide source, simple preparation method and high conductivity. At present, several related research teams have developed and prepared a series of composite electrodes with dual functions on the basis of carbon materials, e.g., Wei [42] prepared alkali metal intercalated MXene composites by using MXene ( $\text{Ti}_3\text{C}_2\text{T}_x$ ) as precursor and treating with different alkali solutions. The specific surface area of the composites was increased, and the maximum specific surface area of M-LiOH was  $100.202 \text{ m}^2/\text{g}$ . Electrochemical tests showed that the M-LiOH composite electrode material had higher specific capacitance ( $174.78 \text{ F/g}$ ) and smaller impedance in the solution of 1 mol/L NaCl. Using a one-step calcination method, the  $\text{TiO}_2/\text{Ti}_3\text{C}_2\text{T}_x$  composite was prepared by Xi and Li [43] (Figure 10); the desalination capacity of  $\text{TiO}_2/\text{Ti}_3\text{C}_2\text{T}_x/\text{llAC}$  reached  $23.8 \text{ mg/g}$  in the initial conductivity of  $3000 \mu\text{S/cm}$  NaCl solution when the operating voltage was 1.2 V in the constant voltage mode, and after 20 cycles the retention rate of the capacity was 78%.



**Figure 10.** Flowchart of  $\text{TiO}_2/\text{Ti}_3\text{C}_2\text{T}_x$  composites

Bai et al. [44] synthesized NiAl-LDHs on nickel foam substrates using a co-precipitation method and successfully transformed them into NiAl-LMO electrodes by forging and firing. The results found that the electrochemical properties of NiAl-LMO electrode were stable, reversible, and the specific capacitance could reach  $577 \text{ F/g}$ . The NiAl-LMO electrode adsorbed 60.9% of  $\text{S}_2\text{O}_3^{2-}$  at an applied voltage of 1.0 V, pH of 7, and temperature of  $40^\circ\text{C}$ , and the desorption rate of  $\text{S}_2\text{O}_3^{2-}$  in the reverse connection of the electrode was 84.9%, as shown in Figure 11 below, indicating that NiAl-LMO electrode has a good removal effect on  $\text{S}_2\text{O}_3^{2-}$  in water.



**Figure 11.** Electro-sorption of  $\text{S}_2\text{O}_3^{2-}$  on NiAl-LMO electrode under different voltage conditions

To sum up, composite electrodes prepared from carbon materials and metal oxides, etc., generally have good electro-sorption performance, as well as specific selectivity and partial degradation. They are commonly used for adsorption



treatment of specific targets. However, the composite preparation method has some potential influence on its electrochemical performance and adsorption capacity. Due to the shape limitation of the substrate material, some composite electrodes are prepared using the binders etc., and such additives have a shielding effect on the effective sites of the adsorption electrode surface. Especially for granular carbon materials, the binder also has an inhibitory effect on the electrical conductivity of the formed adsorption electrode. Therefore, the selection of proper preparation methods is a key concern for the future development of composite electrodes.

## 5. CONCLUSIONS

This paper discusses the EST from two aspects: theoretical research and electrode materials. Firstly, it introduces the classic models of the EST theory, the development history of modern EDL model, and the status of the theoretical research, as well as the application of EST-based electrode materials in water treatment. Besides, as a green and economical water treatment technology, the EST still needs continuous improvement in terms of electrode materials, equipment operation, mechanism and devices. Among the electrode materials, the electrochemical performance and material surface charge capacity of common carbon-based electrodes are constrained by the characteristics of the materials themselves, and their electrochemical performance and adsorption capacity are generally not high. Whereas, metal oxide electrodes have excellent electrochemical activity, but the electrical conductivity is weak and easily affected by the acidity and alkalinity of the solution. To address these problems, composite electrodes can be used to avoid the functional defects of the above-mentioned single materials by integrating different materials, and achieve adsorption storage, degradation deposition or selective separation of target materials on the basis of electro-sorption, thus realizing the function diversification of adsorption electrodes. The composite electrodes for electro-sorption shall be the focus of future research on high-performance and multi-functional electrodes, and also the key research direction of high-efficiency EST.

## REFERENCES

- [1] Shi, X.J., Li, L., Zhang, T. (2015). Water pollution control action plan, a realistic and pragmatic plan - An interpretation of water pollution control action plan. *Environmental Protection Science*, 41(3): 1-3. <http://dx.chinadoi.cn/10.3969/j.issn.1004-6216.2015.03.001>
- [2] Bian, W.B., Pan, J.M. (2021). Research progress on electro-sorption technology and fabrication of adsorptive electrode materials. *CIESC Journal*, 72(1): 304-319. <http://dx.chinadoi.cn/10.11949/0438-1157.20201019>
- [3] Sun, X.W., Zhu, G.F. (2002). Principle and makeup of electrosorb technology in water treatment. *Industrialwater & Wastewater*, 33(4): 18-20. <http://dx.chinadoi.cn/10.3969/j.issn.1009-2455.2002.04.006>
- [4] Caudle, D.D. (1966). Electrochemical demineralization of water with carbon electrodes (No. 188). US Department of the Interior.
- [5] Cao, S.S., Lin, S.S., Jiang, X., Wen, C., Cheng, G. (2016). Progress in research and application of electro-sorption technology in the field of water treatment. *Applied Chemical Industry*, 45(9): 1767-1770.
- [6] Sereych, M., Rodríguez-Castellón, E., Biggs, M.J., Skinner, W., Bandosz, T.J. (2014). Effect of visible light and electrode wetting on the capacitive performance of S-and N-doped nanoporous carbons: Importance of surface chemistry. *Carbon*, 78: 540-558. <https://doi.org/10.1016/j.carbon.2014.07.038>
- [7] Wang, K.J., Fang, K., Gong, H., He, W.Y. (2018). Review on research of capacitive deionization technology in field of environment from low energy consumption desalination to resource recovery. *Chinese Journal of Environmental Engineering*, 12(8): 2141-2152. <http://dx.chinadoi.cn/10.12030/j.cjee.201805064>
- [8] Wu, X.R., Jia, Z.J., Ma, H.Y., Liao, S.D., Wang, B.G. (2013). Fundamentals of electrochemistry (III) - Electrical double layer model and its development. *Energy Storage Science and Technology*, 2(2): 152-156. <http://dx.chinadoi.cn/10.3969/j.issn.2095-4239.2013.02.009>
- [9] Huang, Y., Liu, X., Li, S., Yan, T. (2015). Development of mean-field electrical double layer theory. *Chinese Physics B*, 25(1): 016801. <https://doi.org/10.1088/1674-1056/25/1/016801>
- [10] Xiao, Y. (2009). Research of Ions Transport in Nanofluidic Channels Based on Electrical Double Layers [D]. Shenyang: Northeastern University, 2009.
- [11] Li, D., Niu, Y.Y., Fan, M., Xu, D.L., Xu, P. (2013). Focusing phenomenon caused by soil conductance heterogeneity in the electrokinetic remediation of chromium (VI)-contaminated soil. *Separation and Purification Technology*, 120: 52-58. <https://doi.org/10.1016/j.seppur.2013.09.018>
- [12] Yang, S.C. (2013). Study on the Electrosorption Desalination Technology in the Treatment of Secondary Effluent of Sewage of Petrochemical Enterprises [D]. Lanzhou: Lanzhou Jiaotong University, 2013.
- [13] Xu, C.L., Zhang, X.Y. (2011) Research progress of capacitance adsorption desalination technology. *Guangzhou Chemical*, 39(12): 17-19. <http://dx.chinadoi.cn/10.3969/j.issn.1001-9677.2011.12.005>
- [14] Jia, J.C., Yang, Q. (2010). Application of Gouy-Chapman double layer model to long-range swelling of montmorillonite. *Journal of Dalian University of Technology*, 50(2): 239-244.
- [15] Xu, W.D., Chen, J.F., Li, S.Y. (2004). Preparation of high surface area active carbon electrode and its application in electric double layer capacitor. *Modern Chemical Industry*, 24(z1): 55-58. <http://dx.chinadoi.cn/10.3321/j.issn:0253-4320.2004.z1.016>
- [16] Shapovalov, V.L., Brezesinski, G. (2006). Breakdown of the Gouy - Chapman model for highly charged Langmuir monolayers: counterion size effect. *The Journal of Physical Chemistry B*, 110(20): 10032-10040. <https://doi.org/10.1021/jp056801b>
- [17] Rao, W., Li, D.G. (2009). Dynamics research on ion adsorption of electric double layer. *Journal of Naval University of Engineering*, 21(4): 108-112. <http://dx.chinadoi.cn/10.7495/j.issn.1009-3486.2009.04.022>
- [18] Han, L., Karthikeyan, K.G., Anderson, M.A., Wouters, J.J., Gregory, K.B. (2013). Mechanistic insights into the

- use of oxide nanoparticles coated asymmetric electrodes for capacitive deionization. *Electrochimica Acta*, 90: 573-581.
- [19] Oldham, K.B. (2008). A Gouy–Chapman–Stern model of the double layer at a (metal)/(ionic liquid) interface. *Journal of Electroanalytical Chemistry*, 613(2): 131-138. <https://doi.org/10.1016/j.jelechem.2007.10.017>
- [20] Song, Y.J.(2005). Comparison of Three Double Layer Conductivity Models for Shaly Sands.
- [21] Jiang H , Li S , Ren Y , et al. Electric-triple-layer model based AC electroosmosis flow[J]. *Physics*, 2010.Charmas et al
- [22] Charmas, R. (1999). Four-layer complexation model for ion adsorption at energetically heterogeneous metal oxide/electrolyte interfaces. *Langmuir*, 15(17): 5635-5648. <https://doi.org/10.1021/la980880j>
- [23] Wang, J.,Ying, A.L. (2000). Electrokinetic phenomena of interface and the double electrical layer. *Journal of Lianyungang College of Chemical Technology*, 2000(1): 13-15.
- [24] Ying, T.Y., Yang, K.L., Yiacoumi, S., Tsouris, C. (2002). Electrosorption of ions from aqueous solutions by nanostructured carbon aerogel. *Journal of Colloid and Interface Science*, 250(1): 18-27. <https://doi.org/10.1006/jcis.2002.8314>
- [25] Grahame, D.C., Parsons, R. (1961). Components of charge and potential in the inner region of the electrical double layer: aqueous potassium chloride solutions in contact with mercury at 25. *Journal of the American Chemical Society*, 83(6): 1291-1296. <https://doi.org/10.1021/ja01467a009>
- [26] Hou, C.H., Liang, C., Yiacoumi, S., Dai, S., Tsouris, C. (2006). Electrosorption capacitance of nanostructured carbon-based materials. *Journal of Colloid and Interface Science*, 302(1): 54-61.
- [27] von Sturm, F. (1988). *Carbon materials. Carbon-Electrochemical and Physicochemical Properties*. Wiley, New York.
- [28] Mo, J.X., Gao, C.J. (2007). Inquiry into theory of dual electric layer model in capacitive adsorption-deionized technology. *Technology of Water Treatment*, 33(12): 26-29. <http://dx.chinadoi.cn/10.3969/j.issn.1000-3770.2007.12.006>
- [29] He, F., Biesheuvel, P.M., Bazant, M.Z., Hatton, T.A. (2018). Theory of water treatment by capacitive deionization with redox active porous electrodes. *Water Research*, 132: 282-291. <https://doi.org/10.1016/j.watres.2017.12.073>
- [30] Attard, G.A. (2018). A phenomenological theory of electrosorption. *Journal of Electroanalytical Chemistry*, 819: 481-494. <https://doi.org/10.1016/j.jelechem.2017.12.057>
- [31] Ajay, K.M., Dinesh, M.N. (2021). Performance studies of bamboo based nano activated carbon electrode material for supercapacitor applications. *Materials Today: Proceedings*, 46: 4510-4514. <https://doi.org/10.1016/j.matpr.2020.09.691>
- [32] Han, D.D., Li, H.M., Yang, L., Liu, Y.Q. (2019). [Optimum process for preparation of activated carbon electrosorption electrode by catalytic graphitization. *Journal of Xi'an Polytechnic University*, 33(3): 274-279. <http://dx.chinadoi.cn/10.13338/j.issn.1674-649x.2019.03.007>
- [33] Xu, X., Liu, Y., Wang, M., Yang, X., Zhu, C., Lu, T., Zhao, R., Pan, L. (2016). Design and fabrication of mesoporous graphene via carbothermal reaction for highly efficient capacitive deionization. *Electrochimica Acta*, 188: 406-413. <https://doi.org/10.1016/j.electacta.2015.12.028>
- [34] Yang, Z. Y., Jin, L.J., Lu, G.Q., Xiao, Q.Q., Zhang, Y. X., Jing, L., Zhang, X.X., Yan, Y.M., Sun, K.N. (2014). Sponge - templated preparation of high surface area graphene with ultrahigh capacitive deionization performance. *Advanced Functional Materials*, 24(25): 3917-3925. <https://doi.org/10.1002/adfm.201304091>
- [35] Lv, C., Ma, X., Guo, R., Li, D., Hua, X., Jiang, T., Li, H., Liu, Y. (2023). Polypyrrole-decorated hierarchical carbon aerogel from liquefied wood enabling high energy density and capacitance supercapacitor. *Energy*, 270: 126830. <https://doi.org/10.1016/j.energy.2023.126830>
- [36] Ji, Y.J., He, J.P., Zhou, J.H., Dang, X.J., Liu, X.H., Zhang, C.X., Zhao, G.W. (2007). Fabrication of carbon aerogels with novel structure and its application as electrode material for capacitor. *Journal of Materials Science and Engineering*, 9(4): 501-505. <http://dx.chinadoi.cn/10.3969/j.issn.1673-2812.2007.04.003>
- [37] Shi, Z.Q., Jin, G.Q., Wang, J., Zhang, J. (2017). Preparation of flexible free-standing mesoporous carbon nanofibers and its application in electrodes for supercapacitor. *Journal of Tianjin Polytechnic University*, 36(5): 16-20. <http://dx.chinadoi.cn/10.3969/j.issn.1671-024x.2017.05.004>
- [38] Dong, X.M., Zhang, S.H., Di, J., Wang, Z.L., Qi, W.J. (2022). Research progress of electro-adsorption electrode materials. *Industrial Water Treatment*, 42(1): 48-55. <http://dx.chinadoi.cn/10.19965/j.cnki.iwt.2020-1045>
- [39] Wang, W. (2022). Synergistically enabling the enhanced capacitive deionization performance by preparing polymetallic oxides Faradaic electrodes. Ningxia University.
- [40] Qiao, H.Y. (2018). Arsenic Removal by Calcined Layered Double Hydroxide through Capacitive Deionization. Dalian University of Technology.
- [41] Wang, T. (2016) Preparation of mixed metal oxide films electrode and its capacitive deionization property. Henan University of Technology.
- [42] Wei, W.H. (2021) Preparation of MXene (Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>)-based composites for capacitive deionization and supercapacitor. Ningxia University.
- [43] Xi, W., Li, H.B. (2021). Preparation of TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> composite for hybrid capacitive deionization. *Journal of Inorganic Materials*, 36(3), 283-291. <http://dx.chinadoi.cn/10.15541/jim20200243>
- [44] Bai, Z.Y., Yang, C.F., Dong, J.J., Hu, C.Z., Wu, R.J. (2018). Study on electroadsorption of thiosulfate in water by NiAl-LMO electrode, *Acta Scientiae Circumstantiae*, 38(11): 4306-4312. <http://dx.chinadoi.cn/10.13671/j.hjkxxb.2018.0283>