Renewable and Scalable Energy Storage Materials Derived from Quinones in Biomass

Lianlian Liu

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Renewable and Scalable Energy Storage Materials Derived from Quinones in Biomass

Lianlian Liu

Biomolecular and Organic Electronics
Department of Physics, Chemistry and Biology (IFM)
Linköping University
SE-581 83 Linköping, Sweden
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That person is like a tree planted by
streams of water, which yields its
fruit in season and whose leaf does not
wither — whatever they do prospers.

Psalm 1:3

ABSTRACT

Currently there is an urgent need to reduce the use of fossil fuels, and efficient sustainable energy harvesters from sun and wind have been developed and are widely used for electricity generation. Storage of electrical energy is accordingly necessary to accommodate the time varying supply of wind and solar electricity. Quinones (Q) are attractive as energy storage materials due to their high theoretical charge density and the renewable and abundant source – biomass. Plant-based biomass materials – such as lignin and humic acids – contain redox active Q-groups that potentially could be used for electricity storage instead of simply burning the biomass, which releases CO₂, CH₄, NO_x, and SO_x. Lignin accounts for 20-30% of the biomass weight and contains a sizable fraction of Q-structures. However, utilization of lignin for large scale energy storage is still a challenging task, as lignin is electrically insulating and conductive materials are required to get access to the generated electrons in the bulk. Various relatively expensive materials, such as conductive polymers and various carbon materials (carbon nanotubes, active carbon, graphene, etc.) have been combined with lignin, resulting in hybrid materials for energy storage. However, as the scale required for production of charge storage devices is huge it is of outmost importance to reduce the cost and therefore investigate low-cost conductive materials. In this thesis, common graphite flakes are combined with the lignin derivative lignosulphonate (LS) via a solvent free ball-milling process, followed by treatment with water and resulting in a paste that can be processed into electrodes. Similarly, humic acid derived from peat, lignite that contains a large amount of Q-groups is also fabricated into electrode with graphite via the ball-milling process. In order to further reduce the impact on environment during the extraction of Q-materials from biomass, barks that contain as much as 30% of lignin are directly used for energy storage via co-milling with pristine graphite to generate the biomass/graphite hybrid material electrodes. However, larger weight fraction of Q are required to further improve the electrochemical performance of these electrodes and Q chemicals (QCs) that also originate from biomass are introduced to fabricate the QCs/graphite electrodes with an increased capacity. Additionally, self-discharge mechanism is studied on the LS/graphite hybrid material electrodes, which provides instructions to achieve a low self-discharge rate.

Overall, this study has brought us one step forward on the establishing of scalable, sustainable, and cost-effective energy storage systems using aqueous electrolytes.

POPULÄRVETENSKAPLIG SAMMANFATTNING

Utfasning av fossila energiformer kan ske genom användning av sol- och vind-el. Den stora variationen av el från sol och vind förutsätter att el kan lagras över tid för att möta efterfrågan. Kinoner är attraktiva molekyler för lagring av elektrisk energi, då en kinon har hög laddningstäthet. Förstadier till kinoner och kinoner finns i biomassa, och kinoner är därför förnybara och skalbara på samma sätt som biomassa. Biomassa från växter innehåller lignin, och växters nedbrytningsprodukter innehåller humussyror. Dessa material innehåller kinoner, och kan därför användas för elektrisk lagring, i stället för att förbrännas för värmeutvinning, och samtidigt frisätta koldioxid och andra gaser. Lignin utgör 20-30% av biomassans vikt och innehåller kinoner i avsevärd utsträckning. Lignin är dock elektriskt isolerande, och måste kontaktas av en elektronisk ledare för att kunna lagra laddning i kinoner. Elektroniska ledare i form av kolbaserade föreningar som elektroniska polymerer, nanotuber av kol, aktivt kol och grafen har kombinerats med lignin i hybridmaterial, som dock är relativt dyra. Eftersom behovet av material för elektrisk energilagring kommer att bli mycket omfattande är det viktigt att utveckla skalbara och billiga material. I denna avhandling studeras hybridmaterial i form av en kombination av grafit och lignosulfonat som kombineras i en mekanisk kemisk process utan vätskor, där substanserna mals i en kvarn. Denna produkt bearbetas till en pasta, som används för att forma elektroder. Detta är en skalbar process, som leder till att grafit exfolieras till flerlagergrafen vid malning med den ytaktiva lignosulfonaten. Detta elektrodmaterial är redoxaktivt via kinoner. På samma sätt kan humussyror, från torv, växtavfall eller brunkol, malas med grafit för att bilda ett elektrodmaterial, där kinoner är redoxaktiva. För att ytterligare förenkla tillverkningen av elektroder, och minska energiinsatser i omvandling av trä till lignin i pappersfabriker, kan bark från träd malas med grafit, då lignin ofta utgör 30% av barkmassan. Ett antal olika trädarters bark har kombinerats i barkelektroder, där ekbark ger den bästa laddningskapaciteten. För att höja dessa prestanda kan mängden kinoner i elektrodmaterial ökas. Kinoner i molekylär form har malts tillsammans med grafit, lignin respektive humussyra. Kinonföreningar från biologiska källor kan i sådana hybridmaterial ge 30 ggr högre laddningskapacitet, jämfört med grafit utan biologiska komponenter. Självurladdningen i superkondensatorer med dessa elektroder har också studerats, och visar sig ha bidrag från diffusionsprocesser, aktiveringsenergi och från omfördelning av laddning mellan olika delar av elektrodmaterial.

Studierna av dessa hybridmaterial med grafit och biopolymerer visar hur skalbara, förnybara och billiga elektroder kan framställas för elektrisk lagring av energi med vattenbaserade elektrolyter.

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It is currently a hard time for the whole world. We as human beings are facing big challenges: the global warming, climate changing, pollution, energy issues, famine, poverty, explosion, war, and this deadly pandemic. The future is becoming more and more uncertain. I hope my research will help a little bit the globe and the human beings. I do not know what is going to happen tomorrow, but I have an anchor in the heart.

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Paper I

Scalable Lignin/Graphite Electrodes Formed by Mechanochemistry

*Lianlian Liu, Niclas Solin, and Olle Inganäs**

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Contribution: performed the experimental work and the characterization, wrote the manuscript and contributed to the final editing.

Paper II

Biocarbon Meets Carbon – Humic Acid/Graphite Electrodes Formed by Mechanochemistry

*Lianlian Liu, Niclas Solin, and Olle Inganäs**

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Paper III

Quinones from Biopolymers and Small Molecules Milled into Graphite Electrodes

*Lianlian Liu, Lei Wang, Niclas Solin, and Olle Inganäs**

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*Lianlian Liu, Niclas Solin, and Olle Inganäs**

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Jung Yong Kim, Selvakumaran Nagamani, *Lianlian Liu*, Ahmed H. Elghazaly, Niclas Solin, and Olle Inganäs*

Biomacromolecules, 2020, 21, 1214.

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Paper II

Flexible Solid-State Asymmetric Supercapacitors with Enhanced Performance Enabled by Free - Standing MXene - Biopolymer Nanocomposites and Hierarchical Graphene - RuO_x Paper Electrodes

Leiqiang Qin,* Quanzheng Tao, *Lianlian Liu*, Jianxia Jiang, Xianjie Liu, Mats Fahlman, Lintao Hou, Johanna Rosen,* and Fengling Zhang*

Batteries & Supercaps, 2020, 3, 604.

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Patent Application

Carbon Lignin Electrode, 19155073.0 - 1103. 2019.

Olle Inganäs, *Lianlian Liu*, Niclas Solin

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ABBREVIATION

Anode	the electrode with lower potential in a battery, negative electrode, occurs oxidation reaction and lose electrons into the external circuit during the discharge process
AORFBs	aqueous organic redox flow batteries
AQ	anthraquinone
α_c	cathodic charge transfer coefficient
α_a	anodic charge transfer coefficient
BQ	benzoquinone
C	specific capacitance, in $F\ g^{-1}$
Cathode	the electrode with higher potential in a battery, positive electrode, occurs reduction reaction and gain electrons from the external circuit during the discharge
CCVD	catalytic chemical vapor deposition
CE	counter electrode
CNFs	carbon nanofibers
CNTs	carbon nanotubes
CV	cyclic voltammetry
D	the diffusion coefficient, in cm^2/s
Diamino AQ	diaminoanthraquinone
E	energy density, in $Wh\cdot kg^{-1}$ or $Wh\cdot L^{-1}$
E_p	peak potential, in V
E_{pa}	anode peak potential, in V
E_{pc}	cathode peak potential, in V
E_{eq}	potential at equilibrium of an electrode, in V
E^0	potential of the electrode at standard condition
ECPs	electrically conductive polymers
ECs	electrochemical capacitors
EDL	electrical double layer
EDLC	electricity double layer capacitor
EES	electricity energy storage
HA	humic acid
I_0	exchange current
I_a	anodic current
I_c	cathodic current
I_p	peak current, in A
I_{pa}	anode peak current, in A
I_{pc}	cathode peak current, in A
IEO 2019	international energy outlook 2019

IHP	inner Helmholtz plane
GCD	galvanostatic charge-discharge
k_d	mass transfer coefficient
k_c	reduction charge transfer rate constant
k_a	oxidation charge transfer rate constant
LS	lignosulfonate
MWCNTs	multi-wall carbon nanotubes
NQ	naphthaquinone
O	oxidative species
$[O]_*$	the concentrations of oxidative species at OHP
$[O]_\infty$	the concentrations of oxidative species at bulk solution
QCs	quinone chemicals
OCP	open-circuit potential
OHP	outer Helmholtz plane
ORPs	organic redox polymers
P	power density, in $\text{W}\cdot\text{kg}^{-1}$ or $\text{W}\cdot\text{L}^{-1}$
PS	pseudocapacitor
Q	quinones
ΔQ	specific charge (or charge/discharge capacity) of an electrode, in mAhg^{-1}
R	reductive species
$[R]_*$	the concentrations of reductive species at OHP
$[R]_\infty$	the concentrations of reductive species at bulk solution
RE	reference electrode
RFBs	redox flow batteries
SWCNT	single walled carbon nanotube
TSE	twin-screw extrusion
WE	working electrode

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1 INTRODUCTION

Electrical energy is playing an increasingly important role in modern society. In the report of international energy outlook 2019 (IEO 2019) it was estimated that the global energy consumption will rise nearly 50% between 2018 and 2050, especially in rapidly developing countries that badly need energy sources to drive the growth of economy, for example, India and China. Combustion of fossil fuels is still the dominant primary energy resources, which provides more than 80% of the globe's energy supply and results in severe pollution and carbon dioxide emission. As the largest single source of the world greenhouse gas emissions (almost 25%), fossil fuels face huge environmental, social, financial, and political pressures to decrease carbon emissions.^[1] In order to reduce the reliance of fossil fuels renewable energy emerges. For example, sun and wind are currently widely used for electricity generation since they are economically competitive with fossil fuels. According to IEO 2019, by 2050 renewable energy sources will account for almost half of the global electricity generation, and wind- and solar-power will account for over 70% of the total renewables generation.

However, solar and wind are intermittent energy sources, and the global existing electrical grid systems are generally not capable to handle large-scale intermittent electrical sources.^[1] For example, Germany, US and China have to discard the wind and solar power with negative price during the off-peak time because of the lack of adequate electricity storage capability. Accordingly, large-scale introduction of wind and solar energy sources requires large-scale energy storage systems for stable electricity supply. In addition, renewable sources coupled with local electricity storage are important for the regions that lack distributed power grids.^[2] For instance, in the areas around the equator on African continent, millions of people live without electricity or lack of stable electricity supply. A safe and stable electricity supply from individual household to the community will improve the quality of the residents' life, enable lighting at night and internet access, resulting in promoted education and growth of economy. Such areas are blessed with a rich supply of solar energy, and hence there is a great need to establish local sun-powered electricity sources that are complemented with local charge storage systems, such as secondary batteries and supercapacitors.

It is preferable if the electricity storage materials are produced in a cost-effective manner from sustainable source materials with a low impact on the environment during the extraction process. An outstanding source of such materials is plant-based biomass active materials that can store charge in batteries and supercapacitors, giving so called wooden batteries (or wooden supercapacitors). The key player enabling the charge storage in biomass materials is quinones (Q)-groups, which contain unsaturated aromatic ring structures with carbonyl groups that undergo electron/proton redox reactions with hydroquinone as the product. Plant-based biomass is actually the organic matter derived from plants – sugar or carbohydrates – due to the reaction between carbon

dioxide (CO₂), water and sunlight via photosynthesis.^[3] Remarkably, the redox behavior of Q-groups plays a vital role during a series of photo-induced electron transfer reactions:^[4] in photosystem II in the thylakoid membrane of chloroplasts in green plants, oxygen, electrons, and protons are obtained from water via a four-electron oxidation process:

where the electrons will reduce benzoquinone into hydroquinone and transfer to photosystem I, followed by entering the Calvin cycle where CO₂ is reduced into carbohydrates.^[5] Thereby, the energy stored in biomass in the form of terrestrial and aquatic vegetation originates from the sun, and the photosynthesis enables the conversion of solar energy into chemical energy. This chemical energy stored in biomass can be extracted for human being activities. For instance, plants have been utilized for thousands of year in all known civilization as a major source of energy, via two main process technologies: thermo-chemical (combustion, pyrolysis) and biochemical (digestion, production of biogas, and fermentation, production of ethanol).^[6] Among these, combustion, the burning of biomass in air, is one of the oldest and most widely used conversion method that produces heat, mechanical power and electricity through various equipment, like stoves, furnaces, boilers, steam turbines, which contribute 10% to 14% of the world's energy supply and this number goes up to 39% in the developing countries.^[7] Though biomass is a renewable, abundant and cost-effective energy source, compared with coal, it contains less carbon, more oxygen and hydrogen, lower heating value, which make it similar to the low-rank coals with low energy density. Hazardous components (CH₄, NO_x, SO_x) and CO₂ will be released during the combustion process. In order to convert biomass into high-value products, many researches have been focused to produce chemicals and high-value fuels from biomass via a series of complicated treatments.^[8] Interestingly, fossil fuels can be treated as "old biomass", which spend millions of years for conversion of biomass and are certainly not renewable energy source within a time-scale that humans can consider.

The theoretical charge density for Q-materials, for example benzoquinone, is equivalent to 496 mAhg⁻¹. Compared with the standard lithiated carbon materials (344 mAhg⁻¹), Q-groups are highly promising for electricity energy storage.^[9] Moreover, such biomass materials – i.e. Q-containing biopolymers – can be treated as one sort of the organic redox polymers (ORPs), which contain a non-conductive backbone bearing the redox active Q-groups attached to the backbone.^[10] These electroactive pendant Q-groups contribute to the redox potentials of biomass by accepting extra electrons, biomass can be thereby called *organic radical polymers*, with radicals of semi-quinones in the biopolymers. The employment of the redox active Q-groups for electricity storage can render biomass a high-value energy source. However, biomass-materials are electrically insulating and conductive materials are required to get access to the generated charges at the Q-sites in the bulk. Accordingly, conductive materials, such as conductive polymers and carbon materials (carbon nanotubes, active carbon, graphene,

etc.), have been combined with lignin (accounts for 20-30% of the biomass weight) to obtain hybrid materials for energy storage. However, these conductive materials are relatively expensive for large-scale production. In order to achieve large-scale production of these biomass charge storage devices, it is important to investigate alternative low cost conductive materials. Graphite, one of the cheapest carbon-based materials, is therefore a highly attractive candidate. It contains stacks of graphene layers that can be separated into few-layer graphene and/or single layer graphene by exfoliation, with a highly improved conductivity and specific surface area. Additionally, the cost of the fabrication process of the electrodes is also vital for large-scale production. Mechanochemical techniques are generally considered scalable, cost-effective, clean, and environmentally friendly. They have always played important roles in human civilization with a history dating back to the stone Age; for example in the grinding of wheat and seed, and clay processing. Mechanochemical techniques generally allow for the reduction of particle size, mass transfer, improved contact of particles, and chemical reactions, through impact, shearing, stretching, and compression processes.^[11] Remarkably, mechanochemistry has already been used to exfoliate graphite in the solid state.^[12,13]

The aim of this thesis is to investigate Q-containing biomass materials and incorporate them into electrodes. Cost-effective conductive materials are introduced to combine with these forms of biomass, and scalable fabrication processes are studied to finally obtain sustainable, low-cost, and scalable energy storage systems. Our study is a big step in the direction of industrial application of biomass in electricity energy storage.

In the first part of this thesis, the different energy storage devices and their electrochemical mechanisms will be briefly introduced, followed by the introduction of conductive materials and biomass materials applied in energy storage. Then the electrodes fabrication processes will be discussed. In short, an automated ball mill is used to co-grind graphite with various biomass materials – lignosulfonate (LS), humic acid (HA), barks, and quinone chemicals (QCs) – to create a series of hybrid material electrodes. The physical and electrochemical properties of these electrodes are investigated. Finally, I will try to clarify the self-discharge mechanisms of the LS/graphite hybrid material electrodes for instructions that can lower the self-discharge rate of Q-containing materials.

2 ELECTRICITY ENERGY STORAGE

The electricity storage technologies require high capacity/energy density/power density, long lifetime, low-cost, scalability, and stable performance. However, no single technology can meet all the requirements for the diverse applications in energy storage. In this chapter, some basic electrochemistry, different electricity storage mechanisms, systems and their characteristics will be introduced to provide an overview of the *electricity energy storage* (EES).

2.1 Electrochemistry

Electrochemistry is one branch of chemistry that involves chemical phenomena associated with charge separation.^[14] The first modern electrical battery was invented by Alessandro Volta, in 1800: a voltaic pile containing pairs of zinc and copper discs separated by brine-soaked cardboard could produce a continuous current. Later, Humphry Davy found that the electricity generated from the voltaic pile was due to the chemical reactions between the copper and zinc, which associated electricity and chemistry together the first time. Michael Faraday continued this investigation and developed the understanding of electricity and electrochemistry. He discovered the two laws of electrolysis:^[15]

(1) the amount of the substance liberated or deposited is proportional to the quantity of electricity that passes the solution;

(2) the amount of different substances dissolved or deposited produced by the same amount of electricity are proportional to their equivalent weights.

This theory can be summarized by

$$m = \frac{QM}{Fz} \quad (2.1)$$

where m is the substance in g; Q is the total electric charge passed through the substance in coulombs (C); M is the atomic weight of the substance in g/mol; z is the valency number of ions of the substance, for example, for $Al^{3+} + 3e^- = Al$, the valency number = 3 that means three moles of electrons can be transferred, and the equivalent weight of the substance is $M/z = 27/3 = 9$ g; F is the Faraday constant with $F = 9.6485309 \times 10^4$ C/mol. The quantity of charge carried by a single electron is 1.6023×10^{-19} C, one mole of electrons contain 6.022×10^{23} electrons, therefore one mole electrons carries a charge of $6.022 \times 10^{23} \times 1.6023 \times 10^{-19}$ C = 9.6485309×10^4 C, which is designated *one faraday*; and the amount of electricity carried by one mole of electrons – 9.6485309×10^4 C/mol – is known as the Faraday constant.

In addition, electrochemistry generally includes chemical reactions that result in charge transfer.^[14] As shown in **Figure 2.1**, in an electrochemical cell, there are usually two electrodes (anode and cathode) connected externally via electric wires and in solution (electrolyte) via ionic transport to enable charge transfer. The charge transfer reactions take place in opposite directions at different electrodes immersed in electrolyte to assure the electro-neutrality, and this charge transfer on the electrode surface or in the solution results in a charge separation process. This charge separation at each electrode can be represented by a *capacitance* and the difficulty of charge transfer by a *resistance*.^[14] When the two electrodes display negative changes of free energy during the reactions, electricity is released and the systems are batteries; when the sum of free energy changes is positive, external electrical energy can be converted into chemical reactions, which is electrolysis. Accordingly, the interrelation of chemical and electrical effects results in two fields of study: the chemical production of electricity and the effects of electricity on chemicals. While electricity storage not only involves the chemical reactions, but also physical processes, which will be both discussed in the following section.

Figure 2.1 An electrochemical cell connected externally via electric wires and in electrolyte via ionic transport, with charge transfer and charge separation process.

2.2 Double Layer Capacitance

As pointed out in the previous section, charge separation is associated with charge transfer, which occurs not only in the electrode and/or electrolyte, but also at the interface of electrode and electrolyte, resulting in an interfacial region that includes both the solution and solid. When a potential is applied on the electrode, in this interfacial region, there is an ordering of charge at the electrode surface and an ordering of the opposite charge with equal quantity in the solution, with *electrical double layer* (EDL) formed, as shown in **Figure 2.2**. The proportionality constant between the applied

Figure 2.2 The formation and arrangement of EDL at the interface of electrode and electrolyte as a potential is applied on the electrodes.

potentials and the amount of charge ordering in the solution interfacial region is *double layer capacity*.^[14] This EDL was first modeled by Helmholtz in 1879. He considered these two layers of opposite charge on the two sides of the electrode-electrolyte interface to be as compact as the conventional parallel-plate capacitors, without taking into account the influence from the electrolyte concentration. Later the Gouy-Chapman model was introduced by consideration of the electrolyte concentration and the applied potential. In this model, the electrolyte ions in solution can move freely and create a *diffuse double layer* with variable thickness. However, the problem for this model is to consider the ions as point charge and close to the electrode surface there is no maximum concentration of ions. Thereafter, the Stern model was proposed by combining the Helmholtz model and Gouy-Chapman model: the double layer contains a compact layer of ions close to the electrode followed by a diffuse distribution of ions into the bulk solution, and there is a transition from the compact layer to the diffuse layer at a distance. Then more models were established to further develop the Stern double layer models:

Figure 2.3 The developed Stern double layer models: the arrangement of ions and solvent molecules in the solution.

in the compact layer, ions are strongly adsorbed to the electrode, including the specifically adsorbed ions that lose their solvation to get closer to the electrode; the *inner Helmholtz plane* (IHP) passes through the centres of these specifically adsorbed ions (mostly anions) and the *outer Helmholtz plane* (OHP) passes through the centres of the solvated and non-specifically adsorbed ions, which are generally cations; outside the OHP comes the diffuse layer.^[14] For example, as shown in **Figure 2.3**, in a dipolar solvent, like water, the electrode is regarded as a giant ion, the solvent dipoles are oriented and form the first solvation layer with the specifically adsorbed ions; followed by the second solvation layer of the solvated non-specific ions; then followed by the diffuse layer.^[14]

These models help us to achieve an overview of the double layer structure, which is, however, more complicated in practice, because such EDL theory is built up on the planar electrodes, while the real materials generally contain various pores. For porous materials, the geometry and size of pores highly affect the transfer of ions or/and solvated ions and thus influence the creation of EDL. And in some materials with confined micro-pore structures, the space is not sufficient to form both the compact layer and the diffuse layer.

2.3 Electrode Reactions

Except for the above mentioned EDL process (physical process, in Figure 2.2 and 2.3), the chemical reactions at an electrode are also important.^[14] When considering an oxidation or/and reduction at an electrode, as shown in **Figure 2.4** a, the mechanism contains the following steps:

- (1) diffusion of species from the bulk solution to the electrode-solvent interface;
- (2) rearrangement of the ions;
- (3) reorientation of solvent dipoles;
- (4) adsorption of the reagents at the electrode surface;
- (5) electron transfer;
- (6) de-adsorption of soluble products.

Figure 2.4 (a) Scheme of electron transfer at an electrode; (b) energy distribution of a redox couple of O and R species at the surface of a metallic electrode.

The redox-reaction can be described by:

where ne^- refers to the number of electrons, O and R refer to the oxidant and reductant species. This O|R couple displays an energy level called E_{redox} with a fixed value for a specific substance, as shown in Figure 2.4 b. Associated with E_{redox} there are two distributions of electronic energy levels from the O and R species, respectively. O and R have different charges; and the energy of R is slightly lower than O. Moreover, the energy of Fermi level (E_F) of the electrode that always receive or lose electrons can be tuned by the applied potential. By altering the applied potential the electrode can be induced to supply electrons to O|R couples or, alternatively, to remove electrons from O|R couples, as shown in **Figure 2.5**.

Figure 2.5 Electron transfer between the electrode and the O|R couples by tuning the applied potential.

When the electrode half-reaction (such as reduction) is at equilibrium, the relation between the potential of electrode at equilibrium (E_{eq}) and the standard electrode potential (E^0) is given through the *Nernst equation*:

$$E_{\text{eq}} = E^0 + \frac{RT}{nF} \ln \frac{[O]_*}{[R]_*} \quad (2.2)$$

where R is the universal gas constant, $8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$; T is the temperature in K; n is the number of electrons transferred in the reaction; F is the Faraday constant; $[R]_*$ and $[O]_*$ are the concentrations of R and O species near the electrode surface (at OHP) in mol/L, respectively. E^0 is the potential of the electrode at standard condition with an effective concentration of ions of 1 mol/L and the pressure of 1 atm.^[14]

The tendency of a reduction reaction to occur is given by the standard free energy change:

$$\Delta G^0 = -nFE^0 \quad (2.3)$$

where a material with a negative E^0 will have a positive change in the free energy, meaning that there is a thermodynamic driving force for an oxidation reaction to occur.

The kinetic current I of the electrode reaction is proportional to the difference between the rate of oxidation and reduction reactions at the electrode, which is given by:

$$I = nFA(k_a[R]_* - k_c[O]_*) \quad (2.4)$$

where A is the electrode area; k_a the charge transfer rate constant of oxidation and k_c is the charge transfer rate constant of reduction. The kinetic current becomes zero when the rate of the oxidation and reduction reactions are equal; and the electrode reaches its equilibrium potential.

The electrode reaction rates, $k_a[R]_* - k_c[O]_*$, are not only affected by the reaction itself but also by the transport of species from the bulk solution to the surface of electrode or from the surface of electrode to the bulk solution. The transport phenomena can be separated into processes based on diffusion, migration, and convection. Diffusion process is due to the thermal movement of charged or neutral species in solution; migration is caused by the electric field effects; and convection occurs due to stirring/hydrodynamic transport. Herein, we only discuss the diffusion transport, the rate of which depends on the concentration gradients from the electrode to the bulk solution. As shown in **Figure 2.6**, a diffusion layer is generated with a thickness of δ , where c_0 is the concentration at the electrode and c_∞ is the concentration in the bulk solution.

Figure 2.6 The definition of the diffusion layer δ ; $(\partial c / \partial x)_0$ is the concentration gradient at the electrode surface.

The mass transfer coefficient k_d is defined as:

$$k_d = \frac{D}{\delta} \quad (2.5)$$

where D is the diffusion coefficient in $\text{cm}^2\cdot\text{s}^{-1}$. It can be determined by the current-potential profile, which will be further discussed in section 2.4.1. A smaller thickness of the diffusion layer δ leads to a larger concentration gradient from the electrode surface to the bulk solution, and hence a larger diffusion rate is obtained.

In general, electrode reactions are affected by both kinetics and transport (diffusion) processes. As shown in Figure 2.4 a, the mechanism of electrode reaction includes mass transfer coefficient k_d and kinetic rate constant k_c (or k_a). The former is affected by the diffusion layer thickness; the latter depends on the applied potential E and the standard kinetic rate constant k_0 :

$$k_c = k_0 \exp[-\alpha_c nF(E - E^0)/RT] \quad (2.6)$$

$$k_a = k_0 \exp[\alpha_a nF(E - E^0)/RT] \quad (2.7)$$

where k_0 is the rate constant when $E = E^0$; α_c and α_a are the cathodic and anodic charge transfer coefficient, respectively, which vary between 0 and 1, and for simple one-step redox reaction with n electrons transfer $\alpha_c + \alpha_a = 1$. When comparing the kinetic rate constant and diffusion rate constant, there are: reversible systems where $k_0 \gg k_d$; and irreversible systems where $k_0 \ll k_d$. For reversible reactions, there is always equilibrium at the electrode under any potential, and the electrode reaction current is determined by the electronic energy difference between the electrode (E_F) and the redox pair species (E_{redox}) in the solution, and the rate of transport of the active species. In irreversible reactions, kinetics play a more important role with the need of a higher applied potential to overcome the activation barrier to enable the reaction. The effect of mass-transport, however, can be neglected during the initial stages of a reaction, but it will later affect the electrode reaction and the electrode current.

Another way to express the rate of an electrode reaction is exchange current, I_0 , which is equal to $-I_c$ or I_a at equilibrium potential, based on equation 2.4, 2.6, and 2.7:

$$I_0 = |I_c| = nFAk_0[O]_{\infty} \exp[-\alpha_c nF(E_{eq} - E^0)/RT] \quad (2.8)$$

where there are no concentration gradients near the electrode, thus the concentration at the electrode is equal to that in the bulk. When $[O]_{\infty} = [R]_{\infty} = c_{\infty}$, equation 2.8 can be rewritten as:

$$I_0 = nFAk_0c_{\infty} \quad (2.9)$$

Overall, the rate of an electrode reaction can be both expressed by the standard rate constant k_0 and the exchange current I_0 .

2.4 Electrochemical Characterization

An electrochemical cell normally consists of two electrodes (as previously discussed) that are connected externally via electric wires and in solution via ionic transport. At one such electrode, by controlling the current passing it and the potential on it, the investigation of electrode reaction mechanism can be conducted and this electrode is called working electrode (WE); another electrode is designated as counter electrode (CE) to complete the electric circuit. In addition to this type of two-electrode system (full-cell), which are commonly used for commercial devices, a three-electrode system (half-cell) is more applicable for mechanistic studies: the current passes from WE to CE; and a third electrode, designated as reference electrode (RE), serves as reference to control the potential of WE without current passing through, as shown in **Figure 2.7**.^[14] In this thesis, this type of three-electrode configuration is used for all the electrochemical characterizations.

Figure 2.7 The three-electrode system with WE, CE, and RE.

In general, the WE with redox reactions occurring at the surface is a solid that has high conductivity to lower the background current under a working potential due to the intrinsic resistance, and high stability within the measuring potential. The material used for WE is normally an inert metal such as gold, platinum, silver, or carbon materials. Moreover, the surface of WE can be modified by the deposition of other materials or chemically modified by chemicals to improve the electrochemical performance. As for CE, the most used is platinum plate; for RE the common types are the standard hydrogen electrode (SHE, 0V), calomel electrode (SCE, 0.242 V vs. SHE), and silver-silver chloride electrode (Ag/AgCl/saturated KCl in water, 0.197 V vs. SHE), at 25 °C. In addition, a supporting electrolyte is essential as the source of electrically conducting ionic species in a cell, which can be inorganic or organic salts, acid, base, or buffer solutions, in aqueous or non-aqueous solvents. Each electrolyte, as well as the solvent

and electrode materials, are only stable within a certain potential window and they will decompose when exceeding this potential range. Compared with organic electrolytes, aqueous electrolytes display narrower stable potential window ($\sim 2\text{ V}$, organic electrolytes $\sim 4.6\text{ V}$), but better conductivity, shorter responding time, higher double-layer capacitance, and they are environmentally friendly.^[16] Generally, the potential range utilized in a cell is limited by the decomposition of the supporting electrolyte, solvent, and the electrode materials. Moreover, impurities and oxygen in the supporting electrolyte solutions would introduce undesired redox reactions at the electrode at some potentials, which should be considered or avoided during the measurements.

2.4.1 Cyclic Voltammetry

Potential sweep techniques are widely used for electrode processes investigation, via continuously applying a time-varying potential to the WE within a potential range.^[14] It results in the adsorption of species at electrode, redox reactions (faradaic reactions) of the electroactive species at the electrode or/and in the solution, as well as the double layer charging at the interface of the electrode and solution. Thus the observed current involves the faradaic current and the double layer charging current. Moreover, the sweep rate (or scan rate) of potential ($v = \Delta V/\Delta t$) is an important parameter that affects the profiles of the generated currents: higher scan rate results in higher current and lower scan rate leads to lower current. There are two forms of potential sweep experiments: linear sweep voltammetry, where the potential is scanned in only one direction and stops at a value; and cyclic voltammetry (CV), with the scan direction inverting at the chosen values ($E_{\min}$ and $E_{\max}$) for several cycles, as shown in **Figure 2.8 a**.^[14]

Figure 2.8 (a) The variation of applied potential versus time on WE in CV; (b) the CV profiles of a redox active electrode.

The profiles of voltammetry waves can represent the kinetics and thermodynamics of the electrode reaction. The electrode reaction emerges on reaching a potential, and then the current rises and reaches its peak; thereafter, the current starts to decay due to the consumption of the electroactive species and the creation of a

concentration gradient in the electrolyte near the surface of electrode. For example, in CV, as shown in Figure 2.8 b, after obtaining a peak current I_{pa} and a peak potential E_{pa} from a oxidation reaction, the potential scan direction is inverted and an cathodic curve with the same shape is generated due to the reduction, exhibiting another peak current I_{pc} and peak potential E_{pc} .^[14] For reversible reactions, peak potential E_p and the peak separation ($E_{pa} - E_{pc}$) are independent of the scan rate, and I_{pc} and I_{pa} present the same magnitude.

When the diffusion process of electroactive species is limiting, the peak current I_p is proportional to the square root of scan rate ascribed to the diffusion limitation, according to the *Randles-Sevcik equation* by:

$$I_p = 268600n^{\frac{3}{2}}AD^{\frac{1}{2}}Cv^{\frac{1}{2}} \quad (2.10)$$

where I_p is in amps (A), n is the number of electrons transferred in the redox reaction, A is the electrode area in cm^2 , D is the diffusion coefficient in cm^2/s , C is concentration in mol/cm^3 , and v is scan rate in V/s . When the scan rate increases, the extent of irreversibility of the electrode reaction also increases due to the insufficient time for species transport to the electrode surface, and E_p becomes dependent on the scan rate; the peaks in CV get broader with lower peak value relative to the reversible case, and the peak separation enlarges.^[14] For thin-layer electrode, or if only the adsorbed species on the electrode contribute to the current, there is no diffusion limitation from the electroactive species and I_p is proportional to the scan rate but not to the square root of scan rate. As observed in **paper I** in this thesis,^[17] the lignin/graphite hybrid material electrodes display a changing E_p and a growing peak separation at increasing potential scan rate, indicating the electrode redox reactions to be quasi-reversible at high scan rate; while for the humic acid/graphite hybrid material electrode in **paper II**,^[18] E_p and the peak separation do not vary as the scan rate increases. It is due to the limited amount of redox active species confined in the electrode and the redox reactions are not limited by the diffusion process.

Except for the scan rate, the concentration of electrolyte and the types of electroactive species also have impact on the profiles of CV; for example, if the electroactive species can undergo multiple redox processes or if there are more than one electroactive species in the system, various waves will appear in the voltammetry.

2.4.2 Galvanostatic Charge-discharge

Chronoamperometry and chronopotentiometry are also essential for electrode reaction process study. The former is under potentiostatic control by controlling the potential of WE to be constant and recording the current change over time; the latter applies a constant current through the cell (galvanostatic control) and the potential response with time of WE is recorded. Among these chronoamperometry and chronopotentiometry measurements, galvanostatic charge-discharge (GCD) measurements are widely used to

study the kinetics of electrode reaction, which display different profiles for faradaic and EDL processes (or capacitive process), and will be introduced in section 2.5.

GCD can be used to calculate the *specific charge* and *specific capacitance*, which are employed to identify the electrochemical performance of an electrode or a device, meaning the charge and capacitance per unit mass/volume, respectively. For example, based on the GCD curve in **Figure 2.9**, the specific charge (or charge/discharge capacity) ΔQ of an electrode by normalizing the mass of the active materials can be calculated by:

$$\Delta Q = \frac{I\Delta t}{m3.6} \quad (2.11)$$

where ΔQ is in mAhg^{-1} ; I is the constant charge/discharge current in A; Δt is the charge/discharge time within the potential range in seconds (s); m is the mass of the materials on the electrodes in g. The specific capacitance (C , in F g^{-1}) of an electrode is calculated by:

$$C = \frac{\Delta Q}{\Delta V} = \frac{I\Delta t}{m\Delta V} \quad (2.12)$$

where ΔV is the potential varying during the charge/discharge process in volt (V). In addition, *energy density* and *power density* are commonly used parameters for the performance evaluation of an energy storage device due to their direct relevance to the end applications. Energy density E represents the maximum amount of stored or delivered electrical energy, with a unit of $\text{Wh}\cdot\text{kg}^{-1}$ or $\text{Wh}\cdot\text{L}^{-1}$; power density P describes the rate in taking or delivering energy, with a unit of $\text{W}\cdot\text{kg}^{-1}$ or $\text{W}\cdot\text{L}^{-1}$; both E and P can be calculated from the GCD curves (Figure 2.9):

Figure 2.9 A GCD curve of a capacitor that can be used to calculate the specific charge, specific capacitance, energy density, and power density.

$$E = \frac{C \Delta V^2}{2} \quad (2.13)$$

$$P = \frac{E}{\Delta t} \quad (2.14)$$

where C is the specific capacitance in F g^{-1} .

GCD can also be used for the stability investigation of an electrode or a device by repetitive charge-discharge cycling measurements.

2.5 Electricity Energy Storage Systems

Since the invention of the electric generator by Faraday in 1832, the *electricity energy storage* (EES) field emerged with numerous devices appearing in the late 19th century and developing rapidly during the past century. Nowadays, EES devices mainly include batteries, fuel cells, and electrochemical capacitors (ECs), all composing two electrodes connected via ionic conductive electrolyte and external electric wires, which will be discussed and compared in this section.^[16]

2.5.1 Batteries

Among these EES devices, batteries have the largest commercial market and they are essential components in portable electronic devices, such as mobile phones, notebook computers, vehicles, etc. Batteries operate by converting the chemical energy into electrical energy via redox reactions on the two electrodes, which have different chemical potentials. The electrode with lower potential is designated as anode and the one with higher potential is designated as cathode, as shown in Figure 2.1. The anode and cathode undergo redox reactions as active components as well as function as the charge-transfer medium.^[14] There are mainly two types of batteries: non-rechargeable and rechargeable ones, which are designated as the primary battery and secondary battery, respectively. The most used primary battery is based on zinc-manganese dioxide (Zn-MnO_2); the most popular rechargeable systems include lead-acid, nickel-cadmium (Ni-Cd), nickel-metal hydride (Ni-MH), and lithium (Li) ion batteries.^[16,19,20] Among these secondary batteries, Li-ion battery currently has a big market share because of the high energy density and light weight. It was first commercialized by Sony in 1991,^[16,19] and was awarded the Nobel Prize in Chemistry in 2019. Generally, batteries exhibit relatively high energy density. While several shortcomings are also inevitable:

(1) low power density due to the limited redox reaction rate and the reactive species diffusion limitation, for example, the intercalation and de-intercalation of Li ions within the electrode matrix;

(2) heat generation ascribed to the chemical reactions, which would results in the overheating and fire;

(3) limited cycle life according to the irreversible redox reactions during the recharge process.

Thereby, batteries alone are not capable to satisfy all the requirements for EES.

2.5.2 Fuel Cells and Redox Flow Batteries

Fuel cells, which produce electricity via the redox reactions at anode and cathode, can store or deliver even higher energy density than battery systems. The first fuel cells were invented in 1838 by Sir William Grove, and Thomas Francis Bacon made the first fuel cells for practical use in 1933, which has been applied in the National Aeronautics and Space Administration (NASA) space program since the 1960s.^[21] As shown in **Figure 2.10 a**, the anode and cathode, which are usually noble metal platinum or platinum alloys, serve as charges-transfer media as well as the catalyst to enhance the electrode reactions. The redox active materials are supplied from the outside: oxygen (O_2) from the air and fuels from a tank. The most used fuel is hydrogen gas (H_2), which reacts with O_2 and with water as the final product; hydrocarbon fuels, for example, natural gas, methane and gasoline can also be utilized as fuels via converting into H_2 through a re-forming step. The utilization of gas in the fuel cells, however, requires extra equipment that decreases the volume efficiency of the cells.^[16] Fuel cells are still in the developing stage and have been mainly used in hospitals and some buildings to ensure the steady power supply. They are ideal solutions for vehicle manufacturers in terms of reducing the pollution from the combustion of fossil fuels. Nowadays, the main challenges fuel cells are meeting are high cost, low durability, high demand of pure gas stream, and low volume power density.

Redox flow batteries (RFBs) are electrochemical cells that can be used as fuel cells or secondary batteries. They were first invented in 1970s by NASA for space research and nowadays are treated as the most promising techniques for large-scale EES due to the low-cost and long cycle life.^[22,23] In RFBs, as shown in Figure 2.10 b, the chemical redox active species are dissolved in liquids that are designated as anolyte and catholyte, and they are pumped through the cell from external tanks. In discharge mode, the anolyte

Figure 2.10 The schematic diagram of (a) hydrogen-air fuel cell and (b) redox flow batteries.

flows through an electrode with the redox active elements oxidized at the interface of the electrolyte and electrode; while the electroactive species in the catholyte are reduced at the other electrolyte-electrode interface; the two electrolytes are separated by a membrane that enables ion transfer; and the generated electrons are transferred and collected via the electrodes. In general, the advantages for RFBs involve the independent energy density and power density that can promote separately, excellent cycling stability (20 – 30 years), and short response time. A series of aqueous inorganic electrolytes have been used in RFBs, such as iron, chromium, vanadium, vanadium/bromine, zinc/bromine, soluble lead acid, etc.^[22] Besides, organic reactants have also been applied in RFBs since their redox properties are easily tunable. Therefore, RFBs are further categorized into non-aqueous organic redox flow batteries and aqueous organic redox flow batteries (AORFBs), depending on the solvents used to dissolve the organic redox active components. Among them, AORFBs are more attractive ascribed to the cost-effective and sustainable properties, and Q-materials, which will be discussed in the following section, are widely used in many AORFBs.^[23] However, RFBs also meet several challenges, such as the low volume energy density and low charge-discharge rate.

2.5.3 Electrochemical Capacitors

Electrochemical capacitors (ECs) were first patented by Becker (General Electric) in 1957.^[24] It was found that an EDL with opposite charge was formed at the interface between the electrode and electrolyte, this EC is thus called *electrical double layer capacitor* (EDLC), as shown in Figure 2.2. The specific capacitance of this EDLC was first calculated based on the parallel-plate capacitor:

$$C = \frac{\epsilon_r \epsilon_0}{d} A \quad (2.15)$$

where ϵ_0 is the vacuum permittivity, ϵ_r is the dielectric constant of the interface, d is the thickness of the EDL, and A is the specific surface area of the electrode available to the electrolyte ions. Herein, A of the EDLC electrode can be $1000 \text{ m}^2 \text{ g}^{-1}$ and the thickness of the double layer is in nanometer, accordingly the estimated specific capacitance of this EDLC is several orders of magnitude larger than the conventional dielectric capacitors (usually in pF to μF), and ECs are thus called “*Super-capacitors*”.^[25] Based on the discussion in section 2.2, the electrode surface structure, electrolyte composition, and the chemical affinity between the adsorbed ions and the electrode surface all have impact on the property of EDL, which thus affect the electrochemical performance of EDLC. In addition, the EDL forms and relaxes almost instantaneously and responds rapidly to potential changes, which is much faster (with a time constant of $\sim 10^{-8} \text{ s}$) than the redox reactions (with a time constant of $10^{-2} - 10^{-4} \text{ s}$).^[16] This means that EDLC has an excellent power density, high reversibility and long life time.

However, the amount of energy stored at the surface of an EDLC electrode is much lower than that in batteries and fuel cells.

In order to improve the capacitance and energy density of EDLC, porous and nano-sized materials are developed to increase the specific surface area of the electrodes that is accessible to the electrolyte ions, according to the equation 2.15.^[26] Another approach to increase the capacitance of EDLC is *pseudocapacitor* (PS), which was first proposed by Conway.^[27] He found that the RuO₂ EC stores charge through not only EDL but also the intercalation and redox reactions of the electroactive ions at the electrode and in the electrolyte, and with charge transfer through the EDL.^[28] This renders PS a higher capacitance than EDLC, but at the expense of lower power density and reduced cycle stability.

Compared with batteries, the remarkable high power density, long cycle life (exceed 1 million cycles), good reversibility, simple configuration, and less chemical thermal heat generation render ECs popular for a wide range of applications and thus have a huge market potential. They are mainly used for power capture and supply, for example, to provide the peak power in mobile phones and cameras; for load lifting equipment to reduce the size of the primary energy devices; applied as bridging power support to enable the stable power supply in continuous industry production. They are also important for telecommunication service and data storage centres, to protect the delicate electronics equipment from sudden voltage variation. Moreover, ECs can be utilized as integrated power source for the emergency doors and slide management systems on airplane, due to the robust configurations, a significantly reduction of weight, and low requirement of maintenance.^[25]

2.5.4 Comparison Between the Different EES Systems

The kinetics mechanisms of batteries, EDLC and PS are described in this section by comparing the CV and GCD profiles, as shown in **Figure 2.11** and **Figure 2.12**, respectively. Based on the equation 2.11 and 2.12, we have the current I of the EDL depending linearly on the scan rate of voltage v :

$$I = \frac{dQ}{dt} = C_{dl} \frac{dV}{dt} = C_{dl} v \quad (2.16)$$

where C_{dl} is the specific double layer capacitance. Accordingly, the CV of EDLC display a well-defined rectangular shape (Figure 2.11a, capacitive process) with little deviation upon the increasing scan rate; batteries typically show significant peak currents and peak potentials ascribed to the electrode reactions (Figure 2.11b), corresponding to the profiles in Figure 2.8b; the CV of PS, however, can be rectangular without or with redox peaks, presenting a combination of the former two profiles, as shown in Figure 2.11c.^[28,29] For PS without peaks in CV but with reversible redox reactions, it displays similar profiles to EDLC, making it difficult to distinguish between the EDL and the pseudocapacitance mechanism; when PS displays peaks in CV, it

Figure 2.11 The CV profiles of (a) capacitive process; (b) faradaic process; and (c) mixed capacitive and faradaic process at an electrode.

exhibits a character close to batteries: as scan rate increases, the kinetic of PS convert from reversible to irreversible reactions with the peak potential E_p dependent on the scan rate.^[28] However, the peak separation of PS remains independent with scan rate over a wide range until a critical value is reached and it is smaller than batteries. The relationship between the peak current and scan rate depends on whether PS is capacitive-controlled or diffusion-controlled: for the former the current is proportional to the scan rate, following equation 2.16; and for the latter current is linearly dependent on the square root of scan rate, following equation 2.10.

As for GCD comparison, where the voltage increases or decreases under a constant current, a capacitive process (EDLC, Figure 2.12a) displays a linear dependence of the potential versus charge/discharge time, resulting in a triangular charge-discharge profile originating from the double layer charging at the interface of electrode and solution; a pure faradaic process (ideal batteries and fuel cells, Figure 2.12b) exhibits a flat plateau at the specific potential where the redox reactions occur; a mixed capacitive and faradaic process (PS, Figure 2.12c) presents a combination of the GCD patterns from the former two with less obvious plateaus on the curve, indicating the existence of both the electrode kinetic reactions and EDL formation at the interface of the electrode and the electrolyte.^[28,29]

We have compared the charge storage mechanisms of different EES systems, and the power and energy capabilities of each are summarized in Ragone plot (**Figure 2.13**).^[16] Conventional capacitors display the highest power; supercapacitors (or ECs)

Figure 2.12 The GCD profiles of (a) capacitive process; (b) faradaic process; and (c) mixed capacitive and faradaic process at an electrode.

are high-power systems and fuel cells are high-energy systems; batteries present relatively intermediate power and energy capability compared with the others; RFBs are not included in this diagram, but their performance are expected to be close to the batteries and fuel cells. None of them, however, can individually match the performance of the internal combustion engine. Nevertheless, by combining these power sources high-power and high-energy EES system can be obtained: in such hybrid system, the average output power is provided by batteries/fuel cells and the peak power is provided by ECs, thereby avoiding pushing batteries/fuel cells to the limit of their power capability. For example, vehicles powered by batteries need to frequently accelerate, decelerate, and brake during driving that result in peak power. ECs can release and accept the peak power rapidly thus reducing the use of friction brakes and increasing the lifetime of batteries.

Figure 2.13 The simplified Ragone plot of different EES systems compared to the conventional capacitors and the combustion engine.

Overall, ECs are widely used in hybrid systems for peak power/power quality management and backup sources; however, they are less used as primary energy sources due to the low energy density. It is thus essential to improve the amount of energy stored in ECs, and PS is promising for such purpose as a transition between EDLC and batteries to cover the power and energy density gap between them. Accordingly, the ECs materials we design in this thesis are all with pseudocapacitive performance.

3 MATERIALS APPLIED IN ELECTRICITY ENERGY STORAGE

In the previous chapter, basic electrochemistry, electricity storage mechanisms, and different EES systems were discussed. There are several components that affect the performance of EES, herein in this chapter, we will only emphasize the *materials* applied in EES systems, whose properties have a significantly large impact on the performance of EES devices.

3.1 Conductive Materials Applied in EES

The conductivity of materials is crucial in energy storage devices that require efficient electronic transport. In order to improve the stored energy, these conductive materials are usually fabricated into porous matrix, which will increase the specific surface area and shorten the diffusion path lengths to the reaction sites. In such way, for PS, not only the amount of double-layer charge but also the amount of redox reactions sites increase, thus the current production enhances and a higher capacity is generated. There are currently abundant conductive materials applied in EES systems.

3.1.1 Carbon

Carbon is a nonmetal element with an electronic configuration of $1s^2 2s^2 2p^2$. Electrons localize in atomic orbitals around the nucleus and the atomic orbitals are determined by three quantum numbers: the *principle quantum number* n ($n = 1, 2, 3 \dots$) determines the energy of electrons; the *orbital angular momentum quantum number* l ($l = 0, 1, 2 \dots n-1$) defines the shape of the orbitals; *magnetic quantum number* m_l ($m_l = 0, \pm 1 \dots \pm l$) express the possible orientation of the orbitals. While *spin quantum number* is another quantum number that describe the quantum state of electrons, with a value of $+\frac{1}{2}$ or $-\frac{1}{2}$

Figure 3.1 The electronic configuration of a carbon atom.

½. Taking Pauli Exclusion Principle and Hund's Rules into consideration, the electronic configuration of carbon are displayed in **Figure 3.1**: only two electrons can occupy an atomic orbital and they have opposite spins; p electrons occupy two different 2p orbitals with the same spin. The atomic orbital of one atom can overlap with the atomic orbital from another atom, each containing one electron, to form a chemical bond and a molecular orbital. Interestingly, in order to lower the orbital energy, the atomic orbitals of a carbon atom can form hybrid orbitals that are identified as hybridization sp^3 , sp^2 and sp , as shown in **Figure 3.2**, resulting in three different geometries of the chemical bonds of a carbon atom and thus affecting the properties of carbon materials.

Carbon materials are one of the most important materials applied in EES, which display: various allotropic forms like fullerenes, graphite and nanotubes; several dimensionality from 0 to 3D; different appearance by means of powders, fibres, foams and composites. These materials are generally easily processed, electrically conductive, stable in a wide temperature range, with high specific surface area, and chemically stable; some materials are cost effective. The requirements for a carbon electrode that applied in EES are generally identified as high surface area, low electrical resistance and controllable pore size. Steps in this direction have been taken with achieving a rich variety of carbon materials.

Figure 3.2 The hybrid orbitals of a carbon atom: hybridization sp^3 , sp^2 and sp .

3.1.2 Graphite

Graphite has been found to be used in a ceramic paint for decorating pottery since the 4th millennium BC.^[30] It is one of the cheapest carbon based conductive materials, built up from stacks of graphene layers. Graphite is a crystalline solid of carbon atoms in the form of hexagonal lattice with sp^2 hybridized state, as shown in **Figure 3.3**: the distance between the adjacent carbon atoms in the graphene plane is 0.14 nm and that between the graphene layers is 0.34 nm.^[31] Every carbon atom displays four chemical bonds: three sigma (σ)-bonds and one pi (π)-bond; the σ -bond are connected with its three neighbor atoms and are formed by three sp^2 hybrid orbitals, leading to strong chemical bonds as well as a stable graphene layer; the π -bond are created by the overlapping p_z

orbitals of the carbon atoms within the graphene plane. These π bond electrons are delocalized in the orbitals above or below the graphene sheet thereby resulting in extremely higher electrical conductivity parallel compared with perpendicular to the graphene layer; with the electrical conductivity ranging between $100\text{--}500\text{ S m}^{-1} \perp$ (perpendicular to the graphene layer) and $2 \times 10^6\text{--}2.5 \times 10^6\text{ S m}^{-1} \parallel$ (parallel to the graphene layer).^[31] Graphite electrodes have been widely used in fuel cell,^[32] lithium ion batteries,^[33] sodium ion batteries^[34] and electrolysis^[35] due to the low cost and good conductivity. A way to utilize graphite in EES is to fabricate it into a carbon paste by mechanical milling, which will be discussed in chapter 4.

Figure 3.3 The crystalline solid structure of graphite.

3.1.3 from Graphite to Graphene

As pointed out in the previous section, the π bond electrons within a graphene layer are delocalized and the π -bonding systems are generally weak; the interaction between the adjacent graphene layers is van der Waals attractions, hence the adjacent graphene sheets are easily cleaved away from each other along the basal plane. In such a way, multi-layer graphene or even single-layer graphene materials can be obtained, whose electrical conductivity can reach $10^7\text{--}10^8\text{ S m}^{-1}$.^[36] Geim and his coworkers first isolated the single layer graphene with an atomic thickness from graphite by a tape in 2004,^[37] and this work was awarded the Nobel Prize in Physics in 2010. Usually, organic solvents and surfactants in aqueous environment can help to overcome the van der Waals attractions between the adjacent graphene layers and enable the exfoliation of graphite. N-methyl-2-pyrrolidone (NMP), N,N-dimethylformamide (DMF), benzene, toluene, etc. can reduce the interfacial tension between the solvents and graphite; surfactants with aromatic structures would interact with the graphene carbon rings via π - π interaction and then cause the exfoliation.^[38]

3.1.4 Graphene

The isolated graphene layer presents a two-dimensional (2D) hexagonal lattice structure formed by carbon atoms with sp^2 hybridization and the layer thickness of one-atom.^[39,40] It is promising for energy storage due to the flexibility, good chemical stability, high electrical conductivity and large surface area.^[41] For EDLC, charge adsorption and separation occur at the electrode-electrolyte interface, hence the high specific surface area of graphene (theoretically $2630 \text{ m}^2 \text{ g}^{-1}$) helps to efficiently absorb ions, resulting in a high specific capacitance. The capacity of graphene can be 1000 mAhg^{-1} , which is much higher than that of graphite electrode.^[40] Moreover, partially reduced graphene oxide (rGO) can also be used for energy storage with chemical oxidation of graphite into graphene oxide (GO), followed by reduced to rGO. Generally, the oxidation results in an increasing inter-layer spacing that helps to improve the intercalation of ions between the adjacent graphene sheets, also introduces functional groups on the surface and the edge of graphene sheets, resulting in more redox reactive sites.^[42] However, the use of strong acids, oxidants, and thermal treatments, which result in structural defects that degrade the electronic properties of the graphene sheets, and the release of toxic gas all hinder the industrial production of rGO.

In order to obtain graphene sheets directly and easily, bottom-up – chemical vapor growth, annealing of silicon carbide, building up from molecular building blocks – and top-down – mechanical cleavage and liquid-phase exfoliation of graphite– routes are investigated. The former is efficient to prepare the high quality graphene sheets, which is, however, difficult for scalable production; the latter is promising for scalable production, and organic solvents or surfactants in aqueous solvents are generally needed in a sonication process for the efficient cleavage.^[43] Moreover, graphene sheets suffer from serious re-stacking due to the van der Waals interaction between the adjacent sheets, accordingly, for long-term stabilization, surfactants and/or organic solvents are usually utilized.

3.1.5 Other Carbon Materials

Active carbon (AC) is a carbon material with hierarchical porous structure and high surface area, it is generally fabricated by carbonizing precursors, followed by an activation process with the presence of activation agents. A variety of carbonaceous materials can be used to produce AC, and biomass precursors, such as wood, coal, peat and other agriculture waste products are important resources.^[44,45] The activation processes generally involve physical activation and chemical activation, which employ steam or CO_2 at $800 - 900^\circ\text{C}$, and KOH , H_3PO_4 , ZnCl_2 , etc. at $450 - 650^\circ\text{C}$, respectively. Moreover, the porosity and size of pores in AC can be tailored by the activation process and the activation agents, so as to enhance the ion transportation. The ion-accessible surface area of AC can arrive over $2000 \text{ m}^2 \cdot \text{g}^{-1}$, when applied in EDLC a specific capacity range of $94 - 413 \text{ F} \cdot \text{g}^{-1}$ can be obtained.^[25]

The wide application of carbon nanotubes (CNTs) in EES originates from its high surface area, low resistivity and high stability. There are two types of CNTs: the single walled carbon nanotube (SWCNT) and the Multi-wall Carbon nanotubes (MWCNTs); the former is a single cylinder of crystalline graphene with a well-defined center, the latter are multiple graphene cylinders with a common axis.^[25,46] The most common methods for CNTs production include catalytic chemical vapor deposition (CCVD) with hydrocarbon as the carbon source; electric arc discharge and laser ablation with graphite and hydrocarbon as the carbon sources. CNTs can display an electrical conductivity as high as $1 \times 10^7 \text{ S} \cdot \text{m}^{-1}$ at room temperature and a specific capacitance of $524 \text{ F} \cdot \text{g}^{-1}$.^[25,36] However, the high cost hinders their industrial application as bulk materials in EES, they thus usually act as the conductivity enhancer.

Another important class of carbon materials are carbon nanofibers (CNFs) with a diameter range between 50 to 500 nm and a pore size of 3 to 20 nm. They can be produced from various carbon precursors, such as polymers, via electrospinning process followed by carbonization process; or via the CCVD method with hydrocarbon as the carbon source.^[47,48] The nanostructures of CNFs depend on the stacking manner of the graphene layers, such as perpendicular, inclined or coiled along the fiber axis. CNFs display an open and mesoporous structure, and high conductivity is obtained along the fiber axis, which makes it promising for application in EDLC.^[47] CNFs can also be activated to get a large surface area up to $1200 \text{ m}^2 \cdot \text{g}^{-1}$, more porosity and more active sites, resulting in an capacity up to $300 \text{ F} \cdot \text{g}^{-1}$.^[25] Similarly with CNTs, the cost for CNFs is high that impedes their scalable production and commercial application in EES.

The way to prepare template-derived carbon (TDC) is to fill the carbon precursors into the pores of an inorganic matrix (such as silica) followed by carbonizing the precursors, and then the inorganic matrix is removed by hydrofluoric acid (HF).^[49] In such way, the porous structures of the carbon materials can be controlled; the pores are well connected which results in large surface area and high electronic/ionic conductivity. The surface area for TDC can reach between $500 - 3000 \text{ m}^2 \cdot \text{g}^{-1}$ and a specific capacity as high as $350 \text{ F} \cdot \text{g}^{-1}$ has been demonstrated.^[36] In addition, the pore size of the template can be tuned to match the size of ions in the electrolyte so that the ionic transport is improved. Taking cost and safety (use of HF) into consideration, TDC is however not suitable for industrial utilization.

3.1.6 Metal Oxides and Electrically Conductive Polymers

Metal oxides materials generally exhibit pseudocapacitive behavior due to the double layer capacitance and pseudocapacitance, along with the insertion and de-insertion of ions into the structures, and the total capacitance is higher than that of carbon materials.^[26] Among metal oxide materials, Ruthenium dioxide (RuO_2) displays a high specific capacitance of $850 \text{ F} \cdot \text{g}^{-1}$ originating from the metallic electrical conductivity and the multiple redox reactions operating in a wide potential range.^[25,50] Metal oxides have been combined with graphene to get the composites with high capacity and excellent cycling stability for EES.^[41]

The conductivity of electrically conductive polymers (ECPs) was first reported in 1977 and used in ECs in the mid of 1990s.^[51] ECPs display a conjugated bond system along the polymer backbone and are synthesized via the oxidation of monomers. The conductivity of ECPs depends on the doping process: when the polymer chain is oxidized and cations are created, a p-doped polymer is formed; if the polymer chain is reduced to form anions, an n-doped polymer is formed. Overall charge neutrality of the polymer chain is preserved by the insertion of counter-ions (dopants) into the polymeric matrix. ECPs can highly improve the energy density of ECs since they undergo redox reactions and store charge not only at the surface but also in the bulk of the matrix materials. However, the slow diffusion of ions into the bulk polymer matrix lower the power density of the EES systems. While the excellent flexibility, high charge density, and high conductivity (from a few $\text{S}\cdot\text{cm}^{-1}$ to $500 \text{ S}\cdot\text{m}^{-1}$) render ECPs attractive for EES, and among them the most commonly utilized are polypyrrole (PPy), polyaniline (PANI) and poly(3,4-ethylenedioxythiophene): polystyrenesulfonate (PEDOT:PSS). PPy and PANI have a relatively low cost;^[26] PEDOT:PSS exhibits excellent conductivity, high transparency and relative high electrochemically/thermally stability.^[52] Composites of ECPs and other materials, such as graphene-ECPs composite, are developed for EES.^[53,54] Still, it is difficult to use ECPs for scalable EES application because of the relatively high cost.

Recently, some new materials that display high electrical conductivity and/or versatile structure properties have been explored for EES, such as covalent organic frameworks (COFs), metal-organic frameworks (MOFs), MXenes, metal nitride.^[55] These materials, including the conductive materials discussed above, display good mechanical and electrical properties, rendering EES systems with excellent performance.

In addition to these electrically conductive materials, another electrically insulating material is also attractive for EES, due to the high theoretical charge density and the sustainable sources that are widely distributed and cost-effective – quinone containing materials (as shown in **Figure 3.4**), which will be introduced in the next section.

Figure 3.4 The chemical structures of various quinone chemicals.

3.2 Quinone Materials Applied in Energy Storage

Quinones (Q) is a class of organic compounds with redox reactivity, which contain conjugated cyclic dione structure,^[56] as shown in Figure 3.4. The redox reactions of Q in aqueous solution is commonly described in **scheme 3.1** a (usually with BQ as the example): a reaction of two electrons and two protons; and hydroquinone (QH₂) is the product. Remarkably, there is an intermediate process during this redox reaction between Q and QH₂ – the production of Q radical anion or semiquinone (QH) – due to the one electron and one proton reaction (scheme 3.1b). It is believed that the reduction of Q in aqueous solution results in a mixture of Q²⁻, QH and QH₂.^[57]

Since protons are involved in the redox reactions of Q/QH₂ couples, the kinetics of this reaction are thus pH-dependent: when a two electrons and two protons reduction occurs to Q, the plot of the equilibrium potential versus pH displays a slope of –59mV/pH until pH arrives pK_{a1} = 9.85; as pH further increases, Q undergo one proton and two electrons reduction with QH⁻ as the product, the slope of the equilibrium potential drop versus pH becomes –30 mV/pH until pH = pK_{a2} = 11.84; at this point Q is reduced into Q²⁻ without protons transfer and the slope becomes zero. To conclude, a nine-membered square **scheme 3.2** summarizes the possible *proton-transfer reactions* (vertical) and the *electron-transfer reactions* (horizontal) involved in the Q/QH₂ redox reactions.^[57] On the left column of scheme 3.2, the pK_a of QH₂²⁺ and QH⁺ are extremely negative that means it is difficult to get the protonated forms of Q; while the right column represents the likely *protonation reactions* and QH₂ display weak acidity with pK₁ = 9.85, pK₂ = 11.84, respectively. As for the *electron-transfer reactions*, the top row of scheme 3.2 exhibits two electron-transfer steps with two redox potentials of $E_{Q^{2-}/Q}$ and $E_{Q/Q^{2-}}$, which produce distinguishable waves in CV; if the potential difference is too small, there might be only one wave in CV. In this thesis, 0.1 M HClO₄ with a pH of 1.0 is used as the electrolyte, and under this situation the Q-materials, for example

Scheme 3.1 (a) The redox reaction of Q and QH₂ in aqueous solution with two electrons and two protons transfer; (b) The redox reaction of Q and QH₂ in aqueous solution including the intermediate production of QH.

lignosulfonate, undergo a two electrons and two protons reaction.^[9] It is also found that QH is involved in this two-electron and two-proton reaction, based on the EPR results.

Moreover, within the reaction of Q/QH₂, two electrons and two protons are stored in a structure of six carbon and two oxygen atoms, indicating a theoretical charge density of 2 faraday per 108 g, equivalent to 496 mAhg⁻¹. Compared with a standard lithiated carbon material, 6 carbon per lithium atom with a charge density of 344 mAhg⁻¹, it is a favorable number for EES system.^[9]

Scheme 3.2 Nine-membered square scheme for Q, with pKa's of BQ.

3.2.1 Biomass

As pointed out in section 3.1.5, biomass can be used as precursors to prepare the carbon materials for EES,^[58,59] such as coffee beans, coconut shell, sugar cane bagasse, apricot shell, coffee endocarp, poplar wood, rice husk, peanut shell, fruit seeds, and various tree barks.^[60-62] These biomass derived carbons exhibit large surface area, high electronic conductivities, optimized pore structures and pore size distribution. However, high temperature (as high as 900 °C), chemicals (acids, alkali and salts) and complicated procedures are necessary during the carbonization process. There is still a great need to further simplify and lower the cost of the manufacture process of biomass for EES. Moreover, as pointed out in the introduction section, Q play an important role in the photosynthesis process, which actually exist abundantly in the photosynthesis products – carbohydrates or biomass; and biomass materials can be seen as the ORPs with Q as the electroactive pendant groups. Accordingly, these redox active Q groups would render biomass capable for EES instead of simply carbonization. In the following part, researches related to the redox activity of biomass used in energy storage will be discussed, and among them lignin is a very famous example.

3.2.2 Lignin

Biomass mainly consists of cellulose, hemicellulose, lignin and a small fraction of extractives. Structurally, lignin is chemically interweaved with hemicellulose, both of which wrap outside the cellulose fibers and all of them are long-chain natural polymers.^[3,8,63] Cellulose is a linear homo-polymer that contains β -D-glucopyranose units connected via β -glycosidic bonds, which can be converted into glucose monomers; hemicellulose is a mixture of polysaccharides and a branched polymer with a low degree of polymerization, which binds tightly, not covalently, to the surface of the cellulose micro-fibril; lignin, however, is amorphous polymer with varying structures due to the different biomass sources. Generally, cellulose, hemicellulose and lignin account for 40-50%, 15-30% and 20-30% of the biomass weight, respectively, and they can be separated via chemical, thermal and microbiological processes. There are basically four types of biomass: woody plants, herbaceous plants/grasses, aquatic plants and manures,^[3] among which woody plants and herbaceous plants are most important sources for lignin. Every year there are approximately 70 million tons of lignin produced during the extraction of cellulose in paper industry, however, only 2% weight of lignin is industrially applied as surfactants, dispersants, concrete additives, etc. The remainder is generally burnt as low-grade fuel for process heating in pulp mills.^[63]

Lignin from paper and pulp chemistry is basically identified as four types: kraft lignin (KL), lignosulfonate (LS), soda lignin and organosolv lignin, according to the different pulping processes. KL is the depolymerized lignin that dissolve in alkaline solution, which is thereafter recovered by acidification; when treating the pulp with acidic solution, sulfonate groups are formed onto the lignin biopolymer chains, it is thus called LS and is soluble in water; soda lignin is obtained from the soda pulping process, displaying high purity; based on the treatment with organic solvent, the organosolv pulp is obtained and the extracted lignin is designated as organosolv lignin, which can be dissolved in a wide range of organic solvents and alkaline solution.^[64] The former two pulping processes currently account for most of the lignin production, which thus render

Figure 3.5 (a) The representative molecule structure of lignin and (b) the main monomers included in lignin.

lignin cost-effective. Therefore, lignin is drawing more and more attention to develop into value-added products, and one important aspect is EES application.

Lignin contains abundant six-carbon rings with aromatic functionality, as shown in **Figure 3.5 a**. It is made from three types of monomers, sinapyl alcohol (S unit), coniferyl alcohol (G unit), and p-coumaryl alcohol (H unit), as shown in **Figure 3.5 b**, with softwood lignin containing G units, hard wood lignin consisting of G and S units, and grass lignin including G, H and S units.^[65] These three units are linked via ether bonds or carbon-carbon bonds at random positions, which result in abundant functional groups in lignin: hydroxyl, benzyl, ether, carboxyl, etc.^[63] Among these functional groups, phenol groups can be converted into Q through oxidation process,^[9,66] enabling the redox reactivity of lignin that can be further utilized in EES. However, lignin itself is electrically insulating, conductive materials are thus essential to get access to the Q sites in lignin.

The redox reactivity of lignin was first realized by Milczarek by immersing a polycrystalline gold electrode into a solution of alkali lignin in acetonitrile/0.5 M H₂SO₄ (1/1, v/v).^[66] The alkali lignin strongly adsorbed onto the gold electrode and underwent a 2e⁻/2H⁺ reactions. Importantly, as lignin adsorbed onto an electrode, merely the molecules located closed to the electrode could be used, due to the electrically insulating properties.^[67] It is thereby essential to get access to the Q groups in the bulk materials, which is realized via a ECPs matrix embedded with lignin.^[9] For example, polypyrrole/lignin hybrid material electrodes are fabricated via electrochemical polymerization of pyrrole in the presence of water-soluble LS, whose sulfonyl groups can act as dopants.^[68] This hybrid electrode displays a discharge capacity of 72 mAhg⁻¹, while that of the pure polypyrrole electrodes is merely 30 mAhg⁻¹. However, the cycling stability of this polypyrrole/LS hybrid material electrode is poor with a dramatically loss of Q-capacity after only 100 CV cycles. Thereafter, 3,4-ethylenedioxythiophene (EDOT) is applied to obtain the PEDOT/LS hybrid material electrode, which displays a much better cycling stability with 83% capacity retention after 1000 charge-discharge cycles and a discharges capacity of 34 mAhg⁻¹, with 140% capacity increase compared with PEDOT (14 mAhg⁻¹). Another example is poly(aminoanthraquinone) (PAAQ) that combines with the main units in LS – sinapic, ferulic and syringic acid – to composite a phenolic acid-doped PAAQ material,^[69] whose stability can arrive 70-90% capacity retention after 1000 cycles and the capacity increase from 127 F g⁻¹ (un-doped PAAQ) to 210 F g⁻¹. Herein, the increased capacity of these lignin/ECPs hybrid materials compared with the pure ECPs is the faradic capacity due to the redox reactions of Q-groups in lignin. However, one disadvantage of these lignin/ECPs hybrids is the cost of polymer in consideration of scalable production. It is, accordingly, desirable to substitute these relatively expensive conductive polymers with other conducting materials that is low-cost.

As pointed out in section 3.1, carbon materials are attractive conductive materials, which can actually combine with lignin to enable the access of Q-sites in the bulk, for instance, CNTs,^[70] reduced graphene oxide (RGO),^[71] graphene,^[72] conductive carbon^[73] and HNO₃ treated active carbon (TAC)^[74] have been used to fabricate the

carbon/lignin hybrid materials. The electrochemical performance of these carbon/lignin hybrid material electrodes are summarized in **Table 3.1**, some of them display relatively higher discharge capacity and better stability than the lignin/ECPs electrodes.

Remarkably, graphite is one of the cheapest carbon-based materials with good electrical conductivity. In **Paper I**, graphite was directly used to fabricate the LS/graphite hybrid material electrodes to further decrease the cost of the manufacture. Though the discharge capacity and cycling stability of these electrodes are moderate, however, the low-cost original materials and facile processing method enable these electrodes to be scalable.^[17] The detail about the processing method – mechanical-milling – will be introduced in chapter 4.

Table 3.1 The electrochemical performance of carbon/lignin hybrid material electrodes

Carbon/lignin hybrid material electrodes	Discharge capacity / (mAhg ⁻¹) ^a	Improvement in comparison with the reference electrode ^b	Charge-discharge cycling stability	Ref
KL/CNTs	26 (188 F g ⁻¹)	120%	93% retention after 500 cycles at 1 A g ⁻¹	70
Lignin/RGO	72 (432 F g ⁻¹)	600%	96% retention after 3000 cycles at 1 A g ⁻¹	71
LS/graphene	47 (211 F g ⁻¹)	2000%	88% retention after 15000 cycles at 2 A g ⁻¹	72
KL/conductive carbon	80	120%	No capacity loss after 100 cycles	73
KL/TAC	65 (293 F g ⁻¹)	140%	98.1% retention after 1000 cycles at 1 A g ⁻¹	74

a: The specific capacitance of some electrodes are recalculated into discharge capacity for a better comparison; *b*: the increase of capacity/capacitance.

3.2.3 Humic Acid

Humic acid (HA) and its related humic substances are natural polymers that are widely distributed on earth. They mainly originate from the degradation of organic matter and are presented in various environments, such as terrestrial soil, natural water, sea sediment, peat, lignite and coal,^[75-77] which make HA sustainable and cost-effective. Among these sources of HA, lignite, accounting for 40% of the global coal reserves, is regarded as low-value fuel that is not suitable for direct burning, which results in serious emission of CO₂ and acid rain. If HA can find a valuable way to be utilized then it will enable lignite and coals developing as a feedstock for value-added productions. Actually HA is attracting more and more attention due to the cross-linked aromatic rings structure and wide variety of oxygen-containing functional groups: carboxylic acids, phenolic and alcoholic hydroxyl, ketones, and Q/QH₂ groups, as shown in **Figure 3.6**. The high content of carbon element (more than 40 wt. %) and the sponge-like structure render HA a good precursor for AC and porous carbon fabrication,^[75,78] the rich oxygen containing groups in HA results in the ability of ion-exchange that can be utilized as

medicine^[76] and to remove the heavy metals from water^[79]; the porous structure and acid-base reactions enable their application in removal of waste gas, NO_x, SO₂, H₂S, CO₂, etc.^[80]

Figure 3.6 The representative molecule structure of HA.

The redox reactivity the Q/QH₂ structures in HA has been studied,^[81,82] which is, however, not widely used in EES. Zhu used HA as anode materials in lithium/sodium ion batteries,^[83] and Wasinski added HA into the electrolyte to improve the specific capacitance of EDLC (approximate 10% increase).^[84] We concluded that HA was capable to promote the capacity of EES systems and a HA organic electrode was thereafter invented, this work can be found in **paper II**. Similar to lignin, HA is also electrically insulating thus conductive material – graphite – is employed to combine with HA to fabricate the HA/graphite hybrid material electrodes.^[18] The processing method used is similar to that of LS/graphite hybrid material electrodes in **paper I** - mechanical milling - that also makes these HA/graphite hybrid material electrodes scalable and cost-effective. Though the discharge capacity of these HA/graphite electrodes (20 mAhg⁻¹) is lower than that of the LS/graphite electrodes (35 mAhg⁻¹), it renders another sustainable, abundant and low cost Q-source for EES.

3.2.4 Barks

Plenty of tree barks have been used in EES, however, mainly by means of carbonized materials.^[62,85,86] Lignin accounts for 15-30% of woods mass and as high as 40% of bark's mass,^[87] which suggests barks to be important source for lignin and they contain sizable Q-structures. Since LS and HA have been employed as active materials for EES due to the Q/QH₂ groups, accordingly, the redox reactivity of barks can also be used in EES. In **paper III**, instead of extracting the redox active Q groups from barks, barks are directly used to fabricate various bark/graphite hybrid material electrodes for further lowering the impact on environment. As shown in **Figure 3.7**, a series of barks – beech bark, birch bark, *Quercus robur* bark, *Quercus suber* bark, and *Quercus ilex* bark – as well as other biomass waste – coconut shell, tamarind core husk, and olive core husk –

are separately co-milled with pristine graphite to obtain the biomass/graphite hybrid material electrodes. These electrodes display a discharge capacity range from 1 mAhg⁻¹ to 20 mAhg⁻¹, with *Quercus ilex* bark/graphite electrodes exhibiting the highest discharge capacity. Compared with the HA/graphite hybrid electrodes, *Quercus ilex* bark/graphite hybrid material electrodes exhibit a poorer stability but a similar discharge capacity. These results indicate the possibility to directly use barks or other biomass materials containing a sizable fraction of Q-groups for EES, without extraction and separation of the redox active components from other elements. We believe it is a significant discovery for biomass materials applied in EES.

Remarkably, in barks structure, except for the redox active lignin other compositions such as hemicellulose, cellulose and metal ions also exist, resulting in an increased inactive mass that leads to lower capacity. If taking the literature value, lignin accounts for 30% of *Quercus ilex* bark mass,^[88] and only 15% of the mass of the *Quercus ilex* bark/graphite (1/1, w/w) electrode is lignin. While in **Paper I**, the LS/graphite electrodes display 35 mAhg⁻¹ at a weight fraction of LS of 50 %. Therefore we can further improve the discharge capacity of the electrodes by improving the lignin fraction in the electrodes.

Figure 3.7 The biomass materials used to fabricate the biomass/graphite hybrid material electrodes in this thesis.

3.2.5 Quinone Chemicals

A wide range of organic chemicals containing Q-groups (hereafter labeled as Q chemicals (QCs)) can be extracted from the biomass materials. The widely employed are benzoquinone (BQ), naphthaquinone (NQ), anthraquinone (AQ) and their derivatives.^[4] Representative chemical structures are shown in Figure 3.4. Juglone is presented in leaves, roots, husks, and especially in the bark of black walnut; lawsone can be found in the leaves of the henna plants and in the flower of water hyacinth; alizarin was historically derived from the root of madder plants, and all of them have been used as dyes. Actually, the Q redox function in various QCs have been

widely applied in EES. Polymers based on the conjugated BQ, NQ, AQ, or other polymers with Q-groups on the main chains are used in EES devices that display high specific power and energy;^[89-91] and they can work as dopants in the ECPs with a promoted capacitance and enhanced cycle stability.^[92-94] When grafted or confined within the porous structures of carbon materials, they render the carbon materials as high as 470% increase of capacitance.^[95-97] QCs can also work as the additive in the electrolyte to obtain 2 to 5 times promoted capacitance of the system;^[98,99] and in RFBs a wide variety of QCs have been applied to achieve a high energy density and high stability.^[100,101] However, the drawbacks of these materials are also obvious: the cost of QCs polymers is too high for scalable production; the absorbed QCs on porous carbon materials are limited by the situation of pores that makes the fabrication process complicated, and the reactions can only happen at the surface of carbon; the EES devices containing QCs in the electrolyte display limited volume capacity and poor stability. Taking this into mind and based on the success obtained from the biomass/graphite hybrid material electrodes, we fabricate a series of QCs/graphite hybrid material electrodes to get access to the Q-sites in the bulk. It displays a capacity as high as 70 mAhg⁻¹ with approximate 30 times higher than that of graphite electrode^[102] and the detail results are presented in **paper III**. Herein, the fabrication of the electrodes is conducted by mechanical milling process with protein nano-fibrils as the binder (5 wt. %).

Moreover, in order to improve the electrochemical performance of these biomass/graphite electrodes, an attractive option is to add extra Q-functional groups; one method to achieve this is by introducing QCs into the materials. Therefore, the biomass/QCs/graphite tri-hybrid material electrodes were formed by mechanical milling and their performance were investigated. The LS/juglone/graphite electrode displays a discharge capacity of 45 mAhg⁻¹ with a 30% increase compared with the LS/graphite electrode; HA/BQ/graphite electrode presents a 60% higher capacity than the HA/graphite electrodes; *Quercus ilex* bark/juglone/graphite electrode indicates a 16% increase of the capacity compared with the *Quercus ilex* bark/graphite electrode. However, these tri-hybrid material electrodes lose the QCs capacity relatively fast due to the weak interaction between the small QCs molecules and the other components, thus leading to the loss of QCs into the electrolyte.

4 MECHANOCHEMISTRY APPLIED IN THE FABRICATION OF ELECTRODES

4.1 History and Definition

Mechanochemical techniques are drawing more and more attention due to the solvent-free or nearly solvent-free synthetic routes, which make it a clean, environmentally friendly, and sustainable synthetic method. A definition for mechanochemistry is “reactions, normally of solids, induced by the impact of mechanical energy”,^[103] where the mechanical energy is transferred into the system via various actions, like impact, shearing, grinding, stretching, and compression. These actions can reduce the particle size, create fresh active surfaces and chemical reactive sites, resulting in increasing contact and reaction of the particles. Mechanochemistry has always played an important role in human civilization with the history dating back to Stone Age: processing clay and grinding of wheat and seeds. The earliest written records of mechanochemical reaction dates back to 315 BC in the book “On Stones” by Theophrastus of Eresus, describing a method to generate mercury (Hg) by grinding cinnabar (mercury sulfide, HgS) with copper or bronze mortar and pestle, which is also the first written evidence of inorganic chemical reaction.^[11] Traditionally, mechanochemistry is mainly applied in food ingredients, medicines, minerals or building materials in the form of grinding two or more solids together. Until 1820, Michael Faraday used a “dry way” to reduce silver chloride (AgCl) into silver by grinding it with zinc, tin, iron, and copper. It is then followed by Carey Lea in 1890s, who discovered the decomposition of mercury chloride (HgCl₂) and AgCl into mercury and silver under grinding, respectively, instead of melting or sublimation. This work makes mechanochemical processes distinctive from thermochemical processes, and in 1891, Wilhelm Ostwald defined mechanochemistry as one of the four sub-disciplines of chemistry, along with thermochemistry, electrochemistry, and photochemistry, according to the type of energy input.^[11,104]

4.2 Mechanochemical Processing Techniques

Some of the commonly used mechanochemical tools are showed in **Figure 4.1**. Mortar and pestle, with a long history of human use, are manual mechanochemical tools. Grinding with mortar and pestle can be highly influenced by the ambient situations (humidity) and the manual force, which varies between individuals and it is therefore difficult to control the reproducibility between different preparations. Moreover, mortar and pestle is unsuitable for materials preparations requiring a long milling time. Thereafter, more modern automated mechanochemical tools have been developed and applied, and two important examples are ball mills and twin-screw extrusion (TSE), allowing for good reproducibility and longer reaction time. Ball mills employ sealed

reaction vessels or jars with milling balls added that provide mechanical force to the reagents. There are mainly two types of ball mills, shaker mills and planetary mills: in shaker mills, the reaction jar is shaken from side to side, the milling balls supply impact and shear force to the reactants during the shaking process; in planetary mills, the reaction vessels spin counter-rotatory to the spinning disc that they are mounted on, causing shear force to the reactants in the vessels. The materials used for the jars and milling balls are mainly stainless steel, tungsten carbide, zirconia, and Teflon, the hardness and density of which are vital for the grinding performance due to the different input energy; for example, harder material usually carries higher kinetic energy during the milling process. Other varieties to control the input energy include the shaking frequency or rotation speed of the mills, the operation time, and the filling degree that is also called ball-to-reagent-ratio. The former two parameters are easily tuned on the instruments, the latter is determined by the mass ratio of the milling balls and the reagents. It has been proposed that the volume occupied by balls should not be higher than 25% of the total vessel volume to ensure efficient reaction kinetics.^[105] Moreover, it is essential to consider the chemical resistance (corrosion problems) and wearing problems of the vessels, which would introduce contamination ions to the reactants. Nowadays, ball mills are generally used in lab for scientific research with limited scale, while TES is well established in industries due to the continuous processes: two interlocking screws with counter-rotatory can grind two or several solids together and simultaneously transport the mixture down a barrel along the extrusion path. On the path of extrusion, various parameters can be tuned – temperature, screw speed, and residence time – to optimize the reaction performance.^[106]

Figure 4.1 Some commonly used mechanical tools: (a) mortar and pestle; (b) shaker ball mills; (c) planetary ball mills; (d) twin-screw extrusion.

4.3 Mechanism and Application

Mechanochemical processes are operationally simple, but mechanistically highly complex. To understand more of the mechanochemistry process, several models are proposed, of which the two most important are hot-spot theory and magma-plasma theory.^[104] Hot spot theory is based on the friction processes between two surfaces of slide against each other, causing a dramatic increase of local temperature (above 1000 °C within 1 μm^2) in short period; magma-plasma model is due to the direct impact that allows for the transient plasmas and the ejection of free electrons at impact points. In these situations,

brittle materials would crack under strain and these cracks will propagate over a large distance, where molecular reactions can take place. Generally, during the impact or shearing of two solids or solid/balls at high velocity, reduction of particle size, mass transfer, diffusion of surface molecules, introducing of defects, intimate mixing of reactants, and friction heating in local and bulk are generated.^[11,104]

The merits of mechanochemistry are obvious: rapid reaction rate, solvent free, working at ambient temperature, scalable, independent of reagent solubility. Accordingly, it has been successfully applied in coal industry, catalysts, organic or inorganic chemical synthesis (especially when the reagents are highly insoluble or not all soluble in the same solvent), supramolecular chemistry, crystal engineering, materials engineering (biomaterials, nanoparticles), pharmacy, and food science.^[11,103,107]

4.4 Graphite Exfoliation and Carbon Paste

As mentioned in chapter 3, graphite exfoliation is attractive for the preparation of graphene sheets that display high electrical conductivity and large surface area. Mechanochemistry is actually promising to exfoliate graphite into few-layer graphene due to the solvent-free process. Recently, various solids (or surfactants) have been co-milled with graphite at solid phase to enable the exfoliation of graphite.^[12,13] During the milling process, the aromatic structures in the surfactants interact favorably with graphene sheets via π - π interaction; and the *van der Waals* interaction between the adjacent graphene layers is reduced; then exfoliation occurs; and the exfoliated graphene layers are stabilized by the surfactants molecules, which is a vital process due to the easy re-stacking property of graphene layers. In our study, whether biomass materials can be used as surfactants to exfoliate graphite into few-layer graphene by mechanochemistry? In fact, lignin have been applied to exfoliate graphite and stabilize the obtained few-layer graphene sheets via aqueous sonication.^[108,109] Biomass materials are thereby capable to exfoliate graphite at solid phase by ball-milling, with biomass/graphite mixture generated.

How to fabricate the biomass/graphite mixture into electrodes? Typically, graphene in the form of *dispersion* can be processed into electrodes via various techniques: dip coating, rod coating, spray coating, spin coating, blade coating, screen printing, vacuum filtration, drop casting, etc. Another way to prepare electrodes is to utilize *carbon paste* – a mixture of carbon powder with a non-electroactive liquid binder^[110] – as the precursor instead of carbon dispersion. Keeping the carbon dispersion and carbon paste into mind, a facile process is developed to generate the biomass/graphite hybrid material electrodes for EES in this thesis.

4.5 LS/Graphite Hybrid Material Electrodes

4.5.1 Electrodes Fabrication

In **paper I**, the blackish LS/graphite mixture obtained from ball-milling is dispersed into water; however, drop-casting of this dispersion creates separate aggregates instead of homogeneous films.^[17] The as-prepared dispersion is therefore centrifuged resulting in a pellet and a supernatant that are separated. The films formed from the supernatant display cracks upon drying and partly dissolve into the aqueous electrolyte (0.1 M HClO₄). On the other hand, the materials collected in pellets successfully create homogeneous films without cracks and are stable to electrolytes.^[17] Usually to get a carbon paste it is essential to utilize a liquid binder, which is, however, electrically insulating and does not contribute to the charge storage. Binders can further decrease the conductivity of electrodes which is vital in our case since large fraction of lignin is favorable. Accordingly, this pellets without use of binder preserve a potential high conductivity for this LS/graphite hybrid material electrode. Therefore, the materials in the supernatant are discarded and that in the pellets are collected and coated onto gold substrates via an automated blade coater, creating an electrode.^[17] The whole procedure of the electrodes preparation is presented in **Figure 4.2**.

The properties of the separated supernatant and pellets are both studied: there is a mixture of LS and graphite not only in the supernatant but also in the pellets; the particle size of graphite in the pellets is larger than that in the supernatant; weight of the materials in the supernatant is higher than that in the pellets. It is understandable from the aqueous processing where the larger flakes are less stable under centrifugation and more easily form a pellet; LS is water soluble and prefers to stay in the supernatant that leads to larger amount of LS in the supernatant than in the pellets.

Figure 4.2 The fabrication scheme of LS/graphite hybrid material electrodes via mechanochemistry.

4.5.2 Physical Properties

In addition, the physical properties of these LS/graphite hybrid material electrodes with different stoichiometry from 10 to 1, which is the weight ratio of LS and graphite applied

in the ball-milling process, are investigated. As shown in **Figure 4.3 a**, these LS/graphite hybrid material electrodes exhibit similar CV to the published one, and the discharge capacity of the electrodes with different stoichiometry are approximate 30-35 mAhg⁻¹ (Figure 4.3 b) with 2400% increase compared to the graphite electrode.^[17] As the amount of LS increases, the conductivity of the electrodes decreases gradually from 288 S·m⁻¹ to 139 S·m⁻¹, except for the LS/graphite (1/1, w/w) hybrid material electrode that displays a much lower conductivity of 66 S·m⁻¹ due to the poor morphology.^[17] Taking the faradaic discharge capacity and the actual mass of LS in the hybrid material electrodes into consideration, the discharge capacity due to the mass of LS in the electrodes is recalculated to be 70 mAhg⁻¹, which is in agreement with the published value from the Q-groups in the same LS samples that is 69 mAhg⁻¹,^[9] indicating an efficient interaction between graphite and the Q/QH₂ groups in the electrodes. Other measurements like TEM (in Figure 4.3 c), SEM, Raman, and XRD probe that graphite is exfoliated into few-layer graphene with more disorder and smaller crystallite size during the ball-milling process.^[17] Based on the discussion in section 4.4, LS, containing a large amount of aromatic structures, interact with graphite via π - π interaction and reduce the *van der Waals* interaction between the adjacent graphene sheets, leading to the exfoliation of graphite during the milling process; when treated with aqueous mediate, LS in the LS/graphite mixture help to stabilize the exfoliated graphene sheets; the generated pellets after centrifugation display a viscosity that is enough to form homogeneous films, with LS working as a binder and the redox active component.

Figure 4.3 The (a) CV, (b) charge-discharge curves at different charge rate, and (c) TEM results of LS/graphite (4/1, w/w) hybrid material electrodes.

4.5.3 Investigation of LS Leakage from the Electrodes

During the electrochemical measurements, LS leak gradually from the hybrid materials into the electrolyte as observed by the optical absorption of the electrolyte at 280 nm.^[17] Thereafter the leaking rate of LS and the amount of leaking LS are investigated with a LS/graphite hybrid material electrode immersed into 0.1 M HClO₄ solution and the UV-vis absorption of the HClO₄ solution being monitored over time. The absorption of the solution at 280 nm increased rapidly in the first ten minutes and then gradually became constant; the calculated mass of LS in the solution accounts for around 30% of the primary mass of LS in the electrodes.^[17] We thus hypothesize the LS loosely bound at

the surface of the electrode is washed away by the electrolyte. Then the electrode was immersed into 0.1 M HClO_4 and waited for 10 minutes before running the UV-vis absorption measurements in a new HClO_4 solution, and this time the leaking mass of LS was negligible.^[17] While the discharge capacity of the LS/graphite electrode did not decrease after the washing process and the stability increases from 53% capacity retention toward 80% after 1000 charge-discharge cycles at 4 A g^{-1} .

4.6 HA/Graphite Hybrid Material Electrodes

Based on the fabrication processing of LS/graphite hybrid material electrodes, similar method is used to generate the HA/graphite hybrid material electrodes in **paper II**.^[18] This preparation process contains aqueous treatment of the HA/graphite mixture that helps to disperse the graphene layers, and the solubility of HA in water is vital to obtain a homogeneous film. Dependent on the pH, HA display a protonated or deprotonated form with a HA salt formed at higher pH and an acid at lower pH; at neutral pH (water), the solubility of HA salt is much better than that of HA, thus HA is employed in the form of a sodium salt for the electrodes fabrication.^[18] It demonstrates a mixture of HA and graphite in the pellets and graphite is exfoliated into few-layer graphene in the presence of HA during the ball-milling process. Similarly, the aromatic structures in HA interact with graphite via π - π interaction that enables the exfoliation.

Other properties of these HA/graphite electrodes with different stoichiometry (2/1, 4/1, 7/1, 10/1, (w/w)) are also investigated: as the stoichiometry of HA/graphite increase, the conductivity of these electrodes decrease from 159 $\text{S} \cdot \text{m}^{-1}$ to only 0.34 $\text{S} \cdot \text{m}^{-1}$, which are much lower than that of LS/graphite hybrid electrodes; the mass ratio of HA and graphite in the pellets increase from 1.17 to 4.85, which explains the decreasing and low conductivity.^[18] Moreover, there is a smaller fraction of Q/QH₂ groups in HA than that in LS, these HA electrodes thus display no obvious redox peaks in CV (**Figure 4.4 a**) and a discharge capacity range of 17-20 mAhg^{-1} (**Figure 4.4 b**). Interestingly, the conductivity does not display a high impact on the discharge capacity of the HA/graphite electrodes even with a conductivity of 0.34 $\text{S} \cdot \text{m}^{-1}$. In addition, these HA/graphite electrodes show better charge-discharge cycling stability (84% retention after 1000 cycles, **Figure 4.4 c**) than LS/graphite electrodes (63% retention after 1000 cycles)

Figure 4.4 The (a) CV, (b) discharge curves at different charge rate, and (c) charge-discharge cycling stability results of HA/graphite (4/1, w/w) hybrid material electrodes.

toward HClO_4 solution without rapid loss of active materials.^[18] We assume in the acidic situation, HA sodium salt is in protonation form that is not well soluble into the electrolyte solution, which results in improved stability of the electrodes.

4.7 Biomass/Graphite Hybrid Material Electrodes

Various barks and other biomass materials are directly co-milled with graphite in **paper III**, and they work as surfactants to exfoliate graphite into few-layer graphene via ball-milling process. It is however problematic to fabricate this as-prepared biomass/graphite mixture into carbon paste by aqueous treatment, dispersion, centrifugation, and separation processes. Because these biomass materials display poor solubility in water due to the complex polymer structures, and are unable to disperse and stabilize the exfoliated graphene sheets in water. Moreover, after centrifugation, almost all the carbon and bio-carbon materials go into the sediments (pellets), which exhibit low viscosity and would not create homogeneous films. In order to generate carbon paste from these biomass/graphite mixture, binders are thus used. Protein nanofibrils (PNFs) is an attractive source for binders due to the polymer structures and surface charges. A PNFs dispersion (5 wt. %) generated from Hen egg-white lysozyme via self-assembly in HCl solution ($\text{pH} \approx 1.6$) is used to co-ground with graphite and biomass (wet-milling), and a slurry that can form homogenous films is obtained. However, the resultant biomass/graphite electrodes from this slurry display low discharge capacity of only 0.8 - 3.2 mAhg^{-1} . We assume that during the wet-milling process, with the presence of PNFs dispersion, the π - π interaction between the biomass and graphite is reduced which results in inefficient exfoliation.

Therefore the biomass are first co-milled with graphite in solid phase (dry-milling) followed by grinding this biomass/graphite mixture with PNFs dispersion, with the obtained slurry fabricated into homogenous electrodes. The beech bark/graphite, *Quercus robur* bark/graphite, olive core/graphite and *Quercus ilex* bark/graphite hybrid electrodes fabricated from dry-milling present dramatically increased discharge capacity from 1 mAhg^{-1} to 9 mAhg^{-1} , 2 mAhg^{-1} to 12 mAhg^{-1} , 1 mAhg^{-1} to 6 mAhg^{-1} and 2 to 20 mAhg^{-1} , respectively. Moreover, smaller crystallite size and reduced number of layers of graphene sheets are observed in the dry-milling fabricated electrodes. It

Figure 4.5 The (a) CV, (b) discharge curves at different charge rate, and (c) charge-discharge cycling stability results of *Quercus ilex* bark/graphite hybrid material electrode formed by dry-milling.

thereby illustrates that dry-milling is more efficient than wet-milling to exfoliate graphite and results in higher discharge capacity. The CV, discharge capacity, and charge-discharge cycling stability results of the *Quercus ilex* bark/graphite electrode formed by dry-milling are presented in **Figure 4.5**.

4.8 Quinone Chemicals/Graphite Hybrid Material Electrodes

In **paper III**, quinone chemicals (QCs) derived from biomass are utilized to form the QCs/graphite hybrid material electrodes in order to further improve the discharge capacity of the electrodes. Since the QCs used herein are not water soluble (the quinol form might be water soluble at high pH), similar process to the fabrication of the biomass/graphite electrodes – wet milling and dry milling – are used to fabricate the QCs/graphite electrodes. It is demonstrated that the QCs molecules are capable to assist the exfoliation of graphite into few-layer graphene: from wet-milling to dry-milling, the discharge capacity for BQ/graphite, juglone/graphite, and alizarin/graphite electrodes arise from 6 to 12 mAhg⁻¹, 40 to 60 mAhg⁻¹, and 30 to 70 mAhg⁻¹, respectively. However, the stability of these QCs/graphite electrodes is relatively low. The CV, discharge capacity, and charge-discharge cycling stability results of alizarin/graphite electrodes formed by dry-milling are shown in **Figure 4.6**, with only 39% capacity retention after 120 charge-discharge cycles. We assume that the PNFs enable the creation of homogenous QCs/graphite electrodes, it is however incapable to stabilize the small molecules/graphite matrix and stop the loss of QCs.

Figure 4.6 The (a) CV, (b) discharge curves at different charge rate, and (c) charge-discharge cycling stability results of alizarin/graphite hybrid material electrodes formed by dry-milling.

5 SELF-DISCHARGE STUDY OF LS/GRAPHITE HYBRID MATERIAL ELECTRODES

An ESS system in the charged state is of higher free-energy than that in the discharged state, it will result in a spontaneous drop of free energy over time due to the thermodynamic driving force.^[11] This spontaneous process, in other words self-discharge, means that over time the amount of available charge and voltage of an ESS system will decrease; this moreover leads to a reduced energy density and power density. Self-discharge behavior is therefore an important aspect of EES: primary batteries experience a drop in voltage; secondary batteries require more frequent recharging process; and ECs display lower EES efficiency. In order to minimize self-discharge, it is essential to identify the operating self-discharge mechanisms and thus to modify the EES systems in a way that reduces self-discharge. Self-discharge processes can occur by several mechanisms, generally, they can be classified into two families: 1) processes related to the kinetics of the electrochemical processes at the interface of electrode and electrolyte, involving the faradaic reactions; 2) physical processes, like charge redistribution, which discharges the surface of electrodes and results in voltage decline. Several self-discharge models have been proposed to separate these different mechanisms, which will be discussed in the following section.

5.1 Three-electrode and Open-circuit Potential

The self-discharge measurement can be conducted in a two-electrode configuration or a three-electrode configuration. Even though the former is more similar to the configuration in commercial devices, it is, however, difficult to use for mechanistic investigations. For example, the recorded potential of a two-electrode configuration is the *voltage difference* between the two electrodes. In order to be able to identify the voltage drop of each electrode, a three-electrode configuration is more applicable, which are accordingly used in this thesis.

Float current measurements and Open-circuit potential (OCP) can be both used for self-discharge study. The former employs a continuous current flow to maintain the desired charging potential of the EES system with a record of the current over time; in the latter the EES is charged to a desired potential and then the potential is recorded versus time under an open-circuit configuration. OCP is more commonly used in academic research and the self-discharge models being discussed in this thesis are based on OCP. Hence, OCP is applied for the self-discharge study in **paper IV**.

5.2 Conway Models

According to Brian E. Conway, there are mainly five models that are related to self-discharge mechanisms:^[111-113]

Ohmic leakage – occurs due to the inter-electrode short circuit.

Overcharging – when the EES are overcharged beyond the decomposition potential limit of the electrolyte, self-discharge takes place due to the overcharging current or the decomposed species.

Diffusion-controlled faradaic reactions – is due to the impurities of low concentrations that undergo redox reactions, which discharge the electrode within the potential range on the electrode surface; examples of such impurities are dissolved O₂, or redox active metal ions such as iron ions.

Activation-controlled faradaic reactions – if the redox active species are at high concentration or confined on the electrodes (or part of the electrodes), diffusion limitation no longer exists and the self-discharge process is based on the faradaic reactions of the redox active species.

Charge-redistribution – generally, the outer part of an electrode charge/discharge more rapidly than the bulk, which leads to potential inequality through the electrode; then charge (including electrons and ions) will move through the electrode to equilibrate the potential difference between the surface and the interior of the electrode; if charges move from the surface to the interior of the electrode, the potential of the electrode will decline; if charge move from the interior to the surface of the electrode to offset the reduced charge, the potential will climb. Such process is more significant for porous electrode than planar one since the resistance of electrolyte confined in the pores and the rate of ions movement down the pores strongly affect the charge-redistribution rate, which is also limited by the electronic and ionic resistance of the electrode films.

Among these models, ohmic leakage and overcharging can be avoided by correctly establishing the cell and choosing the potential range, they are thus less important. We only consider the latter three mechanisms in this thesis. It should be noted that the actual self-discharge process will typically be highly complex with a combination of multiple mechanisms. For example, in PS, the charge on electrode is balanced by the counter ions in the electrolyte to form the EDL; then redox active species undergo faradaic reactions and pass electrons across the EDL; charge at the surface of the electrode move and a drop of potential occurs, which is self-discharge.

If the rate-limiting step of self-discharge process is the diffusion of the ions to the electrodes, the self-discharge mechanism is diffusion-controlled and it displays a linear dependence of potential V_t versus the square root of time:^[114]

$$V_t = V_i - \frac{2zFAD^{1/2}\pi^{1/2}c_0}{C}t^{1/2} \quad (5.1)$$

where V_i is the initial charging potential; A is the electroactive area, z , D , and c_0 are the number of charge transferred in the redox reactions, diffusion coefficient, and initial concentration of the redox species, respectively. If the rate-limiting step is the redox reactions, it is faradaic activation-controlled and the V_t profile is linear when plotted with the logarithm (log) of time:^[111,114]

$$V_t = -\frac{RT}{\alpha F} \ln \frac{\alpha F i_0}{RT C} - \frac{RT}{\alpha F} \ln \left(t + \frac{C\tau}{i_0} \right) \quad (5.2)$$

and

$$V_t = V_i - A \log(t + \tau) \quad (5.3)$$

$$\tau = \left(\frac{RT}{\alpha F} \right) \frac{i_0}{i_i} \quad (5.4)$$

where R is the universal gas constant, T is the absolute temperature, α is the charge transfer coefficient, F is the faraday constant, i_0 is the exchange current density, C is the capacitance, t is time, τ is an integration constant, A is Tafel slope constant, i_i is the initial current upon polarization.

Charge-redistribution, however, displays a similar profile to the activation-controlled mechanism – a linear potential drop versus the log of time, after a plateau. It is thus difficult to distinguish charge-redistribution from activation-controlled mechanism. Based on equation 5.2, 5.3, 5.4, the activation controlled self-discharge displays a slope independent on the charging potential, and the length of plateau is consistent with the integration constant τ , which is independent on the charging potential as well. For charge redistribution, the slope and plateau length however are dependent on the charging potential, the former increases and the latter decreases along with the charging potential. Accordingly, varying charging potentials are used to study the self-discharge process in **paper IV**. Besides, varying charging time and repeating charge/discharge processes, which can affect the potential inequality through the electrode, are also applied to distinguish the charge-redistribution from the activation-controlled mechanism.

5.3 Results

LS/graphite hybrid material electrodes are used for the self-discharge mechanism investigation. First, the aqueous electrolyte was purged with N_2 for 30 min before the charging process to avoid the redox reactions of O_2/H_2O on the electrode during the self-discharge process. Electrodes were charged to different potentials and kept for 3600s, then the potential was recorded at open-circuit for 48 hours. Thereafter, the discharge potential was replotted versus the log of time and the square root of time, separately,

and the profiles with different charging potentials are compared and shown in **Figure 5.1**. In addition, the measurements were performed at different temperatures and with different concentrations of electrolyte, respectively, with the initial charging potential of 0.7 V.

Figure 5.1 Self-discharge profiles of the LS/graphite hybrid material electrodes. (a) Potential versus discharge time, (b) potential versus the log of discharge time, (c) potential versus the square root of discharge time.

The self-discharge process indicates different mechanisms with different charging potentials. With a potential of 0.4 V, the time profile follows equation 5.1, indicating a diffusion controlled mechanism. This refers to the redox active species with low concentrations in the electrolyte, which might be the iron species originating from the ball milling process and O₂ adsorbed at the surface of electrode; 0.4 V is not high enough to oxidize large amount of QH₂ groups during the charging process, hence, there is only EDL capacity of the electrode. Moreover, the electrode displays a BET surface area of 3.7 m² g⁻¹ without obvious porous structures, for comparison, the surface area of activated carbons can be 1000 times larger. Thereby, the diffusion of protons and anions from the electrolyte to the surface of electrode and into the electrode also contribute to the self-discharge process. With 0.5 V, the voltage drop versus time displays a combination of diffusion-controlled and activation-controlled mechanisms, attributed to the diffusion of redox reactive ions, as well as the reduction of Q-groups. As the charging potential rises to 0.6 V and 0.7 V, more QH₂ groups are oxidized during the charging process, and the self-discharge plots follow the equation 5.2, 5.3, 5.4, indicating the activation controlled mechanism. However, when the time profiles and plateau length with different charging potentials are compared, their potential dependent properties probe the charge redistribution mechanism. Thereafter, the electrode was charged with different charging time and the charge-discharge processes were repeated for several times, the results further confirm that the charge-redistribution mechanism dominates the primary phase of the self-discharge process. As self-discharge process continues, the self-discharge rate becomes independent on the initial charging potential, activation controlled mechanism thereby becomes dominant. The detailed discussions can be found in **paper IV**.

6 ELECTRODE MATERIAL CHARACTERIZATION

6.1 Infrared and Raman Spectroscopy

Infrared (IR) and Raman spectroscopy are vibrational spectroscopies that are used for molecular structure identification.^[115] Generally, the former is widely applied in the asymmetric vibrations of polar structures and the latter is used in the symmetric vibrations of nonpolar structures. In IR spectroscopy, the IR radiation interacts with the molecular vibrations that results in the absorption of IR radiation and the transitions between the vibrational energy levels are measured. This process involves the electric *dipoles*, and the molecular vibration must result in a change in the dipole moment to be IR active. Raman spectroscopy is a two-photon inelastic light scattering process with a *polarizability* of the molecule. The incident photon interacts with the molecule vibrations and transfers part of the energy to it, and then scatters as a photon with a reduced frequency. The molecular vibration has to cause a polarizability change to be Raman active. IR and Raman spectra both display bands of vibrational energy levels with specific frequency, intensity, and shapes, which are unique to each molecule, respectively. Wavenumbers – $\bar{\nu}$, number of waves per unit length – is usually used to characterize the energy of each vibrational state:

$$\bar{\nu} = \frac{\nu}{(c/n)} = \frac{1}{\lambda} \quad (6.1)$$

where ν is the frequency (number cycles per unit time); λ is the wavelength; c is the speed of light; and n is the refractive index of the medium. The intensity of Raman scattered radiation follows:

$$I_R \propto \nu^4 I_0 N \left(\frac{\partial \alpha}{\partial Q} \right)^2 \quad (6.2)$$

where ν is the frequency of a laser, I_0 is the incident laser intensity, N is the number of scattering molecules, α is the polarizability of molecules, and Q is the amplitude of vibration. Accordingly, the wavelength and flux power of laser highly affect the Raman intensity. Moreover, the two main challenges of Raman spectroscopy are the weak signals and fluorescence disturbances, which is serious in organic molecules.

In this thesis, we applied Fourier transform infrared (FTIR) spectroscopy to identify the molecular structure of the biomass materials and Raman spectroscopy for the intrinsic structure of graphite in the hybrid electrodes. The FTIR results prove the existence of aromatic rings, C-O, C-C, and C-O-C structures in LS and in the LS/graphite hybrid material electrodes (**paper I**); there are phenolic and aromatic

structures in HA and in the HA/graphite hybrid electrodes (**paper II**).

A 532 nm laser was used as the excitation source for the Raman spectroscopy characterization. The pristine graphite displays D band, which is ascribed to the breathing modes of the sp^2 atoms in rings; G band that is due to the in-plane vibrational mode and bond stretching of paired sp^2 atoms in rings and chains; and 2D bands, the overtone of D band due to the two phonon lattice vibrational process, as shown in **Figure 6.1**.^[116] The graphite structures in the LS/graphite hybrid material electrodes exhibit relatively significant D band, much higher intensity ratio of D to G band (I_D/I_G), a stronger shoulder peak of G band, and a blue shift and narrowing of 2D band, indicating more defects, smaller crystallite size, more bond disorder, and the presence of few-layer graphene sheets in the hybrid electrodes. For HA/graphite hybrid material electrodes, they display similar vibration absorptions of graphite that indicates the exfoliation of graphite: higher I_D/I_G , a shoulder peak of G band, a blue shift of 2D band and G band. Similar profiles are also observed for *Quercus ilex* bark/graphite hybrid electrode and QCs/graphite hybrid electrodes, which indicate reduced graphene layers, improved density of defects and disorder, and decreasing size of crystalline graphite. The Raman signals of LS, *Quercus ilex* bark, and the QCs, however, are not obtained due to their strong fluorescence; HA exhibits two bands that are overlapping with the D and G bands of graphite without good resolution, ascribed to the interference of fluorescence.

Figure 6.1 Raman spectra results of LS/graphite hybrid material electrodes.

6.2 XRD

X-ray diffraction (XRD) was used to identify the crystallite structure of the electrode materials, by using a PANalytical X'Pert diffractometer with Cu $K\alpha$ radiation (45 KV and 40 mA). According to Bragg's law:

$$2d\sin\theta = n\lambda \quad (6.3)$$

where d is the interlayer distance, θ and λ is the scattering angle and the wavelength of x-ray, respectively, n is the integer, the pristine graphite displays (002) 2θ peaks at 26.5° , indicating an interlayer distance of 0.34 nm,^[117] as shown in **Figure 6.2**. The (002) peaks at 26.5° in these biomass/graphite hybrid material electrodes indicate no spacing change of graphite layers, while the promoted full width at half maximum (FWHM) of this peak suggests the reduced crystallite size and decreased thickness of graphite.^[118]

Figure 6.2 XRD results of LS/graphite hybrid material electrodes.

6.3 SEM and TEM

Scanning electron microscopy (SEM) was used to characterize the morphology of these biomass/graphite electrodes, by Zeiss Leo 1550 Gemini Scanning Electron Microscope with an acceleration voltage of 5 kV (Zeiss, Oberkochen, Germany). Transmission electron microscopy (TEM) on a LEO 912 OMEGA, operating at an accelerating voltage of 200k eV in a bright-field image mode, was applied to investigate the number of graphene layers in the hybrid material electrodes.

6.4 TGA

Thermogravimetric analysis (TGA) is useful to estimate the stoichiometry of these LS/graphite and HA/graphite hybrid material electrodes, which is uncertain because after aqueous treatment the supernatant is discarded and the stoichiometry in the pellets is unknown. The pre-dried pure materials and hybrid materials were heated to 1000°C under Ar on a STA 449 F1 Jupiter thermal analysis (NETZSCH, Selb, Germany) to obtain the residual mass fraction, respectively. The weight loss of the hybrid materials after heating equals the weight loss of each pure material in the hybrid materials, which provides an equation that can be used to calculate the *stoichiometry* of the hybrid materials. For the details, please refer to **paper I** and **paper II**.

6.5 DLS

Dynamic light scattering (DLS) is a technique to obtain the particles size distribution based on the Brownian motion of dispersed particles in a liquid, and the smaller particle is moving at a higher speed than the larger one.^[119] The speed of particles can relate to the particles size through the Stokes-Einstein equation:

$$D = \frac{k_B T}{6\pi\eta R_H} \quad (6.4)$$

where D is the translational diffusion coefficient that is the speed of particles in m^2/s ; k_B is the Boltzmann constant, T is temperature and η is the viscosity of liquid, and R_H is the hydrodynamic radius that refers to the size of particles that are spherical, smooth, and moving at the same speed. During the measurements, the incident laser with a specific frequency is scattered by the particles in all directions, with a certain angle the scattered light is detected. The intensity of the scattered light will fluctuate over time due to the motion of particles; and the fluctuations of the scattered light can be described by a correlation function, which describes how long a particle can localize at the same spot; as the particle is moving, there is an exponential decay of the correlation function over time and the smaller particles display faster decay than the large particles; thereafter these correlation functions are fitted via CONTIN program to achieve the diffusion coefficient and the hydrodynamic radius. Accordingly, it is not a direct technique to measure the particle size but is based on the motion of particles. In this thesis, DLS was used to measure the graphite particle size distribution in the supernatant and in the pellets, respectively, as shown in **Figure 6.3**. It indicates the larger particle size in the pellets than that in the supernatant, and the size range of graphite in the pellets is consistent with the SEM results.

Figure 6.3 DLS results of LS/graphite hybrid material electrodes.

6.6 Electrical Conductivity

The electrical conductivity of the biomass/graphite hybrid material electrodes was investigated via the four-point probe technique.^[120] From the name, there are four electrical probes with equal spacing between each of them in the system. A current is applied on the outer two probes, and the voltage drop between the inner two probes is measured. When the four probes touch the film, the sheet resistance R_s (in Ω/sq) of the infinite film can be known from:

$$R_s = \frac{\pi}{\ln(2)} \frac{V}{I} = 4.532 \frac{V}{I} \quad (6.5)$$

where I is the applied current on the outer probes in amps (A) and V is the voltage drop between the inner probes in volts (V), $\pi/\ln(2)$ is the geometric correction factor. This equation is only valid when the thickness of materials is no larger than 40% of the spacing between each probes. The electrical resistivity ρ can be known from:

$$\rho = R_s t \quad (6.6)$$

and the electrical conductivity σ :

$$\sigma = \frac{1}{\rho} \quad (6.7)$$

where ρ is in $\Omega\cdot\text{m}$; t is the thickness of materials; σ is in S/m. The sheet resistivity can be read directly from the four-probe instrument and based on the measuring thickness, the resistivity and conductivity of the materials can be calculated based on equation 6.6 and 6.7.

7 CONCLUSION AND FUTURE OUTLOOK

In this thesis, we fabricate a series of biomass/graphite hybrid material electrodes that are sustainable, low-cost, and scalable, by using the Q-groups in biomass for EES. First of all, abundant biomass materials derived from trees and lignite – LS and HA – are co-milled with graphite via a solvent free ball-milling method, respectively. The obtained LS/graphite hybrid material electrodes with different stoichiometry display a conductivity range from 70 to 290 $\text{S}\cdot\text{m}^{-1}$ and a discharge capacity range from 30 to 35 mAhg^{-1} ; HA/graphite hybrid material electrodes exhibit a discharge capacity range from 17 to 20 mAhg^{-1} and a conductivity range from 0.3 to 160 $\text{S}\cdot\text{m}^{-1}$ with different stoichiometry. It is proved that during the milling process LS and HA enable the thinning and breaking of graphite into few-layer graphene with smaller crystallite size. In order to reduce the impact on the environment during the extraction of Q-structures, various biomass materials are directly co-ground with graphite via the ball-milling process and the biomass/graphite electrodes are obtained with the help of protein nano-fibrils. Among these biomass/graphite hybrid material electrodes, *Quercus ilex* bark/graphite electrode presents the highest discharge capacity of 20 mAhg^{-1} , that is similar to the HA/graphite electrodes, due to the high fraction of lignin in this bark. Moreover, a high loading of Q-groups is beneficial for the capacity of electrodes, accordingly, pure QCs derived from biomass are used to get the QCs/graphite hybrid material electrodes. Alizarine/graphite hybrid material electrodes show a capacity of 70 mAhg^{-1} that is approximately 30 times higher than that of pristine graphite. Thereafter, NQ is introduced into the LS/graphite hybrid material electrode and it displays a promoting discharge capacity from 35 mAhg^{-1} to 45 mAhg^{-1} ; BQ is added into the HA/graphite hybrid material electrodes with the discharge capacity arising from 20 mAhg^{-1} to 35 mAhg^{-1} .

The self-discharge mechanisms of the Q-containing electrodes are investigated on the LS/graphite hybrid material electrodes in HClO_4 electrolyte. These self-discharge process are conduct under different conditions: a series of initial charging potentials; electrolyte with varying pH; different charging time; repeating charge-discharge processes; various temperatures. Based on the Conway models, the self-discharge process indicates a combination mechanisms of faradaic diffusion controlled, faradaic activation controlled, as well as charge redistribution. This work is significant to design and modify the electrochemical systems to render slower self-discharge process.

Overall, we have used various abundant and cost-effective biomass materials for the scalable fabrication of EES systems, and the electrochemical performance of these electrodes keeps improving due to the modification of the starting materials and the fabricating process. However, these biomass electrodes present merely moderate capacity, it is thereby essential to further improve their capacity to render them the capability for commercial market.

One way is to increase the Q-loadings in the electrodes, such as further enhancing the Q-fraction in the hybrids or introducing new Q-structures with higher charge capacity into the films. Remarkably, both electronic and ionic conductivity must be sufficient to allow full access to the redox capacity of the electrode material, and the optimal nanostructure is still not known. Ionic conductivity is related to the percolation of ionic transport, and percolation of conducting graphite is necessary in our hybrid material electrodes. The volume fraction of graphite in the biomass/graphite electrodes are above or close to the theoretical percolation transition for metallic spheres in an electrically insulating matrix.^[121] Accordingly, there are some possibilities to form an improved nanostructure, with more elongated graphite flakes, in order to fully utilize the redox active element in the biomass/graphite hybrid materials.

In addition, several metrics of the mechanochemical processing can be tuned to promote the exfoliation performance of graphite, such as the type of graphite, the materials of the milling vessels, the type of milling instruments, the frequency and running time. It can thus improve the interaction between the bio-carbon materials and the carbon materials, and then increase the Q-sites that are accessible in the matrix. New binder materials and carbon materials with low cost are also required to further improve the interaction between the biomass materials and the carbon materials, and the stability of the hybrids.

Generally, these electrodes can only serve as positive electrodes while biomass negative electrodes are still lacking, thereby, Q-structures with more negative potentials are needed to prepare the biomass negative electrodes. Besides, these biomass/graphite hybrid electrodes suffer from serious loss of biomass materials and QCs from the electrodes into the electrolyte during the electrochemical measurements, which has not been efficiently diminished due to the weak interaction between the graphite and biomass materials; the interaction mechanism between the biomass materials and graphite during the exfoliation process is not clearly known and the in-situ measurements might help to clarify the exfoliation and interaction processes; the self-discharge process of the Q-containing electrodes needs more study to further explain the mechanism.

The biomass materials we tried in the thesis are only a small part of the biomass family, thereby more biomass sources with high fraction of Q-structures can be investigated and developed. Our work is significant for establishing the sustainable and cost-effective energy storage systems for commercial application in the large-scale intermittent electrical sources. It will in future benefit the people in the regions that lack electricity, promote the global economy, decrease the environmental pollutions, and decelerate the climate change.

8 SUMMARY OF PAPERS

Paper I

Scalable Lignin/Graphite Electrodes Formed by Mechanochemistry

Lignosulfonate (LS) is a side-product from the paper pulp, it is thus sustainable and cost effective. The large amount of Q-groups in lignin makes it suitable for electricity energy storage (EES). However, a challenging aspect to apply lignin in EES is the electrically insulating property. Therefore, conductive materials are required to get access to the redox active Q-structures in the bulk. Graphite is a low-cost conductive materials that can be used to form the graphite-lignin hybrids via a mechanical milling process. In this paper, LS is co-milled with graphite in the solid state, with a LS-graphite mixture generated. This mixture is treated with aqueous solution and it results in a paste that can be coated on the substrates and applied for EES. This LS/graphite hybrid material electrodes display a conductivity of 280 S m^{-1} and a discharge capacity of 35 mAhg^{-1} . It proves that LS works as a surfactant to exfoliate graphite into few-layer graphene with reduced crystallite size during the milling process. In this way, a facile processing method is proposed to fabricate sustainable, low-cost, and scalable electrodes.

Paper II

Biocarbon Meets Carbon – Humic Acid/Graphite Electrodes Formed by Mechanochemistry

Another biopolymer, humic acid (HA), can be found in lignite and the degraded plants, making it a ubiquitous, renewable, and low-cost biocarbon material. HA contains abundant Q-groups and can be used for EES. Similar to lignin, HA is also electrically

insulating and conductive materials are essential to utilize the Q-structures. A processing method similar to the fabrication of LS/graphite electrode is used in this paper, and the HA/graphite hybrid material electrodes are obtained. Graphene sheets with few layers and smaller crystallite size are observed in these electrodes; these electrodes present a conductivity of 160 S m^{-1} and a discharge capacity of 20 mAhg^{-1} . This work renders another abundant and cost-effective Q-source for EES.

Paper III

Quinones from Biopolymers and Small Molecules Milled into Graphite Electrodes

Generally, lignin accounts for 15-30% of the mass of wood and as high as 40% of the mass of barks. Paper pulp from the processing of wood or barks is thus an important source of lignin. However, to extract and separate lignin from the paper pulp, alkaline/acid solutions or organic solvents are commonly used. Therefore the isolation process is complicated and not environmentally friendly. In this paper, biomass materials – barks – are used directly as redox active materials in EES, with graphite as the conductive materials to get access to the Q-groups within the barks. A protein nanofibrils is used as binder for the electrode fabrication. The *Quercus ilex* bark/graphite electrodes show a discharge capacity of 20 mAhg^{-1} , compared with the electrode

fabricated from isolated lignin, this bark/graphite hybrid material electrode is more environmentally friendly and cost-effective. In addition, plenty of QCs are also co-milled with graphite to fabricate the hybrid material electrodes with an improved Q-loading. The alizarin/graphite electrodes display higher discharge capacity of 70 mAhg^{-1} . This work enables the direct utilization of biomass materials and QCs to build up a library of Q-containing electrodes with a discharge capacity range from 1 to 70 mAhg^{-1} , which are sustainable, scalable, and cost-effective.

Paper IV

Self-Discharge Investigation of Lignin/Graphite Hybrid Material Electrodes

Scalable and low-cost LS/graphite hybrid material electrodes have been developed. However, a high self-discharge rate that results in loss of energy density and power density is observed with these electrodes. It is thus important to investigate the self-discharge mechanism for these electrodes. In this paper, different models are applied to clarify the self-discharge mechanism of the LS/graphite electrodes. It indicates a combination of diffusion controlled, activation controlled, and charge redistribution mechanisms during the self-discharge process at varying charging voltages. These mechanisms are ascribed to the diffusion of the redox active species with low concentrations and the proton diffusion in the electrolyte; the redox reactions of the Q/QH₂ groups in the electrodes; the transfer of charge through the whole electrode to reach a potential equilibrium. Our work could help to develop ways to slow down the self-discharge process.

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Department of Physics, Chemistry and Biology (IFM)

Linköping University
SE-581 83 Linköping, Sweden

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