Electrochemical and Ion Transport Characterisation of a Nanoporous Carbon Derived from SiC

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Dedicated to my wife and my children
Abstract

In this doctoral project, a relatively new form of carbon material, with unique narrow pore size distribution around 7 Å and with uniform structure, has been electrochemically characterised using the single particle microelectrode technique. The carbon has been used as electrode material for supercapacitors. This type of capacitors is used as high power energy buffers in hybrid vehicles and for stationary power backup. The principle for the microelectrode technique consists of connecting a carbon particle with a carbon fibre by means of a micromanipulator. The single particle and carbon fibre together form a microelectrode. Combination of this technique with electroanalytical methods such as cyclic voltammetry and potential step measurements allows for the survey of electrochemical phenomena and for the determination of ion transport parameters inside the nanopores.

A mathematical model based on Fick’s second law, for diffusion of ions inside the nanopores at non steady state, was used for the determination of effective diffusion coefficients ($D_{eff}$). The coefficients were calculated from an asymptotic solution of Fick’s equation, applied for a thin layer adjacent to the external surface of the carbon particles and valid for the current response in a short time region. Another asymptotic solution was obtained, using spherical geometry and valid for the current response in a long time region.

In this doctoral work, the carbon particles have been exposed to potential cycling, which mimics that of large electrodes during operation of a double layer capacitor. The potential-current response, $E$-$I$, for the nanoporous carbon, shows a pure capacitive behaviour between -0.5 V and 0.1 V vs. the Hg/HgO reference electrode. The detection of the faradaic processes beyond these potentials was possible by lowering of the voltammometric sweep rate. The electrochemical processes occurring at positive and at negative potential were investigated separately.

Cyclic voltammometric measurements showed that the chemisorption of hydroxyl groups, occurring between 0.1 and 0.3 V, leads to a mild oxidation of the carbon structure, resulting in surface groups containing an oxygen atom at a specific carbon
site (e.g., phenolic or quinine type). These oxygen-containing surface groups caused an increase of the specific capacitance, which remained constant throughout a number of voltammometric cycles. The $D_{ef}$ decreased on the other hand with the number of cycles. The $D_{ef}$ decreases also with the positive potential. The evaluation of $D_{ef}$ indicates adsorption of hydroxyl groups and an increase of the effective tortuosity of the pore system.

The oxidation of the carbon particles, between 0 and 0.5 V, leads to more extensive oxidation and to surface groups containing two oxygen atoms at a single carbon site, followed by formation of carbonate ions. The oxygen-containing surface groups and carbonate ions formed at these potentials do not contribute to the specific capacitance and drastically retard or obstruct the ion transport inside the nanopores.

At negative potentials the carbon particles show a dominantly capacitive behaviour. The faradaic processes taking place below −0.5 V vs. Hg|HgO reference electrode are generation and adsorption of hydrogen. These processes do not perturb significantly the electrochemical and ion transport properties of the nanoporous carbon particles. It was found that hydrogen generation occurs at −0.5 V vs. Hg|HgO and that two hydrogen oxidation processes take place at positive potentials. The results indicate that the weakly adsorbed hydrogen undergoes oxidation between 0 and 0.1 V and that the strongly adsorbed hydrogen is oxidised at more positive potentials.

The single particle technique was adapted for the determination of diffusion coefficients of an organic electrolyte. The different size of the anions and cations caused different transport characteristics at negative and positive potentials. Slow cycling was found important for ion penetration inside the nanopores and for the evaluation of the effective diffusion coefficients.

The effective diffusion coefficients for the nanoporous carbon using aqueous 6M KOH and 0.1M TEABF$_4$ in acetonitrile were estimated to $1.4 (±0.8) \times 10^{-9}$ cm$^2$ s$^{-1}$ and $1.3 (±0.4) \times 10^{-8}$ cm$^2$ s$^{-1}$, respectively.
Keywords: Cottrell equation, radial diffusion, chronoamperometry, potential step measurements, microelectrode technique, nanoporous carbon, diffusion coefficient, double layer, supercapacitor.
Sammanfattning


En matematisk modell baserat på Ficks andra lag för icke-stationär jondiffusion i nanoporerna har utvecklats för att bestämma effektiva diffusionskoefficienter ($D_{eff}$). Koefficienterna beräknades utifrån en asymptotisk lösning tillämpat på en tunn film nära partikeln yta och därmed gällande för en strömarepons vid korta tider. För långa tider härleddes en annan asymptotisk lösning under antagande av en sfärisk geometri.

I det här doktorskabetet, var kolpartiklarna utsatta för potentialcykling, vilken efterliknar den cykling som stora elektroder utstår under driften av en dubbelsikts superkondensator. Potential-strömareponsen, $E-i$, av det nanoporösa kolet uppvisar ett rent kapacitivt beteende mellan –0,5 V och 0,1 V mot Hg|HgO som referenselektrode. Detektionen av faradaiska processer bortom dessa potentialer var möjligt genom att sänka den voltammometriska svephastigheten. De elektrokemiska processer som äger rum vid positiva och negativa potentialer studerades separat.

Cyklisk voltammometriska mätningar visade att kemisorption av hydroxidgrupper, vilket inträffar mellan 0,1 och 0,3 V, leder till mild oxidation av kolstrukturerna med resulterande ytgrupper som innehåller enbart en syreatom per specifikt kolsäte (t.ex. av fenol- eller kinonliknande typ). Dessa syrebaraande ytgrupper orsakade en ökning i
specific kapacitans. $D_{eff}$ minskade, å andra sidan, med antal cyklar. $D_{eff}$ minskade också med potentialen i positiv riktning. Utvärderingen av $D_{eff}$ visar på att adsorption av hydroxidjoner äger rum och på en ökning av den effektiva tortuositeten.

Oxidation av kolpartiklarna, upp till 0,5 V, leder till en mer intensiv oxidation. Ytgrupper som innehåller två syreatomer per kolsäte resulterar i karbonat bildning. Dessa syreämrande ytgrupper och karbonationerna som bildades vid de hår potentialerna, bidrar inte till den specifika kapacitansen och försämrar drastiskt eller blockerar jontransporten inne i nanoporerna.

Vid negativa potentialer, uppväxer kolpartiklarna ett annat beteende. De faradaiska processerna som äger rum under ~0,5 V mot Hg|HgO referens elektrod är generering och adsorption av väte. De här processerna påverkar inte särskilt de elektrokemiska och jontransportegenskaperna hos de nanoporösa kolpartiklarna. Oxidations processer av det bildade vänet äger rum vid positiva potentialer. Resultaten visar på att svagt adsorberat väte genomgår oxidation mellan 0 och 0,1 V och att starkt adsorberat väte blir oxiderat vid mer positiva potentialer.

Mikropartikelmethoden blev anpassad för utvärdering av diffusions koefficienter för organiska elektrolytter. Skillnader i jonstorlek, mellan anioner och katjoner, orsakar olika transport egenskaper vid negativa och positiva potentialer. Det visade sig att långsam cykling var viktig för inkorporering av joner in i nanoporerna och därmed för utvärderingen av diffusions koefficienterna.

Den effektiva diffusionskoefficienten för det nanoporösa kolet i 6M KOH beräknades till 1,4 $(\pm0,8) \times 10^{-9}$ cm$^2$ s$^{-1}$. Den effektiva diffusions koefficient för 0,1M TEABF$_4$ blev uppskattad till 1,3 $(\pm0,4) \times 10^{-8}$ cm$^2$ s$^{-1}$.

**Nyckelord:** Cotrell ekvation, radjell diffusion, kronoamperometri, potentialstegmätning, mikroelektrodteknik, nanoporöst kol, diffusionskoefficient, dubbelskikt, superkondensator.
List of appended papers

This thesis is a summary of the following technical papers, which are referred to in the text by their Roman numerals I-V.

I. Characterization of ion transport in a nanoporous carbon for double layer capacitors
   Marcelo Zaleta, Martin Bursell and Anders Lundblad

II. Determination of the effective diffusion coefficient of nanoporous carbon by means of a single particle microelectrode technique
    Marcelo Zaleta, Martin Bursell, Pehr Björnbom, Anders Lundblad

III. Effects of pore surface oxidation on electrochemical and mass-transport properties of a nanoporous carbon
     Marcelo Zaleta, Pehr Björnbom and Anders Lundblad

IV. Characterization of the electrochemical and ion transport properties of a nanoporous carbon at negative polarization by means of the single particle method
    Marcelo Zaleta, Pehr Björnbom and Anders Lundblad

V. Determination of diffusion coefficients of BF$_4^-$ inside carbon nanopores using the single particle microelectrode technique
   Marcelo Zaleta, Pehr Björnbom, Anders Lundblad, Gunnar Nurk, Heili Kasuk and Enn Lust

My contribution to the papers in this doctoral thesis

**Paper I-IV**
I am the main author.

**Paper V**
I am the main author. The construction of the cell and the set up for the experiments was carried out by Gunnar Nurk. I carried out the experiments together with Heili Kasuk who also gave contributions to the introduction and the experimental part.
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1. Introduction

1.1 General

The importance of electric power supplies in our modern society became more evident after the technological expansion following the Second World War. It has been even more accentuated with the introduction of computers in the household, the advances in wireless telephony, and nowadays, a higher, if not total, degree of electrification of vehicles for transportation. The requirements to be addressed, in order to carry out an adequate and optimal implementation of power sources for these purposes, are energy devices with high capacity of energy storage and capable of delivering as high power as possible. Portable energy devices were used in transportation for the first time when the electric car made entrance at the end of the 19th century. At that time several technical shortcomings made, among other reasons, the vehicles fail. To date, enormous progress has been made in this field, and there is still expectative for further improvement and development. Therefore, it is not totally surprising with the increasing interest in energy storage devices for modern automobile applications. Hybrid electric, battery or fuel cell driveline prototypes have shown, for instance, good prospective for substitution of conventional combustion engine drivelines. A new technology for transportation of that kind implies, therefore, high commercial demand of electric power devices.

Batteries have commonly been used as power devices due to their high capacity for energy storage in relatively small volume and weight. In addition, modern batteries have been designed for providing suitable high levels of power for several applications at the expense, though, of their energy density [1]. For automotive applications the battery should, at the best, have an operation life corresponding to the life of the vehicle in general. The cycle life is however, still relatively short (~1000 cycles) for most of the modern batteries. Electrochemical capacitors (also called supercapacitors or ultracapacitors) have been developed in the latest decades, in order to provide higher power than batteries, and at the same time, have higher energy density, in comparison with simple capacitors. Supercapacitors of the double layer
type can compete with batteries in price, high cycle-life and power delivery. The principle of energy storage by electrostatic charging and discharging without electron transfer, makes the double layer capacitors (DLC) an attractive alternative instead of batteries in automotive applications, regaining brake energy, and supporting with energy pulses at the start, or during the acceleration of vehicles, for more than $10^5$ cycles. From a commercial perspective, the DLC devices need, however, to achieve higher energy density at lower cost to become an attractive substitute for power batteries. A way of increasing the capacity of energy storage in DLC has been by using high surface materials, suitable cell design and to utilize organic electrolytes, which permit a wider operation than that of aqueous electrolytes. Apart form the knowledge of the faradaic limits, the pore properties of carbon materials have a major effect on the performance of capacitors. The specific capacitance (Farad / g, or Farad / cm$^3$) is proportional to the surface area of the electrode; therefore, the electrode material must contain a considerable fraction of pore volume. Carbon materials can be produced in diverse micro-textures and with different pore size distributions from many primary resources such as wood, biomass, petroleum, etc. Carbons are also available in high surface area, having more than 1000 m$^2$/g and are, therefore, most used for the fabrication of DLC electrodes. Intensive research has been dedicated to characterizing the chemistry involved in different electrochemical processes when using carbon as electrode material. From this research characteristics, common for many carbonaceous materials, have been established [2]. However, carbon is a multifaceted material concerning allotropic forms and structures. Each form of carbon, having a particular micro-texture, usually shows inherent electrochemical and physico-chemical properties, which leads, consequently, to different suitability for the wide range of applications. Other materials, such as conducting polymers and ruthenium oxide have also been used for the fabrication of porous electrode materials for supercapacitors. Carbon is, however, relatively inexpensive, in comparison to ruthenium oxide and its shelf and cycle life is superior in comparison with that for the polymers.

The principle for the energy storage in carbon DLC is the accumulation of associated electric charges with ionic charges at the interface between the solid electrode material and the electrolyte. The region in which this takes place is known as the electrical double layer. In common capacitors, the capacitance value is inversely
proportional to the distance between the charged electrodes. The separation of charges in the double layer is around 1-3 Å [3]. Therefore, high values of capacitance, in the order of 10-50 µF/ cm², depending on the surface area and the structure of the material can be obtained in double layer electrodes. An optimal densification of the double layer per unit volume of a porous material involves the use of micropores (i.e., < 20 Å) to obtain high active surface area. However, a limit is set on the small pores related to the accessibility of the pores to the ions of the electrolyte solution. Therefore, a trade-off between the pore size and the size of the solvated ions is required. A complication addressing this problem, particularly when manipulating pores at the nanoscale level, has been the difficulty of controlling the pore size distributions during the synthesis of the activated carbon materials by current thermo-chemical processes (e.g., pyrolysis).

Recently, carbon materials obtained from metal carbides, such as SiC and TiC, have been produced with high pore size accuracy in angstrom (Å) units, and with controllable pore size distributions [4]. Particularly for the carbide-derived carbons mentioned above, structural measurements have revealed that the carbons possess a fairly uniform structure and narrow pore size distributions around 8 Å [5]. In addition to these peculiar pore properties, a good conductivity and mechanical strength has made these carbons appropriate as DLC electrodes. Carbons derived from silicon and titanium carbide have shown high capacitance values (120-150 F/cm³ in 6M KOH and approximately 70 F/cm³ in TEABF4) and have been successfully used in DLC electrodes [6]. The high values of capacitance obtained for this carbon demonstrate the importance of the nanopores for the energy storage in DLC.

For automotive applications, the supercapacitor has to be able to deliver the stored energy relatively fast (i.e., in order of seconds). In order to meet this requirement, the ion transport has to be effective in the whole cell. The first condition depends on the design of the cell and on the size of the particles, which build up the electrode. The factors which affect the ion transport inside nanopores are more difficult to address because the net transport of species inside the pores is a product of many parameters which are not considered in mathematical models for larger pore electrodes. For instance, as described below, the ion-ion or ion-pore wall interactions leads in many
cases to a strong adsorption or to changes in the molecular configuration of the species being transported inside the pores. The classical models of the double layer and the theory for porous electrodes do not apply correctly for such small pores. Furthermore, molecular simulations oversimplify the real processes taking place inside the pores, and the closer the model to a real situation the more time demanding the calculations are. There are, however, several valuable aspects concluded from these works. 1) The overlapping of the diffuse double layer inside the pores leads to a strong adsorption and to a different accommodation of ions inside the carbon structure. 2) The electrochemical and mass transport properties are different in narrow pores than in larger pores or free bulk solution, and depends strongly on the pore size. The role that the microporosity plays in the contribution to the total capacitance has been discussed in several papers, but there is still no consensus about the specific capacitance achievable from the micropores [2,7,8,9]. However, today high surface area carbons (containing micropores) are most often used for manufacturing of DLC [1]. The transport of species inside micropores differs from the ion transport in larger pores such as mesopores or macropores. This fact is known from previous works, studying species inside zeolites [10,11].

1.2 The aim of this doctoral project

There are several questions to be addressed concerning the transport phenomena inside the nanopores. For instance, it is questionable whether the solvated ions can penetrate the micropores of size smaller than 8 Å. That means that the ions in the bulk solution, especially the cations, drag a shell even when entering the nanopores. Furthermore, the mechanisms responsible for driving the ion transport inside mesopores and macropores is mathematically defined in contrast to that for nanopores, which is not readily understood. The significance that migration and/or diffusion have, as possible mechanisms for the ion transport in nanopores, remains still an open question.

From a physico-chemical point of view, there are interesting questions about the ion transport inside the nanopores and about the constitution of the double layer in confined spaces. Apart from the significance that the transport processes inside
narrow pores has for energy storage devices, transport of species is also important in other fields. Catalysis, nanofiltration, nanotechnology and biotechnology at the nanometer scale often involve transport of species in nanostructured materials or biological membranes (e.g., drugs). For this doctoral work, the electrochemical and mass transport properties of ions inside the nanopores of a carbon material derived from silicon carbide are specifically studied. The derived carbon is completely nanoporous and has a narrow pore size distribution around 7 Å.

An important goal for this doctoral work has been the adaptation of the single particle microelectrode technique to the study of the mass transport properties and the electrochemical characteristics of the nanoporous carbon material. Further objectives of scientific interest in this work are:

1) Make an implementation of the mathematical models by which the ions become transported inside the nanopores. That means, in principle, to verify if diffusion can be used for ion transport modelling in small pores.

2) Estimation of the value of effective diffusion coefficients for various salts in aqueous and organic solvents. This indicates how fast the charge and discharge processes occur inside the nanopores.

3) Survey the faradaic processes taking place inside the nanopores.

4) Elucidate how different activation procedures (so-called training) lead to aspecific electrochemical behaviour of the carbon particles.
1.3 Definition of a supercapacitor

The term supercapacitor means a device with extremely high specific capacitance, in the order of Farad/gram or Farad/cm³ compared to conventional capacitors whose capacitance is around pico, nano or microfarad per mass or volume unit. Supercapacitors are also called ultracapacitors or electrochemical capacitors. The basic construction of a supercapacitor is similar to that of a battery: two separated electrodes immersed in an electrolyte, this is illustrated in Fig. 50. The ability of each electrode to store electricity at a specific voltage depends on the capacitance and is expressed in Farad. The specific capacitance is, thereby, expressed in Farad per unit volume or weight. The classical design laws for conventional capacitors apply in general also for supercapacitors, and are illustrated in Fig.1.

Figure 1. A comparative drawing showing the principle for storage of charge in a conventional capacitor (at the left side) and in the double layer of porous carbon materials (at the right side). Zoomed circles: Carbon particles containing opposite charged ions.
As can be noted from equation (1) in this figure, the capacitance is a function of the surface area (A), and inversely proportional to the separation of charges. The properties of the electrolyte are evaluated from the value of the dielectric constant, equivalent in the capacitor case to the product of the permittivity constant for the dielectricum used and the permittivity at vacuum (ε_0). The energy density (W) is theoretically evaluated according to equation (2) and is a function of the capacitance (C), and the operation voltage (V). The specific power (P) is evaluated from equation (3) and is proportional to operation voltage and the equivalent series resistance (ESR).

The peak specific power of supercapacitors is up to 100 times higher than that of batteries, but the energy density is 20 to 50 times lower [12]. A trade-off has commonly to be made between energy density and specific power in the performance of the electrodes. For instance, thin electrodes are, on the one hand, more appropriate for reaching high power characteristics (due to the lower resistance), but on the other hand, increasing the thickness of the electrodes increases the energy density. Another important parameter, for the performance of porous electrodes, is the time constant (τ), which indicates how fast the electrodes can be charged. The time constant might, in turn, be related to the pore size, the radius of the particle (i.e., spherical geometry is regarded), and to the inverse of the effective diffusion coefficient (D_{eff}).

Supercapacitors differ from batteries in the way the electric energy is stored. In a battery the energy is stored in chemical form as active material in its electrodes. The discharge of the batteries involves phase changes and, even if rechargeable, irreversibility appears with cycling. The voltage is dependent of the active materials and is close to the open-circuit potential (OCP) for the charged electrode. Thus, a battery can deliver energy at constant voltage, whereas the only way to extract energy from a capacitor is to have a voltage variation. The combination between battery and supercapacitor may be, for instance, an economically viable solution for hybrid automotives.

1.3.1 Types of supercapacitors

Covering the definition of supercapacitor in this manner, a variety of diverse devices can be sub-classed depending on different criteria such as charge and discharge
mechanisms, electrolyte, electrode material and capacitor design. Supercapacitors can be divided into three categories according to the mechanism by which the charge and discharge processes take place:

1) Double layer capacitors.

The storage of charge occurs in the electrical double layer formed at the interface between the electrode material and the free electrolyte. The double layer capacitors use high specific surface area carbon materials (>1000 m² g⁻¹) as active electrode component. From this basis, there are several carbon materials suitable for manufacturing of DLC electrodes such as active carbons powders, carbon fibres, carbon aerogels, skeleton carbon, carbon nanotubes [13], etc.

The electrodes are known as “blocking” or ideally polarisable because there are no charge transfer reactions in the operative voltage interval. A device in which this is the dominant storage mechanism will behave as a pure capacitor in series with its internal resistance. Devices of this type that have been developed with large values of capacitance are generally called “Electrochemical double-layer capacitors” (EDLC), supercapacitors or “ultra-capacitors”. The amount of charge that can be stored at the double layer is in the order of 15-40 μF/ar cm². While the energy and power densities are around 2-3 Wh/kg, the power capability of the best carbon based supercapacitors exceeds 2 kW/kg [1]. High capacitance (100-150 Farad cm⁻²) can be achieved in aqueous electrolytes. The common electrolytes are 5-7 M KOH and 1-3.5 M H₂SO₄ [14] and 1-2 M TEABF₄ in acetonitrile or propylene carbonate. The high conductivity of the aqueous electrolytes is suitable in applications which require high power current. However the energy density for these devices is lower in comparison to the energy density obtained in organic electrolytes. The setbacks of using organic electrolytes are lower specific capacitance (60-100 Farad cm⁻²) and lower electrolyte conductivity. Nevertheless, the commercial prototypes, developed by the below mentioned supercapacitor manufactures, have preferably organic electrolytes, particularly tetrathylammonium tetrafluoroborate (TEABF₄) in acetonitrile (in Europe), or in propylene carbonate (in Japan) [15].
The first known carbon supercapacitor was patented by Becker in 1957 and consisted of high surface activated carbon and H₂SO₄ as electrolyte. In 1969 SOHIO launched the first electrochemical DLC in the market. Thereafter, NEC Corporation launched a prototype in 1978. These devices were used principally in low current applications because the energy density and power performance was low in comparison to modern supercapacitors. Just after, Pinnacle Research Institution developed the first high power DLC for military use in 1980. After the good results shown by this institution, the Department of Energy of the United States (DOE) started a program called “Ultracapacitor development program” in 1992. The program was created for the application of supercapacitors in traction vehicles and therefore, high power >1kW/kg and high energy density 1-6Wh/Kg was initially the target of the project. Maxwell Technologies in 2000, and other companies such as NEC, Panasonic and Siemens have developed supercapacitors, which have reached and exceeded these goals. However, the market for these devices is at present still in an emerging phase and there are still many aspects to be further investigated, e.g., better knowledge about the self-discharging process of the electrodes. The challenge today is to fit the technical aspects, which the hybrid vehicle technology requires, in order to make DLC an attractive alternative to batteries.

2) Pseudo-capacitive capacitors

The principle for the storage of energy for these devices involves a change in oxide composition for metal oxides and changes in capacitance, which varies proportionally with the applied voltage. The pseudocapacitive behaviour has been investigated with electrodes using metal oxides with high performance contain ruthenium oxide (RuO) or hydrated ruthenium oxide (RuOOH), obtained by pyrolysis of RuCl₃ [16]. Predicted values of capacitance around 400 F/g (but in practice ~150 F/g) and 700-800 F/g, respectively, make these materials very attractive for supercapacitor manufacturing. However, they are very expensive and their used is limited to military applications.
3) Redox-pseudo-capacitance

The principle for energy storage is a faradic deposition that results in three-dimensional absorption of electroactive species into a bulk solid electrode material by an insertion reaction (known as doping process). The basic polymer supercapacitor includes two identical P-dopable electrodes. Several materials such as conducting polymers are known to act as solid solution electrodes, for instance, polypyrrole, polythiophene or polyaniline. Since the amount of stored energy is proportional to the amount of the electroactive species that can be absorbed by the electrode, this three-dimensional bulk storage mechanism can lead to higher values of energy storage per unit volume of electrode structure than can any surface-related process. Capacitance values around 200 F/g can be achieved, but the cycle life of the polymers is rather low compared to carbon or metal oxides.

4) Unsymmetrical capacitors

The principle for these devices is to combine a blocking electrode such as a carbon electrode with a pseudo capacitor electrode such as nickel oxide or iron oxide. The main advantage of the unsymmetrical system is higher specific capacitance and operating voltage compared to the corresponding DLC. Thus, the total capacitance equals the capacitance of the blocking electrode (100 –150 Farad cm$^{-3}$) because the asymmetric capacitor is designed with a much larger pseudocapacitor electrode. The drawbacks are a limited cyclability and a higher ESR coming from the pseudocapacitor electrode.

1.3.2. Applications

Double layer capacitors (DLCs) are available in various sizes and shapes for selection according to the intended application. The principal applications of the supercapacitors can be divided into three main categories [12,17]:

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1) Power backup applications:

A) Currents less than 500 µA (1 hour - 2 weeks, 1.8-5.5 V, ∼0.05-5 Farad).

Personal wireless, Integrated circuit (IC) back up, Solar watch, Complementary metal-oxide semiconductor (CMOS) microcomputers, CMOS random access memory’s (RAMs), IC for clocks, Radio, Video cassette recorders (VCR), Camera.

B) Medium capacity power supply, currents up to 50 mA (1 hour- 2 weeks, 3.5-6.5 V, 0.4-3.3 Farad).

Electric typewriters, Electric cash register, Computer terminals, Sequence controller, Synthesizer tuner, Video compressor manager (VCM) timer, Video disks, Record players.

2) Power supply replacing batteries

C) Up to 1 A (3 sec- 30 min, 1.8 V, 0.3-10 Farad).

Secondary power source for undesirable voltage drops, Primary power supply for light emitting diode (LED), Displays, Toys, Electric buzzers, Lamps.

D) 10-100 A (1-30 sec, 12-24 V, 50-2000 Farad)

Automobile, Bicycle, Cordless apparatus, Solar car, On-off skylight

3) Electric hybrid vehicles

The most interesting and with high market prospective is the concept of an electric hybrid power source for vehicles. Battery performances are a compromise between energy and power to meet the requirements of hybrid applications. Electric hybrid vehicles are equipped with two separate power systems, commonly an electric motor and an internal combustion engine,
assisted by an electronic interface unit. The benefits of both forms of propulsion may be exploited and their disadvantages reduced. In stop-and-go traffic for instance, the electric motor takes over propulsion, which reduces both fuel consumption and emission of pollutants. When the vehicle brakes or drives downhill, generated energy can be buffered and later regenerated.

1.3.3 The double layer

It is difficult to directly measure the interface between the conductive material and an electrolyte interface. However, there are theoretical models, which can predict capacitance and the charge storage associated with the double layer. The Helmholtz model (formulated in 1853 by Helmholtz and Perrin) assumes that the potential difference in the double layer is linear and confined in a discrete layer adjacent to the electrode surface. Thus, the metal with its excess charge is one side of the double layer; the solution with its counter charge is the other side of the double layer. Therefore, the capacitance can be evaluated in a similar way as that for conventional capacitors, i.e., using equation (1) in Fig. 1. However, this model does not take into consideration the adsorption of water molecules and of counter ions at the pore wall (called contact adsorption), as was established by the surface tension-potential curves obtained in experiments with mercury electrodes [3].

The Gouy-Chapman model assumes that there is no distinct layer, and that the charges are distributed from the conductive metal throughout the electrolyte, decaying rapidly as a function of distance from the metal surface. The distribution of ions in the electrolyte, according to this model, follows a Boltzmann distribution, where $C_j$ is the

$$C_j = C_j^\infty \exp \left[ -\frac{z_j F \psi}{kT} \right]$$

(7)

concentration of species $j$. $C_j^\infty$ is the concentration of species $j$ in the bulk electrolyte, $T$ is the temperature, $k$ is the Boltzmann constant, $z_j$ is the charge of species $j$, $\psi$ is the electrostatic field. Combined with the Poisson equation,
\[ \rho = \sum \zeta_i z_j F = -e \frac{d^2 \psi}{dx^2} \]  

(8)

A value for the net charge is obtained and, thereby, the capacitance in the diffuse layer, which is identified by several researchers as the differential double layer capacity \( C_d \):

\[ C_d = \left( \frac{2 \zeta_i^2 e^2 \varepsilon_0 \zeta_j}{kT} \right)^{1/2} \cosh \left( \frac{z e \psi}{2kT} \right) \]  

(9)

For a given electrolyte the above reduces to

\[ C_d = \frac{K}{T^{1/2}} \cosh \left( \frac{K \psi}{T} \right) \]  

(10)

where \( e \) is the charge of the electron, \( K \) and \( K_1 \) are constants, \( \varepsilon_0 \) is the vacuum permittivity constant and \( \varepsilon \) is the relative permittivity. This model predicts both temperature and potential dependence for the capacitance. A discrepancy is that the capacitance of the double layer calculated from the equation above varies sharply with the potential. This theory has been proven very successful at a low electrolyte concentration and at low surface charge density. When overlapping occurs as in the case of nanopores, the structure of the double layer is distorted by the steric effect as well as the hydration force. However, none of these forces are considered in the Gouy-Chapman model.

Yang et al. (2002) [18] calculated the ion concentration profile in nanopores of different sizes by simulations using the Gouy-Chapman model, and compared the results with molecular calculations. The first model showed high concentration of counter ions at the pore wall. This feature implies an ion-exclusion effect in pores leading to repulsion of coions out of the pores by strong electrostatic force and, therefore, only counterions can exist. For large pores around 20 Å, the counter ion concentration was still higher than the co-ion concentration throughout the entire pore space. Their values, however, were closer in the central region, meaning that equal numbers of both ions exist in this region and the bulk phase can be reproduced. No
differences were observed in this respect between the Gouy-Chapman model and the primitive model (regard water as a continuum) for Monte Carlo simulations.

The Gouy-Chapman model predicts that an excess number of positive ions (e.g., potassium ions) accumulate adjacent to the negatively charged surfaces and then decay exponentially toward the middle of the pore. However, using the non-primitive model together with canonical (i.e., collection of replicated system in thermal contact) Monte Carlo in a 10 Å pore, the maximum counterion concentration was located at the middle and the concentration decays toward the surfaces. This feature was explained by a water layer being strongly adsorbed at the pore wall. Thus, water molecules are more favoured at the charged surfaces than ionic species are. The Gouy-Chapman model does not neither predict, the contact adsorption of anions inside the pores.

The Stern model is a summation of the two previous theories. In this model it is suggested that both the finite size of the ions adsorbed and specific chemisorption interaction of the ions with the metal and the diffuse layer should be taken into account. The capacitance is the sum of the two capacitances of the Helmholtz fixed layer, $C_{fP}$ and Gouy-Chapman diffuse layer, $C_{GC}$:

$$\frac{1}{C} = \frac{1}{C_{fP}} + \frac{1}{C_{GC}}$$  \hspace{1cm} (11)

However, this model, as the previous models, does not take into account that water populates the double layer and the specifically adsorption of ions. The problem of solvent dielectric polarization was envisaged by Conway [8] and by Grahame [19]. In the modern model of the double layer, there is a contribution of specifically adsorbed ions and adsorbed water dipoles to the capacitance of the interface. The picture of the double layer as it is understood today, is illustrated in Fig. 2. However this model is not valid inside the nanopores. An overlapping of the diffuse layer and strong ion-ion and ion-wall interactions inside the pores has to be considered when modelling the double layer. Using high concentration of electrolytes, the diffuse layer loses significance (the diffuse layer is around 5 Å in thickness) and other complications
related to phenomena specific for nanopores (e.g., ion pairing, increase tortuosity, limited mobility, etc), makes it difficult to apply the models described above.

**Figure 2.** The double layer. Pictures at the right illustrate the initial models suggested by Helmholtz (at the top) and Gouy-Chapman (middle) and Stern (bottom). The picture at the left is a drawing of the suggested double layer after the conjunction of the other models and contributions of Stern and Grahame.

### 1.3.4 Characteristics of transport inside the nanopores

In the experiments of this doctoral work, the carbon particles were subjected to a thermo-chemical pre-treatment and, thereafter, to electrochemical measurements. The thermo-chemical pre-treatment is an aid to wet the internal surface of the particle. Several particles were, thereafter, subjected to cycling in order to obtain electrochemically stable conditions (e.g., oxidation/reduction of oxygen inside the particles and wetting by electrochemical cycling). In order to envisage a picture of how the transport of the studied species take place inside the nanopores, it is
necessary to appeal to simulations obtained from theoretical studies done by means of semi-empirical and thermodynamical methods.

The first aspect to be considered is the transport and distribution of water molecules inside the carbon nanopores. The common feature found by the theoretical simulations is that water molecules in narrow pores behave differently than those of the bulk. Kirsh et al. [20] found, for instance, that water inside the nanopores and in different concentrations, does not crystallize between 0 and –50 °C. The evaporation of water at different temperatures higher than 100 °C (120 °C and 150 °C) revealed several coexisting states of water. Thus, the properties of the water molecules in the material and the mechanism of their association are governed by the size of the pores. For pore having a size of 20 Å, or larger, water showed the bulk properties. This was confirmed in the extraordinary observations with transmission electron microscope (TEM) in the work of Naguib et al. [21]. On the other hand, water diffusivity is lower in the nanopores than in the bulk and decreases with pore size. For pores smaller than 20 Å, the density profile is not uniform [22] and water is distributed in the form of clusters.

The studies, made by Jorge et al. [23], showed that water adsorption in carbons is strongly affected by the presence of oxygen surface groups on the carbon surface, whereas the chemical nature of the oxygenated groups does not have significant effect on the studied adsorption parameters. They also found that the maximum affinity for water adsorption occurs for a pore width around 0.65 nm. Pore filling occurs via the adsorption of water on surfaces sites with consecutive formation of adsorbed monolayers growing with the addition of other water molecules. The thermo-chemical wetting of the nanoporous carbon particles, which was applied in this doctoral work, creates oxygenated groups on the carbon surface. Hence, the investigations by Jorge et al. indicate that wetting of the carbon particles occurs, probably, in form of clusters. Cycling in a capacitive region, after the pre-treatment, seems also to be a way of wetting the particles.

A second aspect that is interesting to consider is the transport characteristics of electrolytes inside the nanopores. The trend observed in the simulations by means of
energy calculations [24,25,26,27,28], in pores smaller than 10 Å in diameter, are the following:

1) The diffusion coefficient decreases dramatically as a function of pore size. Studies show that conductivity increases with decreasing pore radius and then decreases rapidly to zero when oppositely charged ions cannot get past each other (i.e., forming a sort of ion pairing).

2) Diffusion coefficients decrease with increasing ion density inside the nanopores. In the narrowest channel, severe confinement leads to more ion pairing, less solvation, less hydrogen bonding; clustering of ion pairs can also give capacitive effects.

A third aspect important for the application of the mechanism of solid diffusion is the interaction of the ions with the pore wall. The energy calculations made by Floess et al. [29] and Everett et al. [30] reveal that the adsorption energies of carbon pores is much higher than that for plane surfaces, particularly when the pore size is smaller than 10 Å. According to the study by Floess, the maximum adsorption energy is obtained in a pore size 6.8 Å. For pores smaller than 7.7 Å the adsorption potential is a maximum in the middle of the pore.

According to Kastening et al. [31], the double layer inside micropores is charged at one side of the potential by the solely counter-ions. The amount of co-ions decrease substantially with the potential and only some ions remain adsorbed inside the micropores.
1.4 The nanoporous carbon

The nanoporous carbon material was produced at the Central Research Institute of Materials in St. Petersburg. The starting material is silicon carbide, which reacts with chlorine at 700-1000 °C gas according to the reaction:

$$\text{SiC} (s) + 2\text{Cl}_2 (g) \rightarrow \text{SiCl}_4 (g) + \text{C} (s)$$

Chlorine removes layer by layer the metal atoms from the crystalline structure without changing the template of the material. Argon gas is used to remove residual silicon tetrachloride from the carbon structure. The remaining product is a rigid skeleton material with good mechanical properties and with carbon atoms forming a disordered amorphous nanoporous structure.

The nanoporous carbon was available for this work in three sizes, denominated after the SiC precursor particles: 1) f 60, 10-24 µm; 2) f 240, 50-150 µm; 3) f 120, 100-250 µm. The structural analysis of the skeleton carbon [32,33] has revealed small clusters (4-6 nm in size) of bent graphite planes, and gas-porosimetry measurements have shown that the pores in the carbon are around 7 Å wide and extremely uniform in size.

The specific surface area (SSA) is approximately 1200 m²/g, and is represented principally by a nanoporous structure. Analysis of pore size distribution reveals that about 97% of the SSA stems from pores smaller than 20Å [34]. The open pore and homogeneous structure shown by the nanoporous carbon, as illustrated by the structure model of Bursill et al. (1995) [35] (see Fig. 3), has, in a similar way as carbon nanotubes and carbon fibres, high significance for the transport properties of ions inside the nanopores [36].
Figure 3. Sketch of the amorphous carbon nanostructure illustrating its pore structure. Taken from Bursill and Bourgeois (1995) [35], by courtesy of the journal Modern Physics Letters B. (bar=0.14 nm).

A reduction of the pore tortuosity is favoured in comparison with materials having heterogeneous pore systems. The effective diffusion coefficients depend on microgeometry of the porous material (37). The uniform structure of the nanoporous carbon and the narrow pore size distribution make this material suitable for determination of parameters necessary in modelling of porous electrodes containing micropore structure.

1.5 The single particle microelectrode technique

One of the main goals of this work has been to make an adaptation of the microelectrode technique, developed by Bursell and Björnbom (1990) [38] at KTH to the study of electrochemical and mass transport characteristics of a nanoporous carbon, available in the form of particles in different sizes. The technique was initially used for the study of agglomerates in gas diffusion electrodes for oxygen reduction and has been cited later by other researchers in different electrochemical investigations. For instance, catalytic material properties for fuel cells [39,40,41,42], transport parameters for hydrogen in metal hydrides [43,44,45,46,47,48], material characterisation for batteries [49,50] and microanalysis of metals in pyrite [51,52].
Figure 4. Schematic picture of equipment used in the experiments by means of the single particle microelectrode technique: (1) optical microscope; (2) micromanipulator; (3) gold probe; (4) counter electrode; (5) Hg/HgO (6 M KOH) reference electrode; (6) nitrogen inflow; (7) nitrogen outflow; (8) separator; (9) carbon fiber contacting the carbon particles.

The principle for the single microelectrode technique consists of contacting a carbon fibre to a single particle of the material to be investigated by means of a micromanipulator. The carbon fibre is nanoporous and the contribution from the fibre’s surface to the total capacitance is insignificant. The diameter of tip of the fibre is approximately 10 μm. Thus, the electrochemical measurements realized on the smallest particles (10-30 μm) are markedly affected by the contact resistance of the fibre.

The principle for the design of the electrochemical cell was to reduce the external resistance of the electrochemical system to be measured by surrounding the single particle with a large non-polarizable counter electrode. This electrode constellation allows for the decreasing of the IR drop in direct proportionality to the radius of the particle. The sketch of the cell is shown in Fig. 4. Important for the experiments is to maintain a chemical inert atmosphere inside the cell by continuous circulation of a
nitrogen flow. Otherwise, the cathodic current obtained from the reduction of oxygen becomes dominant at negative potentials (−0.25 V vs. Hg|HgO reference electrode).

At positive potentials, on the other hand, oxygen might react with carbon causing changes on the carbon structure. Therefore, the backflow of oxygen was tested by voltammetric cycling of a perowskite material, a catalyst material sensitive to the reduction of oxygen. Cycling was conducted with and without inert atmosphere. In the absence of inert atmosphere, an increase in current was observed at −0.1 V vs. Hg|HgO. The faradaic current is eliminated when having an inert atmosphere inside the cell.

The measurements were realized by means of standard electrochemical transient methods such as cyclic voltammetry and a potential step method (amperometry). Cyclic voltammetry is particularly useful for surveying electrochemical processes of both faradaic and non-faradaic character. Cyclic voltammetry, in combination with the single particle microelectrode technique, results in a highly sensitive analytical method for monitoring of, for instance, faradaic processes.

2. Results - Summarized from Papers I-V

2.1 Material characterisation

The carbon shape and the composition of the particles were analysed using the scanning electron microscope (SEM) and the pore properties were established by gas porosimetry measurements. The images obtained from SEM (see Fig. 5) revealed that the carbon particles showed different geometries and surface roughness but had similar morphologic appearance and shape as they had before the thermal treatment of the starting material SiC. That means that the chemical reaction with chlorine gas removes principally the metallic silicon atoms in the crystalline structure of SiC, leaving the porous template rather intact. Another feature observable from the SEM pictures, and relevant for the interpretation of the mathematical models, is the shape of the particles. As can be seen in Fig. 5, the major part of the particles is of
significant extension in three dimensions, allowing for the assumption of the radial diffusion model inside the particles at long times. The mechanical pre-treatment of the SiC particles (milling) seems to cause cracks, fissures and edges on the external surface of the particles.

![SEM micrograph showing particles with sizes 50-100 nm (f240).](image)

**Figure 5.** SEM micrograph showing particles with sizes 50-100 nm (f240).

The roughness and the possible macroporosity at the external surface have significance for the transport processes because the ion transport is much faster at these locations. Consequently, the inside of the particle adjacent to the external surface is not completely homogeneous and the expected semi-infinite diffusion in a perfect particle arising at short times does not appear in this time region.

The chemical mapping of the particles conducted simultaneously during the SEM observation revealed that the particles consisted principally of carbon. Traces of silicon and chlorine were also detected. The carbon content after the thermal treatment has been reported to be higher than 99.6% [13].

The pore size distributions for particles f240 and f120 obtained from the porosimetry measurements are shown in Fig 6A and 6B, respectively. The results indicate that the silicon carbide particles f240, show after the thermal treatment a BET surface area of
1163.0 m²/g and consist principally of micropores (1156.8 m²/g). The surface area for the carbon particles obtained from SiC particles f120 was lower in comparison to f240.

![Pore size distribution for carbon particles of size A) 100-200 µm (f120) and B) 50-100µm (f240), determined by gas (N₂) porosimetry.](image)

**Figure 6** Pore size distribution for carbon particles of size A) 100-200 µm (f120) and B) 50-100µm (f240), determined by gas (N₂) porosimetry.

According to the gas-porosimetry measurements, the total surface area was 774 m²/g and the median pore diameter for the particles f120 and f240 are 6.48 Å and 5.39 Å, respectively. These values are approximately 1 Å smaller than the values obtained for the same nanoporous carbon material by other researchers [53]. Depending on the isotherms of the selected gas [54], or the pore model assumed (e.g., slit-like, cylindrical or crack-pore model), the pore size obtained from the porosimetry measurements may differ slightly (~ 1 Å) in value (e.g., N₂, Ar, CO₂; in our case N₂ was used, which according to Jagiello and Thommes (2004)) [54] gives lower values than the other gases mentioned).

The ratio volume / external surface area for the particles does not approach the relation for a spherical geometry for all the particles. The equivalent radius, used for the calculations of the diffusion coefficient, using the radial diffusion relation is, however, calculated assuming a spherical geometry. An important implication of using this radius becomes evident when the shape of the particle deviates markedly from the spherical geometry. The higher the deviation, the greater the disagreement of the $D_{eff}$ values calculated from the asymptotical solutions.
2.2 The electro-analytical method for determination of $D_{eq}$

(Paper II)

An uncomplicated way of characterising the mass transport properties of the ions inside the pores is evaluating qualitatively the transient response at the reversal of the potential in a cyclic voltammetric experiment: the longer the transient, the larger the mass transport hindrance. Another simple way is recording the current response with the time after a potential step measurement. Thus, a potential perturbation performed on a carbon particle, previously in equilibrium, leads to general changes of the electrochemical potential, $\mu_{eq}$, between the particle and the electrolyte solution. Electrons are removed from, or added to, the carbon structure. On the electrolyte side a transport of ions is created in and out of the pores of the particle. The current pulse will decline exponentially until charge equilibrium has been reached at the new potential.

The effect of electrochemical potential gradients on mass transport is usually expressed in terms of migration and diffusion, two different mechanisms responsible for the transport of ions. Migration is the movement of ions produced by an electric field. The ions being transported acquire a specific orientation exerted by the field. The electrical work exerted by, or on the system, $\varepsilon \phi$, is a function of the inner potential, $\phi$, the outer potential ($\Psi$) and the surface potential ($\chi$). The contribution to the total current caused by the migration of ions is undoubtedly significant for the transport process of the ions from the free electrolyte to the external surface of the particle.

We assume that, before the perturbation, the particle has sufficient counter ions to balance instantaneously the excess or deficiency of charge. Therefore, $\Psi=0$ inside the nanopores. The conductivity of the carbon material is much higher ($\kappa = 33.33 \ \Omega^{-1} \ \text{cm}^{-1}$ [55]), than to the conductivity of the 6M KOH solution ($\kappa = 0.63 \ \Omega^{-1} \ \text{cm}^{-1}$ at 25 °C [56]); therefore, $\chi$ is assumed to be constant in the whole particle. The ions become strongly adsorbed in the nanoporous carbon due to the high adsorption energy showed for comparable pores in similar carbon materials [29,30]. The ions are assumed to
associate an opposite charge, located at the pore wall and be randomly transported into the particle. Considering these assumptions, the gradient of $\mu_0$ becomes equal to the gradient of the chemical potential of the ions inside the carbon particle. Meaning that the transport of ions into the NP carbon may be considered as a surface diffusion process, analogous to the diffusion of species into condensed structures (solid-state diffusion). For instance the transport of lithium intercalated into graphite, or absorbed hydrogen in metal hydrides, is usually regarded in this way. In this work it is assumed that the transport by diffusion obeys Fick’s second law. Taking, for instance, the transport of species $i$, inside the nanopores, the expression for ion transport at negative potentials is given by equation (12):

$$\frac{\partial C_i}{\partial t} - D_{\text{eff}} \frac{\partial^2 C_i}{\partial e^2} = 0$$  \hspace{1cm} (12)$$

The concentration of concern is the net concentration obtained after the perturbation of the potential at equilibrium, $\Delta C_i = C_{i,e} - C_{0,i}$. Therefore, the initial concentration, before the perturbation, is set to zero. The concentration, $\Delta C_i$, can, in turn, be expressed in terms of specific capacitance per volume of particle, $C_s$, and the change in potential ($\Delta V$) divided by the Faraday constant ($F$).

$$\Delta C_i = \frac{C_s \Delta V}{F}$$  \hspace{1cm} (13)$$

Equation (12) can be solved by means of a Laplace transformation using the following boundary conditions (semi-infinite diffusion model):

At $t=0$ for all $z$: $C=C_{0,i}=0$
At $t>0$, $z=0$: $C=C_{i,0}$, and at $z=\infty$: $C=0$

We are interested in the solution for the elementary case of a semi-infinite slab after a potential step. The solution of equation (12) gives equation (15), for the ionic current density, $j$, at the outer surface of the particle:
\[ j(0,t) = -nFD_{\text{eff}} \left( \frac{\partial C_i}{\partial z} \right)_{z=0} = -nFD_{\text{eff}} \Delta C_i \left( \frac{1}{D_{\text{eff}} \pi t} \right)^{1/2} \] (14)

Combining equations (13) and (14), an expression for the current response, \( I \), against the inverse square root of time, \( t \), is obtained:

\[ I(0,t) = -AD_{\text{eff}} C_s \Delta V \left( \frac{1}{D_{\text{eff}} \pi t} \right)^{1/2} \] (15)

In this equation, \( D_{\text{eff}} \) is the effective diffusion coefficient in \( \text{cm}^2 \text{s}^{-1} \), \( t \) the time elapsed and \( A \) the geometrical area of the particle. A typical transient response for the carbon particles is shown in Fig 7. The current decays very fast at short times (0-2 seconds). Thereafter, at long time, the decay is slow in a low current region. A fast decay means a relatively fast mass transport process or vice versa. The Cottrell relation (equation (15)) was deduced in order to describe the semi-infinite diffusion process. The equation is thus an asymptotic solution of equation (12) valid for the diffusion layer generated at, or adjacent to, the interface between the carbon particle and the electrolyte solution.

That means that the evaluation of the mass transport properties is made for a relatively short time period and the ion transport responsible for the current response takes place at a thin layer adjacent to the external surface. The value of the active area for the electrochemical process can therefore be approximated to the geometrical area. Hence, the effective diffusion coefficient may be determined from the slope of the linear relation by plotting the current \( I \) versus \( t^{-1/2} \).
The ion transport process occurring inside a porous carbon particle differs, however, considerably from that of a flat electrode. As can be seen in Fig 8, plotting \( I \) vs. \( t^{1/2} \), does not give the typical linear relation obtained from the Cottrell relation for flat
electrodes. However, it is possible to distinguish two linear regions on this curve. At very short times, less than 1 second, a linear relation seems to be useful for the calculations of $D_{eff}$. However, the line does not go through the origin, a peculiarity commonly used for distinguishing processes with diffusion control. The other linear trend appears at very low current levels, making it difficult to extract reliable data for the estimation from the graph.

![Graph](image)

**Figure 9.** The analysis of the data for determination of the Cottrell region.

By making an analysis of the data by plotting $I^{1/2}$ against $t^{1/2}$, the Cottrellian behaviour may be determined from the data, as the constant product of $I^{1/2}$ (see Fig. 9), with more accuracy.

The extracted data is then re-plotted as in Fig 10, and the diffusion coefficients are calculated from the slope of equation (15). The linear relation has to pass through the origin if the process is diffusion controlled.
The integration of equation (15) gives the transient relation for charge $Q$ and a integration constant, equation (16). Thus, plotting $Q$ vs. $t^{1/2}$ also has to be a linear relation.

$$Q(t) = -2AC_3 \Delta V \left( \frac{D_{eff}}{\pi} \right)^{W/2} + \text{Const.} \quad (16)$$

Figure 10. Data obtained from the Cottrell region in Fig. 9.

Figure 11. The integrated form of the data for the Cottrell relation.
As can be seen in Fig. 11, the integration leads to a smooth line making useful the plot for elimination of signal noise. The diffusion coefficients estimated according to equation (15) and (16) should show consistency. Otherwise the data is not useful for the calculation of \( D_{\text{eff}} \).

In the case that faradaic processes occur simultaneously at the particle surface, the Cottrell equation can be used only if the prerequisite of fast kinetics is fulfilled. Otherwise, it is more convenient to assess the problem of ion transport using equation (17) for the currents caused by diffusion of ions inside the particles during long time regions. As discussed previously, the shape of the particles permits the assessment of the ion transport problem regarding it as a radial diffusion of ions inside spherical particles. Thus, expressing equation (12) in spherical coordinates, equation (16) is obtained.

\[
\frac{\partial C_i}{\partial t} - D_{\text{eff}} \left( r \frac{\partial^2 C_i}{\partial r^2} + \frac{2}{r} \frac{\partial C_i}{\partial r} \right) = 0
\]  

(17)

The solution of equation (17) using the boundary conditions below, gives the radial concentration distributions for a particle of radius \( a \). A corresponding flux of ions expressed as the current entering the particle is given as equation (18).

At \( t=0 \) for all \( r: C=C_{0i}=0 \)

At \( r > 0 \), \( r = a: C=\Delta C_i \), and at \( r = 0: \frac{\partial C_i}{\partial r} = 0 \)

\[
I = \frac{2AD_{\text{eff}}C_s \Delta V}{a} \exp \left( -\frac{\pi^2 D_{\text{eff}} t}{a^2} \right)
\]  

(18)
Equation (18) corresponds to an asymptotic solution of equation (17) at long times. The asymptotic solution is valid from the time the ions have reached the middle of the particle (discussed below).

The transient data for the long time region has to be a linear relation when plotted as $\ln I$ vs. $t$, illustrated in Fig. 12.

![Graph](image)

$y = -0.001x + 19.301$

**Figure 12.** Current response at long times for the data from Fig. 7.

The effective diffusion coefficients are estimated from the slope of this linear relation. The value of the intercept ($\ln I$ at $t=0$) of this relation can also be used for the estimation of $D_{ef}$. However, it can be influenced by faradaic reactions occurring at the external surface. The slope from the linear relation is, on the contrary, less sensitive for these reactions under the presumption that they occur solely on the external surface of the carbon particle and that they decay rapidly to zero value [57]. Thus, equations (15) and (18) might be used for the evaluation of effective diffusion coefficients of ions inside the carbon particles, at short time periods and long time ranges, respectively.

That means that the calculated diffusion coefficients from the Cottrell equation (15), are applied to the situation when the ions penetrate the pores adjacent to the particle.
surface, and equation (18) (filling up), is valid from the time the ions have reached the middle of the particle. The concentration profile in a particle is illustrated in Fig. 13.

![Graph](image)

**Figure 13.** Simulation of the diffusion process inside a particle showing the concentration profiles valid for the solution at short times (semi-infinite diffusion model) and long times (radial diffusion model for log times). C is the concentration inside the particle, C₀ the concentration at equilibrium, θ is the dimensionless time, L is the particle radius and r the distance from the particle’s centre.

The assessment of the $D_{eff}$ using equation (18) is done using the radius of a particle regarded as having spherical shape. The ratio volume/external area of a sphere divided by the same ratio for the observed volume and external surface is a shape factor, which indicates the deviation from the spherical geometry of the particle. For instance, the shape factor of the activated particle (42 cycles between 0 and –0.5 V) used in the figures, illustrating the electroanalytical method above, is 0.86. The $D_{eff}$ from the semi-infinite diffusion and radial diffusion models was estimated for the particle from Figs. 10 and 12 to $1.8 \times 10^6$ and $2.0 \times 10^{-9}$ cm$^2$ s$^{-1}$, respectively.

The value of the specific capacitance for an ideal DLC has to be constant everywhere in the potential of operation. Most carbon particles show an ideal capacitive behaviour especially at negative potentials. Therefore, $C_s$ can be obtained in this potential region simply from the integration of the cyclic voltammograms.
\[ C_i = \frac{\Delta Q}{\Delta E} \]  

(19)

or by dividing the constant current by the sweep rate [2]:

\[ C_i = I \cdot \left( \frac{dE}{dt} \right)^{-1} = I \cdot \nu^{-1} \]  

(20)

Another method to obtain the \( C_i \) is directly from the integration of the data from the potential step measurement. A charge process has to culminate in a constant maximum value with time, at the equilibrium point. However, background currents are usually present in electrochemical experiments and therefore the value of \( Q \) might continue to increase with time. Thus, the charge provided from the background currents has to be extracted from the capacitive charging.

Figure 14. Determination of \( Q \) for the calculation of \( C_i \) from the integrated \( I-t \)-current response shown in Fig. 7.
Plotting the transient data as $Q$ vs. $t$, and applying linear regression of data in a region of constant increase, the value of the capacitive charge is obtained at the intercept, shown in Fig. 14. For instance, the value of specific the capacitance calculated from the extrapolated $Q$ value ($Q$ vs. $t$) is 48.1 Farad cm$^{-3}$, which is a close to the value obtained from the cyclic voltammograms (44.8 Farad cm$^{-3}$).

Concluding remarks at this point.

1) The implementation of the asymptotic solutions of Fick’s second law was possible for the carbon particles due to the use of the expression of concentration as function of capacitance and potential difference for the step.

2) The analysis of the Cottrellian behaviour is necessary to corroborate diffusion control.

3) The current response at short times is sensitive for faradaic reactions, which take place at the external surface. The Cottrell relation can be used if the kinetics occurs very fast.

4) Possible errors in the estimation of $D_\text{eff}$ using the radial diffusion equation:

- Gas evolution (e.g., hydrogen or oxygen) has a negative effect due to fluctuations of the area available for the electrochemical process.
- Conducting potential steps when faradaic processes take place simultaneously at the carbon surface inside and outside the particle, violates the condition of fast kinetics.
- If the geometry deviates largely from the spherical shape, the $D_\text{eff}$ values calculated from equation (18) differ from the values calculated from the Cottrell relation (15). The estimation become erroneous if $D_\text{eff}$ disagrees markedly with the $D_\text{eff}$ calculated from the Cottrell relation (more than one order of magnitude).
- Estimation of the volume and external surface is erroneous, particularly, for particles with large surface area.
- The time region for the application of this equation is too short.
2.3 Electrochemical properties of the NP carbon

(Papers I)

Preliminary experiments, conducting cyclic voltammetry, confirmed the typical rectangular current response of the pure capacitive behaviour for capacitors for the carbon particles. This is illustrated in Fig.15 (a) and (b). However, as can be seen from these figures, the $E-I$ responses are not the same at positive and negative potentials. This disagreement becomes more accentuated the more negative or more positive the potential is. However, after further cycling the current reaches a stable value. The expected potential window of operation for carbon was difficult to define because the capacitive current becomes dominant in comparison with other faradaic currents. The voltammograms shown in Fig 15 suggest that the faradaic and capacitive processes occur simultaneously inside the nanopores. It is known, from the literature, that the electrochemical properties of carbon materials differ depending on the carbon allotropic form, microtexture, purity and porosity. At slow sweep rate, 0.2 mVs$^{-1}$, the nanoporous carbon used in this work shows a clear current peak at 0.5 V vs. Hg$|$HgO (see Fig 15 (c)). At this potential oxygen evolution commonly starts to occur in other carbon materials. As can be seen, the current peak decreases with the number of cycles. The current peak, typical for a faradaic process occurring at plane electrodes, can shift with the potential due to changes in the electrode surface. A decrease of the current might mean, on the other hand, loss in catalytic capability at the electrode surface (e.g., deterioration of the electrode), or dramatic reduction of the mass transport to the electrode surface (e.g. formation of a thin oxide layer at the electrode surface). In the case of the nanoporous carbon particles, the second alternative does not apply. The advantage of using micrometer-size particles is the reduction of the external mass transport resistance. The second alternative is neither conceivable because a total blockage of the particle external surface should imply a total deterioration of the current response even at other potentials. This is not the case for potentials between 0 and $-0.5$ V; the $E-I$ behaviour is approximately constant at those potentials. The decrease in current reflects, consequently, a complexity of processes occurring simultaneously inside the nanopores at this potential.
Figure 15. Cyclic voltammetry between different potentials vs. Hg/HgO. Scan rate 0.01 V/s. a) at negative potential scanned 10 times. Scan 1 at the bottom and scan 10 at the top. b) At positive potential. Scan 1 at the top and scan 10 bottom. c) cycling 29 times. Scan rate 0.001 V/s. Scan 8 at the top and scan 25 at the bottom.

The potential step measurements conducted at negative and positive potentials, depicted in Fig. 16, indicate that at negative potentials, the adsorption process is diffusion controlled, at a difference from the processes at positive potentials. The process between 0 and 0.3 V seems to be of mixed control and the process between 0.3 and 0.6 seems to be kinetically controlled [58].

According to the cyclic voltammograms above, the processes are affected principally inside the carbon particles and, therefore, may therefore, generally be related to a problem of mass transport hindrance inside the pores. The maximum in current, $I_{\text{max}}$, in this case, is proportional to the diffusion coefficients of ions inside the nanopores. Therefore, it can also be concluded that the mass transport becomes more hindered at positive potentials than at negative potentials. Furthermore, the processes affecting the mass transport differ even at positive potentials. $I_{\text{max}}$ has a higher value for the potential step from 0.3 to 0 V compared with the potential step from 0.6 to 0.3V.
Further findings from paper I.

1) An important aspect extracted from the voltamograms is the fact that cycling at different potentials is necessary to obtain electrochemical stability of the carbon particles. Thus, an activation process is necessary before using the carbon particles (or electrodes) in order to obtain reliable capacitance values.

2) The study of the characteristics of the electrochemical and mass transport properties should be arranged by studying the electrochemical processes at positive and negative polarisation separately.

3) The current response inside nanopores differs from the current response obtained using smooth electrodes. Therefore, an appropriate analytical method has to be developed in order to calculate effective diffusion coefficients.

2.4 Ion transport and electrochemical properties at positive polarisation
(Papers III)

With an adequate method for the calculation of effective diffusion coefficients, the next step in this doctoral project was to study the ion transport properties inside the nanopores for the carbon particles acting as small electrodes for DLC. The results
obtained in paper I suggest that the ion transport characteristics of the nanoporous carbon are governed by the chemistry involved at different positive potential regions. Therefore, the study was focused on mass transport characteristics at positive and negative polarisation, respectively.

The electrochemical processes which take place at positive potentials, such as oxidation, corrosion and intercalation, have been studied broadly. The literature related to oxidation and corrosion is vast due to the fact that activated carbons have been important electrode materials used in different large industrial processes such as aluminium refining, chlor-alkali production and battery manufacturing [2]. The principal task at this time was to avoid the negative impact that corrosion exerts on the carbon electrodes, leading to an appreciable deterioration of the electrode performance. However, several studies [59,60,61,62,63,64] have aimed at taking advantage of oxygen containing surface groups for other applications such as modification of electrocatalytic activity of carbons involving electrochemical reactions [65], improvement of adhesion properties of carbon fibres with epoxy resins [66], improvement of wetting, etc. The most common electrolytes used in these investigations, are acid aqueous solutions (e.g., H₂SO₄, HNO₃, H₃PO₄) or alkaline media (e.g., KOH, NaOH, LiOH).

The oxidation of carbon materials causes, in general, changes in the surface structure. A moderate oxidation (by chemisorption of hydroxyl ions) leads to a complexity of oxygen functional groups of phenolic type, carbonyl (e.g., of quinone type R(C=O)-R'(C=O)). Even some minor amounts of carboxyl groups (R(OH)(C=O)) and lactones (R-O-(R')(C=O)) are able to be found causing physico-chemical changes on the carbon surface. A stronger oxidation causes an intensive oxidation leading to carbon corrosion and, thereby, changes on the surface topography.

The results obtained in Paper I revealed that a faradaic current appears around 0.5 V vs. Hg|HgO. However, no perceivable evidence of gas evolution could be detected in the microscope at room temperature. The voltammograms show also that the capacitive response is different at positive potentials, in comparison to that for the negative potentials. According to the studies by Ross et al. [67,68] the corrosion process for carbon blacks starts at 0.45 V vs. Hg|HgO. That means, production of
carbon dioxide, carbon monoxide and oxygen evolution. At more positive potentials, oxygen evolution is the principal electrochemical reaction. On the other hand, the onset of corrosion of carbon materials may take place at around 0 V, e.g., acetylene black in KOH. The oxidation processes are, thereby, strongly related to the carbon structure. On the graphite plane, the oxidation occurs, preferentially, on the edge planes than on the basal plane (0001) [2].

2.4.1 Survey of the chemistry

![Image of cyclic voltammograms](image)

**Figure 17.** Cyclic voltammograms conducted at sweep rate 0.1 mVs⁻¹ (figure at the top) and 0.2 mVs⁻¹ (figure at the bottom), for a carbon particle at positive potentials.

The skeleton structure of the nanoporous carbon is rich in edge planes. This facilitates the incorporation of oxygen-containing groups in the structure. Oxygen evolution could be observed for potentials more positive than 0.65 V vs. the Hg|HgO reference electrode. At lower potentials than 0.45 V, the capacitive currents are very high and do not permit the electrochemical detection of the oxidation process, particularly at
high sweep rates. On the other hand, conducting the cyclic voltammograms at slow sweep rate allows for a higher reduction of the capacitive currents in comparison with the reduction of the faradaic currents. Therefore, it is possible to monitor the chemistry of the carbon material in different potential regions. Fig. 17 illustrates the improved electrochemical resolution obtained by conducting the cyclic voltammogram between 0 and 0.5 V vs.

![Cyclic voltammograms](image)

**Figure 18.** Cyclic voltammograms and calculated capacitances for a) particle A, cyclically activated from 0 to 0.3V, scan rate 10 mV/s, b) particle B, activated from 0 to 0.5V; scan rate 10 mV/s, c) calculated specific capacitances.

Hg|HgO, at slow sweep rate, 0.1 mVs, in comparison with 0.2 mVs. As can be seen from these figures, three different potential regions may be distinguished. In the first region, between 0 and 0.1 V, the E-I response behaves approximately purely capacitively. In the second region, between 0.1 and 0.3 V, a current increase is observed. The current decreases though to an approximately constant value with further cycling. The increase of current of the third region, between 0.3 and 0.5 V, is very pronounced and decreases very dramatically. Consequently, continuous cycling in these regions, separately, leads to different electrochemical characteristics of the nanoporous carbon, when considering it as an electrode material for DLC. As shown
in Fig. 18 a and c, the specific capacitance value increases, and remains constant, with cycling in region 2. On contrary, cycling in the third region, where it is well known that strong oxidation and corrosion processes can occur, a dramatic decrease of the specific capacitance is observed (see Fig. 18 b and c). A peculiar increase of the specific capacitance is observed after the first cycle between 0 and 0.5 V.

After cycling several times between 0 and 0.3 V, an extensive oxidation of the nanoporous carbon occurs resulting predominantly in oxygen surface groups of the type R-OH (e.g., phenolic) or R(C=O)-R’(C=O)) (quinone type). These functional groups [2] and, in general, surface groups containing a single oxygen atom on a carbon site, are the sites responsible for the rise of the capacitance [69,70,71] (i.e., the observed increase in capacitance in Fig 18 a).

The existing oxygen groups can catalytically react with other hydroxyl groups to produce higher oxides. According to Chen and Zeng [72], the carbon surface oxidised to >C-OH can be re-oxidised with an OH a second time according to the reaction:

$$>\text{C-OH} + \text{OH} \rightleftharpoons >\text{C}=\text{O} + \text{H}_2\text{O}$$

Cycling from 0 to 0.5 V leads to oxygen surface groups with two oxygen atoms on single carbon sites (e.g., carboxyl). Therefore, the high capacitance obtained after the first cycle suggests that the carbon surface was covered initially with surface groups containing a single oxygen atom. Further cycling at these potentials seems to have an electrocatalytic effect favoring the production of larger oxygen groups and eventually, corrosion products (CO and CO$_2$). The formation of carbon dioxide inside the pores might also explain the decrease of $D_{off}$ through the formation of carbonate ions according to the reaction:

$$2\text{OH} + \text{CO}_2 \rightleftharpoons \text{CO}_3^{2-} + \text{H}_2\text{O}$$

The carbonate ions contain three oxygen atoms in the surface group and might, therefore, strongly block the nanopores. Fig. 19 illustrates the possible oxidation processes of the nanoporous carbon in different potential regions.
Figure 19 Possible oxygen groups on the carbon surface after mild and strong activations and, beside the asterisk, a suggested mechanism of enhancement of the total capacitance by a reversible redox system.

The following points can be concluded from the results:

1) Processes occurring between 0 to 0.1 V are of capacitive character
2) The oxidation processes occurring between 0 and 0.3 V yields principally surface groups containing a single oxygen in a carbon site.
3) Extensive oxidation and corrosion occurs between 0.3 and 0.5 V
2.4.2 Effects of the positive polarisation on the mass transport properties

The oxidation processes in regions 2 (0 to 0.3 V), for particle A, and 3 (0 to 0.5 V), for particle B, influence the ion transport in different ways. This can be seen qualitatively appreciated at the reversal of the potential on the cyclic voltammograms in Fig. 18 a and b. Thus, the more prolonged transient indicates a larger mass transport hindrance of particle b, after cycling 13 times (see Fig. 18 b). The ion hindrance was quantitatively confirmed for this particle by calculating the effective diffusion coefficients after each activation cycle, shown in Fig 20a. The \( D_{\text{eff}} \) calculated from the Cottrell relation, decreased considerably after the 10\(^{\text{th}}\) cycle.

In contrast to the previous case, the voltammogram for particle A (Fig. 18 a) does not show an appreciable decrease in transient current response with cycling. However, as can be seen in Fig. 20a, the values of \( D_{\text{eff}} \) decreases significantly with the number of cycles for this particle and reach a level around 0.5 \( 10^{-6} \) cm\(^2\) s\(^{-1}\). \( D_{\text{eff}} \) for particle B has decreased, in comparison, by almost two orders of magnitude after the 10\(^{\text{th}}\) cycle.

![Figure 20. a) left: dependence of the effective diffusion coefficients on the degree of activation for particles A and B, activated as shown at the bottom in Fig. 17; b) right: Dependence of the diffusion coefficients on the potential of an NP carbon particle of size 130 \( \mu \text{m} \). The change in potential was 0.1V for all the steps. The arrow shows the decreasing trend of \( D_{\text{eff}} \) along the positive potentials.](image)

These results suggest that the chemisorbed hydroxyl groups inside the nanopores retard and obstruct the transport of ions. Thus, the mass transport hindrance is more accentuated the bigger the oxygen-containing surface group. At positive polarisation, the adsorption of hydroxyl groups is potential controlled, and consequently, the ion transport properties are also dependent on the potential. Fig. 20b shows the
dependence of $D_{\text{eff}}$ on the applied potential for a nanoporous carbon particle after 14 activation cycles, between 0 and 0.3 V. The observed trend is a decrease of $D_{\text{eff}}$, particularly with more positive potentials.

The results have practical implications for the performance of carbon electrodes for double layer capacitors. Cycling from 0 to 0.3 V will improve the capacitance of the carbon electrode on the one hand. However, the electrode will lose power capacity by decreased diffusivity on the other. This effect is important for high current applications, which require an optimal energy density.

Concluding remarks

1) $D_{\text{eff}}$ of ion species inside the nanopores is largely influenced by species adsorbed on the carbon surface, which affects the tortuosity of the nanopore system.

2) $D_{\text{eff}}$ decreases at positive potentials.

2.5 Ion transport and electrochemical properties at negative polarisation

(paper IV)

Carbon materials are regarded, in general, as poor electrode material for the electrocatalytic production and oxidation of hydrogen [2]. Thus, the overpotential for hydrogen evolution is very large for carbon materials, principally, in alkaline solutions. However, carbon materials have shown high capacity for storage of hydrogen, comparable to the hydrogen absorbed in metal hydrides [73]. The large overpotential for hydrogen generation has made carbon materials suitable as negative electrodes in asymmetric battery-capacitor cell configurations, such as $\text{+NiOOH|KOH|C}$ [74]. The porous carbon electrode acts, in such case, as a double layer electrode having a potential window of operation of around 0.8 V (between 0 and ~0.8 V vs. Hg|$|$HgO). At more negative potentials the adsorbed hydrogen can give rise to a pseudocapacitance, being added to the double layer capacitance.
2.5.1 Survey of the chemistry

Galvanostatic and cyclic voltammometric measurements performed between 0 and 0.9 V, and \(-1.5\) V, respectively, do not clearly reveal the onset for hydrogen adsorption. However, an anodic peak between 0 and 0.1 V vs. the \(\text{HgHgO}\) reference electrode appears on the cyclic voltammograms, conducted between \(-1.0\) and 0.5 V (depicted in Fig. 21).

![Cyclic voltammograms performed between \(-1.0\) V to 0.5 V at 1 mV/s\(^{-1}\), start potential is 0 V. Particle volume \(5 \times 10^3 \text{ cm}^3\). The number of scans is depicted at the right of the voltammograms and the arrows show the sweep direction.](image)

This peak is, otherwise, absent if the cyclic voltammometric measurement is conducted between 0 and 0.5 V (see voltammogram at the bottom, in Fig. 17).

Hence, the anodic peak occurring between 0 and 0.1 V is related to the processes, which take place at negative potentials (i.e., hydrogen generation and adsorption). Therefore, the anodic peak was used as indicator for the establishment of the potential for hydrogen generation inside the nanopores at negative potentials, by fixing, successively, the potential during a period of time. It was found that the start potential for hydrogen generation in this carbon material is at \(-0.5\) V vs. the \(\text{HgHgO}\) reference electrode. Cyclic voltammograms were conducted from a specific fixed potential to
0.2 V and the rise of the anodic peak was monitored. This is illustrated in Fig. 22. Performing a similar procedure as previously described, other anodic peaks (at around −0.1 V and −0.3 V) are found when the potential is fixed at ≈0.7 V. These peaks appear also for other particles.

However, the origin of the current peaks is not understood. Nevertheless, the peaks disappear completely after the conduction of the first voltammometric cycle between −0.9 and 0.1 V, indicating that the faradaic process responsible for these peaks occurs very slowly and that it is reversible.

![Graph](image)

**Figure 22.** Determination of the potential for the process which causes the occurrence of the anodic peak between 0 and 0.1 V. The cyclic voltammograms were conducted after fixing the negative potential for 3 h. The circle and arrow show where the potential was fixed, likewise, the starting potential and sweep direction, respectively. Scan rate: 10 mVs⁻¹

The first oxidation process of hydrogen (H-H or C(H)) is regarded to take place between 0 and 0.1 V vs. Hg|$\text{HgO}$. The current peak decreases with the number of cycles in this potential region, indicating a consumption of the weakly adsorbed hydrogen (i.e., probably H-H). After reaching a flattening of the current peak between 0 and 0.1 V, a voltammometric analysis performed at more positive potentials (−0.08 to 0.5 V) reveals a second oxidation process. Thus, an increase of the current upon
cycling is observed, contrary to the results obtained when cycling solely at positive potentials as illustrated in Fig. 17.

The oxidation processes performed separately in the two potential regions have different electrochemical impact with additional cycling between $-0.5$ and $-1$ V. As can be seen in Figs. 23 after oxidation in the first oxidation process (case III), a larger generation of hydrogen (C-H) seems to occur during the additional cycling.

![Graph showing current density vs. voltage for different cases](image)

**Figure 23.** First oxidation process of hydrogen species. Cyclic voltammograms for a carbon particle (volume= 4.8 $10^{-9}$ cm³) performed after generation of hydrogen at 10 mVs⁻¹. Case I: cycling between $-0.5$ V and $-1$ V followed (10 times) by relaxation at the OCP during 15 hours. Case II: 10 new cycles between $-0.5$ to $-1$ V, followed by hydrogen oxidation. Case III: 10 additional cycles were conducted between $-0.5$ to $-1$ V, followed by new hydrogen oxidation. The voltammogram starts at 0 V, the abrupt observed at the end of the cycle is due to a slight reversibility of anodic reaction between 0 and 0.1 V.

On contrary, the additional cycling after the oxidation in the second process shows a peak current approximately equivalent to the initial current peak obtained before the experiments, shown in Fig. 24. Thus, the results suggest that a stronger oxidation occurs between 0.1 and 0.5 V vs. the Hg/HgO reference electrode. The cyclic voltammograms show approximately similar peak current for the carbon particle. Therefore, it seems that the carbon particles recovers the physico-chemical state they had before cycling.
The hypothesis concerning the electrochemical processes involved at different potential regions are summarised in Fig. 25 and further discussed in Paper IV.

![Graph showing current density vs. voltage](image)

**Figure 24.** Comparison of the effects of the first and second oxidation process on the current intensity of the peak between 0 V and 0.1 V. Case IV, the particle was exposed to initial cycling, 10 times between −0.5 V to −1 V with subsequent oxidation between 0 and 0.1 V (shown by empty squares, scan 1); Case V, the particle was subjected to additional cycling between −0.5 and −1 V followed by oxidation in the second process.

The main idea is that hydrogen generation starts at −0.5 V vs. Hg \(\text{HgO}\) reference electrode, and is adsorbed in different graphite planes in the carbon structure. Thereafter, hydrogen can be oxidised at more positive potentials.

Weakly adsorbed hydrogen is oxidised at lower potentials than strongly adsorbed hydrogen. The oxidation of the strongly bound hydrogen produces water leaving the particle at similar initial conditions as before the electrochemical treatment. The experimental results support this hypothesis.
Figure 25. Schematic drawing showing the processes for hydrogen generation and hydrogen oxidation at different potentials. A) Pure capacitive process; B) Hydrogen generation and adsorption; C) Hydrogen evolution; D) first oxidation process of weakly adsorbed hydrogen; E) Second oxidation process of strongly adsorbed hydrogen.

Concluding remarks

1) Hydrogen generation starts inside the nanopores at \(-0.5\) V vs. Hg/HgO

2) Two regions of oxidation have been identified which means, therefore, oxidation of hydrogen in different adsorption states. According to theoretical studies, molecular hydrogen is weakly adsorbed (physisorbed) and dissociative hydrogen strongly adsorbed (chemisorbed) on the edge planes. The results from the experiments suggest the presence of both molecular and chemisorbed hydrogen inside the nanopores.

3) The oxidation takes place between 0 and 0.1 V vs. Hg/HgO and from 0.2 to 0.5 V.
2.5.2 Effects of the negative polarisation on the mass transport properties

Cycling between 0 and −1 V also causes a decrease of $D_{\text{eff}}$. However, the decrease is of the same order of magnitude as if the particles were exposed to cycling in the purely capacitive region. Hence, the hydrogen generation at negative potentials seems not to affect the ion transport significantly. The decrease of $D_{\text{eff}}$ with cycling is affected approximately in the same manner as if the carbon were subjected to cycling in the purely capacitive region (i.e., between 0 and −0.5 V). Cycling in this region involves a transport of ions in and out of the pore structure. A pore modification must also occur which hinder the ion transport.

The oxidation in the first potential interval (0 to 0.1 V) does not have a special impact on the ion transport properties (seen qualitatively on the voltammogram in Fig. 26A). On the contrary, additional cycling between −0.5 and −1 V causes a significant decrease on $D_{\text{eff}}$. This is not understood. The hypothetical reaction in the first region is that H-H reacts with OH− to produce H2O and H. The dissociative H is then chemisorbed at a carbon site. Thus, the water molecule and the adsorbed H are produced simultaneously in this reaction, and can therefore form hydrogen bonding. This water molecule, subject to the adsorbed hydrogen, can act, in turn, as a nucleus for clustering of water in the pore in a similar way as the water molecules do in the presence of oxygen containing groups (according to the theoretical studies described in 1.3.4).

Molecular simulations of ions inside very narrow pores [75] have shown that water can be strongly adsorbed on functional groups on the carbon surface causing mass transport limitations. The effects that the second oxidation process has on the ion transport are illustrated in Fig. 26B. As can be seen qualitatively from this figure, the ion transport becomes less hindered after the second oxidation process. Additional cycling between −0.5 and −1 V has, in contrast to the cycling after the first oxidation process, a favourable effect on the ion transport.
Figure 26. Comparison between the I-E responses and the $D_{ef}$ for the particle used in Fig. 23 before and after hydrogen oxidation in the two oxidation regions, A) ($\Delta$) before electrochemical treatment, ($\star$) after 10 cycles between −0.5 to −1 V, ($\bullet$) after complete oxidation at the first potential stage (Case II), ($\blacksquare$) after 10 new cycles between −0.5 V to −1 V (Case III), B) ($\blacksquare$) same voltammogram as in A), ($\clubsuit$) after oxidation at the second stage of potential (Case IV), ($\triangle$) after 20 new cycles between −0.5 V to −1 V (Case V).

The similar values of $D_{ef}$ and the electrochemical response for the carbon particles after the second process of oxidation indicate that the particles acquire approximately the conditions they had before the initial cycling.

Concluding remarks

1) The results show that cycling at the negative potentials does not significantly affect the ion transport of KOH inside the nanopores. That means that nanoporous carbon is suitable as negative electrode.

2) The oxidation of the carbon in the first potential region might cause transport hindrance and, thereby, a loss of power.
2.6 Ion transport properties of organic electrolytes

(Paper V)

The most common organic salt used as electrolyte for DLC is tetraethylammonium tetrafluoroborate (TEABF₄) in acetonitrile (preferred in Europe), or propylene carbonate (most used in Japan). The crystallographic diameter of TEA⁺ ions is 6.8 Å, while the corresponding size for the BF₄⁻ is 4.5 Å. Due to the high dominance of the resistance promoted by the electrolyte solution, the carbon fibre and the contact between conducting media, a fraction of larger particles was selected for the experiments using organic electrolyte. The particle size was between 100-200 µm (f120). The gas porosimetry data for these particles is illustrated in Fig. 6 A.

Figure 27. Contamination by crystallisation of Ag⁺ ions on the carbon fibre.

This was observed for instance in the preliminary experiments realized using the house-made Ag|AgNO₃ reference electrodes.

The Ag⁺ ions from the reference electrode became electrodeposited on the carbon fibre and on the carbon particles. Fig. 27 shows the electocrystallisation product on the carbon fibre after some minutes. In order to avoid contamination, the measurements were conducted using a two-electrode configuration thus, excluding the reference electrode.
A comparison between the electrochemical $E-I$ response for 0.1 M TEABF$_4$ and 6 M KOH is illustrated in Fig. 28. The cyclic voltammogram for 6 M KOH show symmetric capacitive behaviour (i.e., anodic and cathodic currents are of similar value) without remarkable changes in the current with the potential.

![Cyclic voltammogram for 6 M KOH (top) and 0.1 M TEABF$_4$ (bottom)](image)

**Figure 28.** Comparison between cyclic voltammogram for 6M KOH (at the top), sweep rate 10 mV s$^{-1}$ and 0.1 M TEABF$_4$ (bottom) 50 mVs$^{-1}$.

Working with organic electrolytes in electrochemical experiments demands use of high purity chemical [76, 77]. That means that the electrokinetic or mass transport measurements have to be conducted before the current product of the adsorption processes becomes significant, causing uncertainty and errors in the calculations of the kinetic parameters. By means of the single particle method, the possible contamination, in ppm, has a higher impact on the current response.

The cyclic voltammograms for 0.1 M TEABF$_4$ show a noticeable variation of the current between positive and negative potentials and a less symmetrical anodic and cathodic capacitive behaviour. Charging the double layer at negative potentials, in the
case of 6M KOH, involves transport of potassium ions inside the nanopores. As can be seen in the Fig. 28, a charging process also occurs for 0.1 M TEABF4 at negative potentials. This result indicates that the TEA⁺ ions are adsorbed on the carbon structure. However, the transport of the TEA⁺ is much slower in comparison to the BF₄⁻ ions (i.e., charge / discharge processes at positive potentials).

The mathematical models for calculation of effective diffusion coefficients were tried after cycling the particle at a relatively fast / slow sweep rate, respectively. The carbon particles were initially analysed by means of cyclic voltammetry, at a sweep rate of 50 mVs⁻¹.

![Cyclic voltammetry for particle 5 before, during and after the slow sweep rate activation (SSRA) cycling: (A) Before the SSRA, scan 28, sweep rate 50 mVs⁻¹, (B) SSRA cycling, scan 10, sweep rate 1 mVs⁻¹, C) after SSRA, scan 3, sweep rate 50 mVs⁻¹.](image)

**Figure 29.** Cyclic voltammetry for particle 5 before, during and after the slow sweep rate activation (SSRA) cycling: (A) Before the SSRA, scan 28, sweep rate 50 mVs⁻¹, (B) SSRA cycling, scan 10, sweep rate 1 mVs⁻¹, (C) after SSRA, scan 3, sweep rate 50 mVs⁻¹.

The transient measurements were performed after the cycling. The effective diffusion coefficients, calculated using the Cottrell relation, showed variations, differing by 2-3 orders of magnitude, within a wide potential interval. The current response decays quickly, after 50-100 s, and the transient data for the estimation of $D_{ij}$ using the radial diffusion relation, was not available (see Fig. 30 A). An interpretation of these results is that the ion transport processes occur at the external surface of the carbon particle. This interpretation was also confirmed by non-activated particles generally having a lower capacitance than activated ones. The low value of specific capacitance,
measured principally at potentials more positive than 0.3 V vs. Ag|AgNO₃, for most of the particles treated in this manner support this hypothesis (i.e., \( C_e < 45 \) Farad cm\(^{-3}\)).

A slow sweep rate activation (SSRA) procedure consisted of cycling the particles at scan rate \( \nu < 1 \) mVs\(^{-1}\). The slow cycling gives time for ion penetration, specially, for TEA\(^+\) ions, which has an ion diameter size commensurate with the pore size. The assessment of the diffusion coefficients after slow sweep rate activation of the particle leads to less variation in the \( D_{eff} \) values with the potential (see Fig. 30). The effective diffusion value calculated for the TEABF₄ ions (1.5 ±0.8 \( 10^{-9} \)) is unexpectedly higher than the effective diffusion coefficient obtained for 6M KOH (1.5 ± 0.510\(^{-9} \)).

![Figure 30](image.png)

**Figure 30.** A) Plot of \( E \) vs. \( D_{eff} \) for the a carbon particle before activation. The data were measured after scan 28 at 50 mVs\(^{-1}\), shown in A in Fig. 29. B) Plot of \( E \) vs. \( D_{eff} \) for particle 5 after cycling at low sweep rate. The coefficients were calculated after activation scan 9, C in Fig. 29.

Therefore, the results suggest that the anions are transported very fast inside the carbon structure and that they are responsible for the capacitive behaviour of the particle. Furthermore, the decaying capacitive current at more negative potentials, during cycling at high sweep rates, indicates that even at this condition, anions are present inside the carbon structure. At negative potentials, the free energy of the anions increases with the potential. Thus, the difference in the electrochemical potential causes a flux of anions in the bulk direction. The anions may become energetically stable whether being associated with cations, or being transported away from the particle to the bulk solution. However, the transport of TEA\(^+\) is much slower
in comparison to that for BF$_4^-$ leading to a pore obstruction and a possible formation of ion pairing inside the pores. The pore obstruction means an increase of the effective tortuosity (i.e., defined as permanent tortuosity and the tortuosity due to strong adsorption of TEA$^+$ ions). A schematic drawing of the hypothesis for charging and discharging is shown in Fig. 31.

![Schematic Diagram](image)

**Figure 31.** Simplified picture of the ion transport inside the nanopores of a particle after SSRA A) accumulation of ions inside the particle seen at potential of zero charge (pzc), B) at positive potentials the TEA$^+$ are desorbed leaving open pores and the tortuosity of the pore system is reduced, and C) at negative potentials, adsorbed TEA$^+$ are transported slowly, blocking open pores for other ions, and increasing, thereby, the effective tortuosity of the pore system. The arrows indicate the transport direction of the ions.

Cycling at slow sweep rate causes a deeper ion penetration in the carbon structure, which, at the potential of zero charge (PZC), is depicted in Fig. 31 A. During a potential perturbation, towards more positive potentials, the BF$_4^-$ ions inside the nanopores become almost immediately adsorbed on the pore wall, creating a deficiency of anions inside the carbon particles. At the same time, the free energy of TEA$^+$ increases and the ions, very slowly, become transported out the pore structure. Due to the concentration gradient, created inside the pores, anions from the bulk
solution are transported inside the pores and compensate for the deficiency of anions. This is illustrated in Fig. 31 B. Potential perturbations at more negative potentials than PZC causes, in similar way as for the anions in the previous case, an instantaneous adsorption of the TEA$^+$ ions inside the pores, but even an adsorption at the pores close to the external surface. Therefore, the BF$_4^-$ ions have to leave the pore structure, following longer pathways. This is illustrated in Fig. 31 C.

Concluding remarks

1) The single particle microelectrode technique was successfully used for determination of TEABF$_4$ effective diffusion coefficients.
2) Cycling at slow sweep rate appears to be a good method for the penetration of ions into the inner surface area of the particle.
3) The presence of both TEA$^+$ and BF$_4^-$ ions inside the carbon particles is an important condition for the validity of the mathematical models used for the determination of $D_{eff}$.
4) Inside the nanopores, the $D_{eff}$ values ($\sim 10^{-6}$ cm$^2$s$^{-1}$) for the TEABF$_4$ ions in acetonitrile are unexpectedly higher than the values ($\sim 10^{-9}$ cm$^2$s$^{-1}$) for aqueous 6 M KOH.
3. Discussion

The transport of species inside nanopores is a new discipline evolved from the intensively growing field of nanotechnology. Mass transport phenomena in small channels is very important for medical, energy and separation technology applications. The transport of species in nanopores was first studied in zeolites, and was called configurational diffusion [11], today, hindered diffusion is also used. In these studies the hydrocarbons subjected to catalytic activity seem to change their molecular configuration when passing inside the zeolite nanopores. In order to address the problem of mathematically describing the ion transport phenomena, a series of transport parameters have first to be established. The existing double layer models, as was discussed in section 1.3.3, do not apply correctly at the nanoscale level. An approach to meet this problem has been by means of theoretical energy calculations using different methods and models such as semi-empirical molecular dynamics, ab initio and Monte Carlo simulations. These methods are suitable for obtaining transport parameters and to determine physico-chemical transport trends. However, the models used are often simplified and the calculations time demanding. The other approach adopted in this doctoral work is the determination of transport parameters such as effective diffusion coefficients by applying mathematical models and interpreting the data accordingly.

The transport of species inside nanopores is a new world full of surprising and complex phenomena. The sum of the different processes at the nano scale results in what we can perceive or detect in the macro world. This situation occurs also in the system studied of this doctoral project. The capacitive currents are more dominant than the current provided from other processes and, therefore, what it is observed becomes somehow different when the phenomena are dissected. The single-particle microelectrode technique permits investigating phenomena inherent to a specific material, eliminating a part of the processes occurring around the particles. The technique is, therefore, a powerful tool for the study of the diversity of processes, occurring inside the nanoporous carbon. However, the results obtained using this
technique need an adequate interpretation. A complication is to separate the effects produced by the technique from the effects due to the phenomena in question. Furthermore, the experimental conditions, e.g. temperature, cell design, trace contamination, etc, may cause a noticeable impact on the process at the nanoscale.

The results have been explained by diffusion of adsorbed ions on the wall of the nanopores (i.e. similar to solid diffusion). The gas porosimetry measurements show a pore structure with a narrow pore distribution with a peak around 7 Å. According to the adsorption energy studies discussed previously, this leads to a strong adsorption inside the pores. This interpretation of ion transport governed by diffusion is also commonly used for other electrochemical systems such as intercalation of lithium in carbon and transport of hydrogen in metal hydrides. However, the true transport mechanism has not been established in this work. Nevertheless, the results contribute with transport parameters useful for ion transport modelling inside nanopores of the studied system. Further, the results are a basis for understanding of the phenomena occurring inside the nanopores. Another possible mechanism for the ion transport is migration. Due to the analogy in the mathematical expressions between Fick’s law for transport of ions driven by a concentration gradient force, and Ohm’s law for ion transport driven by an electric field force, it is not, in fact, straightforward to establish which mechanism predominates inside the nanopores. For instance, starting from the Ohm’s law a similar differential equation, as for Fick’s second law, is obtained. When solving this equation in a similar way as for the diffusion case, and using the specific boundary conditions, an asymptotic solutions at the thin layer close to the external surface of the particle, also at long times, may be obtained. The interesting parameter from these equations is the specific conductivity, which calculated from the equation for short times, \( I = A i(0, t) = -A K_{eq} \Delta V \left( \frac{aC}{K_{eq} \pi t} \right)^{1/2} \) gives a conductivity value of \( \sim 10^{-2} \Omega^{-1} \text{cm}^{-1} \). The low value can also be explained according to the results obtained in the previously mentioned thermodynamic studies [24]. In these studies it was shown that analogous to the diffusion coefficients, the general trend for conductivity is a decrease in value with pore size. Thus, assuming both mechanisms separately and using the same mathematics, the characterisation of the ion transport inside the nanopores from the experimental data obtained, should give equivalent results. What
it is important for the evaluation of the results is the compatibility of the mathematical models with the experimental results, obtained using electroanalytical methods.

For the aqueous 6M KOH electrolyte, the nanoporous carbon has been investigated in the technical operation potential interval of double layer electrodes (and in some experiments beyond that interval). The results indicate that oxidation/reduction reactions of the electrolyte solution (and contaminants) occurring at one side of the potential (i.e. potentials more negative or more positive than p.z.c.) have impact on the reactions occurring at the other potential side. This is very important because it opens possibilities for chemical manipulation inside the nanopores. The results of these manipulations can radically influence the ion transport and electrochemical properties of the carbon. The effect of the chemical manipulation also depends on the pore structure. It probably also depends on other phenomena neglected in this work, for example quantum phenomena.

The results from this doctoral work, and the obtained understanding, thereby, can be used as a basis for improving the performance of electrodes not only made of nanoporous carbon, but also of other activated carbons having a substantial amount of micropores (< 20 Å). For example, the value of the diffusion coefficients gives an idea of how large the particles have to be in an optimised composite electrode. The time constant, \( \tau \left( \equiv \frac{a^2}{D_{ef}} \right) \) \[78\], indicates how fast an electrode can be charged depending on the particle size, \( a \), and on the effective diffusion coefficient, \( D_{ef} \). For a complete charge/discharge time of 1-10 seconds using this carbon material and having \( D_{ef}=2 \times 10^{-9} \text{ cm}^2 \text{s}^{-1} \), the particle size should be 0.5-1.4 \( \mu \text{m} \). However, particles of this size need larger transport channels for fast transport of electrolyte to the surface of the particles.

The results show that ions and reaction products easily become strongly adsorbed in nanopores. At positive potentials, adsorption of hydroxyl ions starts already at approximately 0.1 V vs. the \( \text{Hg}\text{HgO} \) reference electrode, while at negative potentials hydrogen generation and adsorption starts at -0.5 V. This hydrogen generation potential is more positive than what has been observed for other carbons in alkaline solutions \[79,80,81,82\]. The single particle technique has been a good aid for this
potential determination. The specific experimental conditions applied (i.e., fixing the potential during several hours) have had significance for detecting these relatively slow processes.

It is important that the carbon structure is properly wetted before starting an experiment. Therefore, the particles were subjected to thermo-chemical pre-treatment before the electrochemical measurements. What happens during this treatment is not really clear, but the treatment probably leads to wetting of the nanopores through an oxidation of the carbon surface, which improves its hydrophilic properties. The results obtained from the Raman measurements in Paper III, indicate a slight change in the carbon structure after the pre-treatment, caused probably by oxidation of the carbon surface. Furthermore, the theoretical studies by Jorge et al. (2002) [23] indicate that water adsorption starts close to oxygen-containing surface groups with the consecutive adsorption of water monolayers.

The results in Papers I to III suggest that an activation procedure, consisting of cycling the particles between different potentials including positive potentials (0 to 0.3V in this case) improves the electrode performance. Thus, the electrodes treated in this manner acquire a maximal and stable value in capacitance. Probably, the hydrophilic properties are also enhanced. However, increasing the concentration of chemisorbed hydroxyl ions inside the nanopores causes a decline in mass transport properties. The adsorption of hydroxyl ion affects, particularly, the electrode performance when the nanoporous carbon material acts as a positive electrode. The activation process is still important as a pre-treatment for using the nanoporous carbon as negative electrode.

Furthermore, Paper IV shows that at positive potentials, the oxidation of adsorbed hydrogen is more favoured than the oxidation of the nanoporous carbon. This process yields water as principal product. One hypothesis is that this water might be very useful for the improvement of the wetting properties of the electrodes of the nanoporous carbon. Thus, it is possible that cycling to hydrogen evolution potentials may be used to control wetting. On the other hand, the results in Paper IV show that the oxidation of hydrogen in the first oxidation process (0 to 0.1 V) has a negative impact on the ion transport properties inside the nanopores. Unfortunately, is difficult
to investigate the location of the water molecules in the carbon nanopores. However, this might be an interesting task for a future research project.

The results obtained using organic electrolytes are very elucidating concerning the validation of the mathematical models and also for the mechanisms responsible for the ion transport. The low values of capacitance, the fast decay of the current-time response and the strong variation of the effective diffusion coefficients with potential suggest that TEA⁺ ions do not penetrate particularly deep into the carbon structure when cycling the carbon particle rapidly. The capacitance values for the particles treated in this manner were between 10 and 45 Farad cm⁻¹. The capacitance becomes higher after slow cycling of the carbon particles. In addition, the diffusion coefficients show less dependence on the potential and data for long times was available. Thus, these results are an indication of penetration of TEA⁺ inside the structure. The electrochemical conditions satisfy in this manner the boundary conditions for the validation of the mathematical models and for the assumption of diffusion as transport mechanism. However, the results indicate that before to the activation at slow sweep rates, the BF₄⁻ anions penetrate the carbon structure without the presence of cations. The effective diffusion coefficient obtained using TEABF₄ in acetonitrile (Paper V) was an order of magnitude larger than the diffusion coefficients for 6M KOH in water. The role that the solvent plays in the ion transport characteristics is, in my opinion, very important for the performance of the electrodes and in general for processes related to the transport of species inside nanopores.

Concerning the phenomena inside the nanopores, this work has answered some questions I had, but at the same time it has raised many others.
4. Conclusions

- The single particle microelectrode technique was successfully used for the determination of effective diffusion coefficients using both aqueous and organic electrolytes.
- It is important to conduct an electrochemical activation procedure, consisting of slow cycling of the particles (and, consequently, the electrodes) in a potential region covering both positive and negative potentials in order to obtain electrochemical stability and high performance.
- The asymptotic solutions of Fick’s second law for semi-infinite diffusion, Cottrell and radial diffusion relations, were successfully applied for the estimation of effective diffusion coefficients.
- The single particle microelectrode technique, combined with electroanalytical methods, is a powerful method for monitoring the faradaic processes when the electrochemical detection is influenced by mass transport hindrance or by dominance of other electrochemical processes such as charging of the double layer or adsorption. The nanoporous carbon has an operation potential interval of pure capacitive behaviour between -0.5 V and 0.1 V vs. the HglHgO reference electrode.
- The effective diffusion coefficients show a dependence on the potential for 6M KOH at positive potentials vs. the HglHgO reference electrode, caused by the adsorption of hydroxyl groups. For TEABF_4, the effective diffusion coefficients show a dependence at potentials more negative than p.z.c. caused by the adsorption of TEA^+.
- The potential for hydrogen generation in 6M KOH starts at -0.5 V vs. HglHgO.
- The oxidation of adsorbed hydrogen in 6M KOH occurs in two potential regions. Weakly adsorbed hydrogen oxidises between 0 and 0.1 V and more strongly adsorbed hydrogen oxidises between 0.1 and 0.5 V vs. HglHgO.
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## List of Symbols

- $a =$ particle radius \hspace{1cm} [cm]
- $A =$ external surface area \hspace{1cm} [cm²]
- $D =$ separation between charges \hspace{1cm} [cm]
- $C =$ capacitance \hspace{1cm} [Farad]
- $C_1 =$ capacitance for electrode 1 \hspace{1cm} [Farad]
- $C_2 =$ capacitance for electrode 2 \hspace{1cm} [Farad]
- $C_{df} =$ differential capacitance \hspace{1cm} [Farad]
- $C_{GCU} =$ Capacitance at the Gouy-Chapman diffuse layer \hspace{1cm} [Farad]
- $C_{HP} =$ Capacitance at the Helmholtz layer \hspace{1cm} [Farad]
- $C_j =$ Concentration of species $j$ \hspace{1cm} [mol cm⁻³]
- $C_j'$ = Concentration of species $j$ in bulk solution \hspace{1cm} [mol cm⁻³]
- $C_p =$ specific capacitance = \hspace{1cm} [Farad cm⁻³ or Farad g⁻¹]
- $C_v =$ total capacitance \hspace{1cm} [Farad]
- $D_{ef} =$ effective diffusion coefficient \hspace{1cm} [cm² s⁻¹]
- $e =$ electron charge $=1.6 \times 10^{-19}$ \hspace{1cm} [C]
- $E =$ potential \hspace{1cm} [V]
- $ESR =$ equivalent series resistance \hspace{1cm} [Ω cm]
- $F =$ Faraday constant $=96485.33$ \hspace{1cm} [C mol⁻¹]
- $I =$ current \hspace{1cm} [Amperes]
- $k =$ Boltzmann constant $=1.38 \times 10^{-23}$ \hspace{1cm} [J K⁻¹]
- $K =$ electrolyte constant $=ze/2k$
- $K_e =$ electrolyte constant
- $P =$ specific power \hspace{1cm} [W/kg or W/m³]
- $V =$ voltage \hspace{1cm} [V]
- $W =$Energy density \hspace{1cm} [Wh/kg or Wh/m³]
- $s =$ external surface area from spherical geometry ($4\pi a^2$) \hspace{1cm} [cm²]
- $T =$ absolute temperature \hspace{1cm} [°K]
- $z =$ magnitude of the charge of the ions
Greek

\[ \varepsilon_0 = \text{vacuum permittivity} = 8.85 \times 10^{-12} \quad [\text{Farad m}^{-1}] \]

\[ \varepsilon = \text{The relative dielectric constant (for water} \ v = 78.5 \ \text{at} \ 25 \ ^\circ\text{C)} \]

\[ \kappa = \text{conductivity} \quad [\text{S m}^{-1}] \]

\[ \phi = \text{Outer potential} \quad [\text{V}] \]

\[ \tau = \text{time constant} \quad [\text{s}] \]

\[ \psi = \text{electric field} \quad [\text{V cm}^{-1}] \]

\[ \mu_{el} = \text{electrochemical potential} \]

\[ \chi = \text{surface potential} \quad [\text{V}] \]
References


