COMPARISON OF MESOPOROUS CARBON/CARBON SUPERCAPACITOR AND NiO / MESOPOROUS CARBON HYBRID ELECTROCHEMICAL CAPACITOR

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LIST OF ABBREVIATION

1.1 EC - Electrochemical Capacitor
1.2 SC - Supercapacitor
1.3 UC- Ultracapacitor
1.4 EDLC - Electrochemical Double layer Capacitor
1.5 ESR - Equivalent Series Resistant
1.6 CV - Cyclic Voltametry
1.7 EM2K- Emperor 2000
1.8 BP2K – Black Pearls 2000
1.9 AB – Acetalyne Black

LIST OF PUBLICATIONS & SEMINARS

1.1 **Nanostructured NiO for Electrochemical Capacitors: Synthesis and Electrochemical properties** 140
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Solid State Electrochem
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1.2 **Low temperature Synthesis of Nanostructured NiO for Electrochemical Capacitors**, *Teressa L Nathan, Azizan Aziz, Ahmad Fauzi Noor , SRS Prabaharan,* Presented at the 4th COE Workshop on Regional Network Formation for Enhancing Research and Education on Materials Engineering, Bandung (Indonesia) June 26-28, 2006 organised by Institute Technology Bandung Indonesia and Nagaoka University Technology, Japan. Paper submitted to Advances in Technology of Materials and Materials Processing Journal (ATM ISSN 1440-0731)

PERBANDINGAN ANTARA KARBON/KARBON SUPERKAPASITOR DAN NIO/ KARBON MESOOLIANG KAPASITOR ELEKTROKIMIA HIBRID

ABSTRAK

Kapasitor elektrokimia adalah satu teknologi mantap yang mempunyai potensi tinggi sebagai peranti penyimpan tenaga. Keupayaannya memenuhi keperluan tenaga semasa, dari sudut ketumpatan tenaga dan kuasa yang tinggi, membolehkannya menjadi alternatif kepada bateri dalam aplikasi-aplikasi khusus yang memerlukan kuasa output yang besar. Bahagian pertama kajian tertumpu kepada pencirian bahan berkarbon tanpa grafit, khususnya karbon hitam Emperor 2000 (EM2K). Sel elektrokimia dibentuk dengan pellet EM2K yang kemudiannya direndam ke dalam larutan elektrolit 2M NaOH dan diuji pada pelbagai ketumpatan arus untuk melihatkan kelakuan cas/discasnya. Voltametri siklik dan ciri-ciri impedans juga dianalisis dan disimpulkan memberi kapasitans sebanyak 20F/g. Kekonduksian elektrod adalah penting mempengaruhi rintangan bersiri ekuivalen (ESR) bagi sel kapasitor. Pengurangan ESR dapat dilakukan dengan meningkatkan kekonduksian elektrik untuk elektrod karbon dengan cara menambahkan karbon hitam berkekonduksian tinggi, seperti asetalin hitam (AB) dan/atau Black Pearl 2000 (BP2K). Komposit elektrod yang mengandungi karbon hitam berkekonduksian tinggi ini, dengan 10% berat AB dan/atau BP2K, telah menghasilkan kapasitans tentu 24 F/g dan 39 F/g masing-masing. Dalam kajian ini juga, nikel oksida (NiO) dipilih sebagai elektrod positif disebabkan sifat-sifat redoknya melibatkan pengoksidaan Ni^{2+} /Ni^{3+} yang menerbitkan keupayaan discas spesific berbalik yang besar. NiO berstruktur nano disintesis melalui keadah nitrat-sitrat, menggunakan $Ni(NO_3)_2$ sebagai bahan mula dalam kehadiran asid sitrik serta menggunakan gabungan metanol/aseton. Struktur nano hasil akhir telah dipastikan dengan analisis TEM dengan butiran primer dalam julat 7-15 nm. Kelakuan redoks (penurunan/pengoksidaan) satu kebolehbalikan hasilan disintesis telah ditentu pasti dengan kajian voltametri siklik 3 elektrod. NiO (+)/C(-) hybrid EC telah difabrikasikan menggunakan pellet NiO yang ditekan dan dipanaskan pada 400 º C sebagai elektrod positif melawan EM2K dalam larutan 2M NaOH. Kapasitans spesifik setinggi 16 F/g pada 1mHz telah dicapai. Ketumpatan tenaga dan ketumpatan kuasa yang dihitung daripada keluk cas/discas adalah masing-masing 3.9 Wh/kg dan 2727 W/kg dan kemudian dianalisa menggunakan plot ragone (Ketumpatan tenaga lawan ketumpatan kuasa). Keupayaan sedemikian bagi hibrid EC adalah disebabkan penyimpanan cas pada permukaan dan pukal bagi aktiviti redoks.

COMPARISON OF MESOPOROUS CARBON/CARBON SUPERCAPACITOR AND NiO / MESOPOROUS CARBON HYBRID ELECTROCHEMICAL CAPACITOR

ABSTRACT

Electrochemical capacitors (EC) are superior breed of technology that is regarded as highly potential energy storage device. Its ability of fulfilling the current demand of energy, in terms of high energy and power density simultaneously, turns out to be a very promising alternative to batteries in niche applications requiring significant power output. The first part of the thesis focused on investigating non-graphitized carbonaceous materials namely Emperor 2000 (EM 2K) carbon black (courtesy of *Cabot Malaysia*). An electrochemical cell, assembled using EM2K pellets as similar electrodes immersed in aqueous electrolyte medium (2M NaOH) was tested at a different current density to reveal its charge/discharge behavior. Cyclic voltammetry and the impedance characteristics were analyzed deducing a capacitance of ~20 F/g. Electrode conductivity is one of the important parameters affecting the equivalent series resistance (ESR) of the capacitor cell. In order to reduce the ESR, conducting carbons such as acetylene black (AB) and/or Black Pearl 2000 (BP2K) were added. Accordingly, the composite electrode consisting of these highly conducting black carbons (10 wt %) AB and/or BP2K providing a specific capacitance of ~24 F/g and ~39 F/g respectively. This being a negative electrode, nickel oxide was chosen as positive electrode which is one of the transition metal oxides known to possess excellent pseudocapacitive due to its redox properties involving oxidation of Ni^{2+}/Ni^{3+} giving rise to a large reversible specific discharge capacity. Nanostructured NiO was synthesized via a nitrate-citrate method using $Ni(NO_3)_2$ as starting material in the presence of citric acid by using solvolysis agents such as methanol/acetone mixture. The product thus obtained was subjected to thermal treatment at 400°C for 1hr in air showed a single phase cubic structure as confirmed by XRD. The nanostructure of the final product was confirmed by TEM analysis with primary particles within the range 7-

15 nm in sizes. The redox behavior (reduction/oxidation) and its reversibility of the synthesized product were confirmed by 3-electrode cyclic voltammetry studies. Hybrid EC (NiO(+)/C(-) asymmetric combination) was fabricated utilizing pellet pressed NiO annealed at 400 °C as positive electrode against EM2K in 2M of NaOH aqueous solution. The specific capacitance of 16 F/g at 1mHz was achieved. The energy density and power density calculated from the charge/discharge curve were 3.9 Wh/kg and ~2747 W/kg respectively and analyzed using the Ragone plot (Energy density vs. Power density). Such a performance of hybrid EC was attributed to charge storage in both surface and bulk redox activity.

CHAPTER 1
INTRODUCTION

1.0 Introduction

Electrical energy storage devices are mandatory in myriad applications viz., telecommunication devices (cell phones, remote communication, walkie-talkies etc), standby power systems, and electric hybrid vehicles in the form of storage components (batteries, supercapacitors and fuel cells). These prompted the need for advanced power sources offering high power density (Conway, 1999). The electrochemical capacitors (ECs) or supercapacitors (SCs) represent a new generation of electrochemical energy storage components with very high capacitance for energy storage. ECs store energy in either capacitive (double layer of electrostatic charges) or pseudocapacitive (a faradic battery-like reaction) nature. Exploiting both the advantages of battery (high energy density) and conventional capacitors (high power density), ECs easily offer higher specific capacitance values up to several thousand Farad for applications requiring pulse power (appliances requiring high power bursts in the seconds range). They can also be cycled several hundred thousand times. Being an entity of ECs, hybrid capacitors (incorporating a battery-like anode (+) and a carbon-based cathode (-) having non-faradic character) have more to render in terms of power and energy (Conway, 1999).

This class of energy storage device is commonly known in many names such as supercapacitor, ultracapacitor (SC) or electrochemical double-layer capacitor (EDLC). It is capable of condensing energy, by arraying electrical charges, electrostatically at the electrode/electrolyte interface, known as the helmholtz layer, achieving capacitance in the order of Farads. The term “EC” is referred commonly in this thesis. Penetrating into the current market as a feasible alternative to batteries, ECs are paving ways for researchers to investigate all possible materials that could deliver enhanced performances in terms of power and energy density, charge-discharge characteristics, cycling stability and reversibility (Conway, 1999; Burke, 2000; Kotz and Carlen, 2000). New materials for electrodes such as activated carbons, nanostructured carbon, carbon nanotubes, activated fibers and graphite of high porosity, nano sized transition metal oxides, conducting polymers etc provides high specific surface area with good electrical conductivity. Since electrical capacitance of ECs is quite dependent on the number of ions (anions or cations) present at the electrode/electrolyte interface, highly increased specific surface area of these new electrode materials is essential for the ECs to obtain remarkably increased number of ions adsorbed on the surface of electrodes so as to realize the so-called "super-capacitance".

To be specific, the term supercapacitor (SC) is commonly used to describe carbon/carbon symmetrical cells exhibiting "super-capacitance" with several tens of hundreds of farads. SCs in general, are attributed to the purely non-diffusional charge reaction during the polarization. Hence, SCs do not exhibit redox (reduction/oxidation) reaction for electricity storage. Thus, the charge-discharge cycle life of SCs can be over 300,000 cycles (charge/discharge) and the turn around efficiency is up to 96% without significant degradation between the operating temperatures of –25 and +50^{o}C. In addition, the charge time becomes very rapid up to a few seconds and the specific power density is at least two order higher than the secondary or rechargeable batteries (Conway, 1999; Burke, 2000; Kotz and Carlen, 2000). These are the most distinctive outstanding characteristics as a new type of energy storage power source that any other types of electric storage devices such as advanced lithium-ion and lithium polymer rechargeable batteries cannot offer power density as high as what SCs could offer. However, the specific energy density of the SCs is hitherto one order of magnitude less than that of rechargeable lithium batteries.

Research into ECs is presently classified into two main areas that are based primarily on their mode of energy storage, namely: (i) the electrochemical double layer capacitor also referred to as pseudo capacitors. The former stores energy (electricity) in the form of electrostatic means that is typically the same way as a traditional capacitor and secondly (ii), the redox supercapacitor exhibits reversible Faradaic-type charge transfer and the resulting capacitance is not electrostatic in origin and hence the name pseudo capacitors (Conway, 1999; Burke, 2000; Kotz. and Carlen, 2000).

Invoking the developmental pace of advanced materials such as nanostructured transition metal oxides, carbons and electro-conductive porous polymers, the electrochemical capacitor (EC) and the battery (lithium battery) will soon be rolled in the same area of energy storage in which energy is paramount in the so-called hybrid energy storage device. It is with the above-astounded advantages and applications in mind, the present work was embarked at developing ECs using novel nanostructured metal oxides and inexpensive nanoporous carbonaceous materials as potential electrodes focusing on high power ECs in general and pulse power applications in particular.

1.1 Research Background

Research activities have been intensified over the decades to identify plausible materials as candidate electrodes for energy storage applications. The priority has been given to high energy, easily available, cheap and environmental friendly material. In view of the mentioned rationale for choice of materials, activated carbons are the most commonly used electrode material in commercial supercapacitors (SCs) at present. Carbon in its various forms is currently the most extensively examined and widely utilized electrode materials in EDLCs with development focusing on achieving high surface-area with low matrix resistivity. Carbons being an attractive as electrodes for supercapacitors arise from a unique combination of chemical and physical properties, namely: (Conway, 1999; Burke, 2000; Kotz and Carlen, 2000).

- High conductivity.
- High surface-area range (~ 1 to 2000 m^2g^{-1})

- Good corrosion resistance
- High temperature stability
- Controlled pore structure
- Processability and compatibility in composite materials
- Relatively low cost.

Nevertheless, the first two of these properties are critical to the construction of supercapacitors. As will be discussed, the properties of carbon allow both conductivity and surface area to be manipulated and optimized. Carbon has four crystalline (ordered) allotropes: diamond (obtained through sp^3 hybridization), graphite (sp^2 bonding), carbine (sp^1) and fullerenes (distorted sp^2 bonding) (Mc Enaney and Burchell, 1999).

Due to the wide range of carbon materials and to avoid confusion, the term 'carbon' is typically used to describe the element rather than its form. Carbon blacks are group of materials that are characterized by having near spherical carbon particles of colloidal size, which are produced by the partial combustion or thermal decomposition of hydrocarbons. The key properties of carbon blacks are considered to be fineness (primary particle size) structure (aggregate size/shape), porosity, and surface chemistry. Carbon blacks are routinely used as conductive agents in many types of batteries and supercapacitor electrodes (Zheng, 1999; Osaka *et al*,1999; Osaka *et al*, 1998; Liu and Osaka, 1997). The conductivity of carbon blacks is typically in the range 10^{-1} to 10^2 (Ω cm^{-1}) (Donnett *et al*, 1993). Supercapacitor electrodes have been produced from high surface-area blacks (containing a binder) with specific capacitances up to 250 Fg^{-1} (Richner *et al*, 2002). On the other hand, the "active" carbons are obtained through carbonised organic precursor (a 'char') referred to as activated carbons. Chars usually have a relatively low porosity and their structure consists of elementary crystallites with a large number of interstices between them. The interstices tend to be filled with 'disorganized' carbon residues (tars) that block the pore entrances. Activation opens these pores and can also create additional porosity.

Activation can be done by means of two general categories: thermal activation and chemical activation (Pierson, 1993; Bansal *et al*, 1988).

Yang *et al* (2002)employed a commercial activated carbon (AC) as electrodes for SCs. In order to enhance more active sites within the pores, they performed a secondary activation under steam in the presence of $FeCl_2$ catalyst in the temperature range of 800-950°C . Consequently, the re-activation of AC enhances both the specific capacitance and high rate capability of electrochemical double-layer capacitors (EDLCs). For AC treated under optimized conditions, its discharge specific capacitance compared to the original AC, exhibits increase in capacitance up to 55.65 Fg^{-1}, an increase of about 33% and the high rate capability was increased significantly. On the other hand, Laforgue & Simon obtained more than 25 Fcm^{-2} per electrode, with a time constant close to 3s, and power outputs compatible with automotive applications using electrode composition: activated carbon and SFG44 (Laforgue and Simon, 2003).

The influence of pore size distribution in carbon material that τ in turn improvises the accessibility of the pores to the electrolyte was studied by Frackowiak, et-al, Endo et-al and Linares-Solano et-al. The mobility of ions within the pores is different to the mobility of ions in the bulk of the electrolytic solution, and is greatly influenced by pore size. If the pores are too small to allow easy access to electrolyte ions they will not contribute to double-layer capacitance (Frackowiak and Be´guin, 2001; Lozano-Castello *et al*, 2003; Endo and Maeda, 2001)

Nanoporous materials are a subset of porous materials, typically having large porosities, and pore diameters between 1-100 nm. The definition of pore size according to the International Union of Pure and Applied Chemistry (IUPAC) is that micropores are smaller than 2 nm in diameter, mesopores 2 to 50 nm and macropores larger than 50 nm. Prabaharan *et al* fabricated symmetric carbon/carbon electrochemical capacitors employing mesoporous carbon black (MCB) powders (nongraphitized) having modest surface area and studied their double layer capacitance (Prabaharan *et al*, 2006). They observed rectangular shape cyclic characteristics confirming the double layer behavior of these carbon electrodes. The mechanism of double layer formation and frequency dependent capacitance were deduced from the ac-impedance analysis. Specific capacitance, power density and energy density were derived from constant current charge/discharge measurements. MCB powders demonstrated a specific capacitance of about 39 Fg^{-1} and the power density of 782Wkg^{-1} at a current density of 32 $mAcm^{-2}$. The test cells demonstrated the stable cycle performance over several hundreds of cycles. Interestingly, the measured specific capacitance values obtained using the above methods are very much comparable. The results suggest that the present mesoporous carbon could be useful as candidate for the development of EDLCs.

There is considerable interest in the application of carbon nanotubes (CNTs) as electrode materials for supercapacitors and other energy-storage devices (Lee *et al*, 2002). Nanotubes offer a new possibility for carbon electrodes, but least preferred due to high manufacturing cost. Figure 1.1 shows the FE-SEM image of the as-grown single walled CNT.

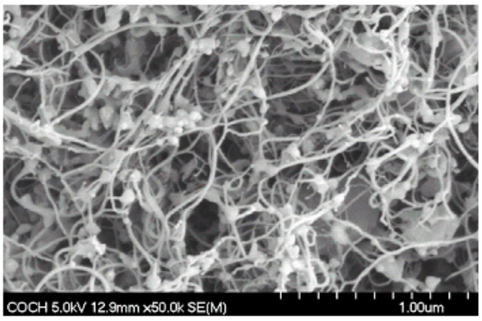

Fig. 1.1: FE-SEM image of the as-grown single walled CNT (An *et al*, 2001)

Considerable interest has also been shown in conducting polymer materials, and research suggests that high specific capacitances could be attainable. Work at Los Alamos National Laboratory has reported prototype polymer film capacitors with an energy density of 39 Wh/kg and a power density of 35 kW/kg (Li *et al*, 2005)

The current trend in supercapacitor technology is called the hybrid supercapacitor of an asymmetrical configuration in which a battery type electrode replaces one activated carbon electrode (Li *et al*, 2005; Naoi *et al*, 2002; Sugimoto *et al*, 2003). The battery electrodes accumulate charge through Faradaic electrochemical process (redox reaction), which increases not only the specific capacitance of the capacitor, but also extends the working voltage. This facilitates the energy density of the capacitor is enlarged considerably. Generally, there are three categories of redox-reaction materials are used in the hybrid supercapacitors nowadays, metal oxides, conductive polymers and intercalation compounds. Transition metal oxides have always been an attractive electrode material due to their low resistance and high specific capacitance, but their excessive cost has generally ruled them out as a commercially viable option. Traditionally a strong sulfuric acid has been used as an electrolyte with metal-oxide electrodes in order to increase the ion mobility, and hence the rate of charge/discharge is increased. This however limits the choice of electrode materials because of the fact that most material becomes unstable and corrodes in a strongly acidic electrolyte.

The most promising results seem to lie in the use of hybrid configurations, which consist of activated carbons and conducting polymers or metal-oxides. Seung *et al* (2003) prepared ruthenium/carbon composite materials by impregnating ruthenium(III) acetylacetonate into a mesoporous carbon (average pore diameter = 12 mn, pore volume = 3.6 cm^3/g) and then heat treated it at 320°C for 2 h under an argon atmosphere. The metallic ruthenium nanoparticles were converted to pseudo-capacitive hydrous ruthenium oxide by electrochemical oxidation at 0.75V (versus SCE) for 2 h in 2.0 M H_2SO_4. The specific capacitance of the composite electrodes, which is the sum of the double-layer capacitance of mesoporous carbon and the pseudo-capacitance of hydrous ruthenium oxide, reached 243 F/g with heavy loading. The rate capability of composite electrodes also decrease with increase in ruthenium loading, due to an increase in both the equivalent series resistance (ESR) and the overall capacitance value. The ESR increment is caused mainly by the increase in the electrolyte resistance within pores which, in turn, results from a pore narrowing with ruthenium loading hindered by ionic motion in narrowed pores can explain this feature (Seung et al, 2003).

Transition metal oxides like RuO_2 and IrO_2 exhibit faradaic pseudocapacitance with capacitance reported to be as large as 760 F/g (Zheng *et al*, 1995). However the high cost of these materials limits their commercialization. To circumvent the draw back, metal oxides such as nickel oxide (Nam and Kim, 2002; Wang and Qin, 2002; Srinivasan *et al*, 2000) cobalt oxide (Lin *et al*, 1998) and manganese oxides (Pang *et al*, 2000) are studied because they are inexpensive and capable of exhibiting pseudocapacitance behavior similar to that of RuO_2 and IrO_2. Nickel oxide has received a considerable amount of attention over the last few years due to its large surface area, and high conductivity pseudocapacitive behavior. It is applied in diverse fields, such as smart windows, active optical fibers, catalysis (Sheela *et al*, 1995), electrochromic films (Chigane and Ishikawa, 1992), fuel cell electrodes (Makkus *et al*, 1994), gas sensors and others (Yoshimura *et al*, 1995).

NiO (Nickel Oxide) electrode has high resistivity, which is a serious drawback to apply for practical applications to ECs. It is crucial to enhance the electrode conductivity in order to improve the energy density and power density of electrodes. Moreover, the specific surface area of electrodes is directly related to the specific capacitance. However, the specific surface area of the NiO in general is not high enough for high capacitance. The carbon nanotube has been known to yield high conductivity and large specific surface area (Niu *et al*, 1997; Ray *et al*, 2002; Frackowiak *et al*, 2001; An *et al,* 2001). With a view to improvise the electrode conductivity of NiO, Nam et-al studied Nickel oxide/carbon nanotube ($Ni_{1-x}O$/CNT) film nanocomposite electrodes for electrochemical capacitors, which were prepared by electrochemically precipitating nickel hydroxide onto a CNT film substrate and heating it in air at 300°C. For comparison, nickel oxide thin film and nickel oxide/carbon paper $Ni_{1-x}O$/C paper electrodes were also prepared via electrochemical route. The nickel oxide layers (~5 nm thickness) in the $Ni_{1-x}O$/CNT film electrode were coated uniformly on the surface of the individual CNTs, constructing a 3D nanoporous network structure through the entire thickness of the film. In comparison to the thin film and $Ni_{1-x}O$/C paper electrodes, the $Ni_{1-x}O$/CNT film electrode showed a very high specific capacitance of ~1000 F/g with a high rate capability in 1M KOH. The high specific capacitance and good power characteristics of the $Ni_{1-x}O$/CNT nanocomposite electrode can be attributed to the construction of an electrode with a very thin film of electroactive materials with a nanometer thickness on a CNT film substrate with a 3D nanoporous network structure (Nam *et al*, 2005).

Zhang *et al* synthesized nanocrystalline NiO by a simple liquid-phase process. A specific capacitance approximately to 300 Fg^{-1} could be achieved with NiO in the range of 0.0–0.5V (Zhang *et al*, 2004). Liu and Anderson studied the capacitance of sol-gel derived NiO films heated in different atmosphere and concluded that the sample annealed in air show only a slightly higher capacitance compared to the one heated in pure nitrogen or oxygen (Liu and Anderson,1995).

Lee et-al (2005) have fabricated supercapacitor electrodes employing nickel oxide (NiO)/carbon nanotubes (CNTs) nanocomposite formed by a simple chemical precipitation method. The presence of CNT network in the NiO significantly improved (i) the electrical conductivity of the host NiO by the formation of conducting network of CNTs and (ii) the active sites for the redox reaction of the metal oxide by increasing its specific surface area. In addition, it was also found that the power density and cycle life were improved. Their work explained the simple chemical precipitation method for formation of the NiO/CNT nanocomposite and the close relationship of specific surface area and the specific capacitance of the composite. The CNTs in the NiO/CNT nanocomposite form electrically conductive network, decreasing the electrical resistivity of electrode materials, and thereafter decreasing the ESR of supercapacitors. The CNT with high specific surface area is required to form high electrical double-layer capacitance and more active sites for redox reaction of metal oxides. Their approach created avenue for practical applications of metal oxides by improving the electrochemical properties.

1.2 Justification of Study

Electrochemical capacitors (ECs) offer extended battery life in mobile communications equipment using the battery/supercapacitor combination (Battery Energy Saving Technology Capacitor). Additionally, it is suitable for use in hybrid battery packs to reduce peak power on demand and extending the battery life.

It is a well known fact that rechargeable batteries such as lithium-ion and lithium polymer though advanced cannot offer high power density as certain applications still do demand power density. Example being the near future electric and/or hybrid electric vehicle (EVs or HEVs) which require high power density devices for load leveling. That is, to propel electrified vehicles, most of the energy is focused at the on-board battery pack. Nevertheless, batteries cannot sustain high power during peak powering and hence demands high power devices to compensate the peak power loss during load leveling. EDLC or EC is the only choice to meet such peak power demand. That is, EC can serve as a peak power provider in conjunction with high-energy batteries. Therefore, this proposal aims at developing electrochemical capacitor materials and devices based on carbon materials and metal oxide.

In the past, stored energy was provided by capacitor banks, which proved to be bulky and more prone to failure. EC is needed where space was at a minimum. In this sense, the focus of the present proposal has been designed carefully to address this major issue and also to design and develop a high power EC for low voltage applications at < 0.5 Hz (DC applications).

ECs are energy storage devices that display high pulse-power capabilities. Various types of materials such as activated carbon (Osaka *et al*, 1999; Osaka *et al,* 1998; Bansal *et al,* 1988) highly crystalline carbon (Richner *et al,* 2002; Pierson, 1993) carbon nanotube (CNT) (Lee *et al*, 2002; An *et al*, 2001; Niu *et al,* 1997 and An *et al,* 2001), transition metal oxides (Zhang *et al*, 2004; Lee *et al*, 2005) and conducting polymers (Arbizzani *et al*, 1996) have been used as thin-film electrode materials for the fabrication of ECs.

Nanostructured materials are found to demonstrate unique properties in terms of electrode conductivity and particle to particle contact due to their nanometer sizes where electron tunneling is quicker than micron-sized particles. The latter aspect is vital for supercapacitor as it directly influence the equivalent series resistant (ESR) of the cell. Therefore, employing nanosized particles as electrode for such application would certainly help to achieving such high rate capability within the cell. It is in this context, the present work has thus been justified as timely and important to develop such high rate power sources namely hybrid supercapacitors. Obtaining uniform nanograin sizes in metal oxide powders is a crucial challenge for material scientists. This requires an appropriate synthesis approach. Therefore, the present work has been aimed at developing uniform sized NiO spherical nano-sized particles with a view to enhancing the electrode properties and characterizing its electrode-active qualities in electrochemical supercapacitors.

The motivation for the present work thus far has been centered on the above aspects focusing on the preparation of nanocrystalline metal oxide namely porous NiO adopting a simple solvothermal approach and to characterize the metal oxide thus obtained in an aqueous electrochemical cell (against a calomel reference electrode) to determine its single electrode capacitance and in turn to use it as a positive electrode against a mesoporus nanocomposite carbonaceous negative electrode fabricating a hybrid supercapacitor namely NiO(+)/C(-) with a view to study the energy/power density for pulse power applications.

1.3 Objectives of present research

Several objectives have been set for this study. They are:

- To study the characteristics of commercially available mesoporous carbon based similar electrode electrochemical capacitor - EM2K (Cabot), BP2K(Cabot) and AB(Denka)
- To synthesize nanostructured transition metal oxide based on nickel and study the nanostructure characteristics using FESEM, HR-TEM and XRD techniques for use as electrodes for fabricating electrochemical capacitors
- To evaluate single electrode capacitance of the synthesized NiO using three electrode measurements by employing aqueous electrolyte.
- To fabricate and test the hybrid capacitors with nanooxide/mesoporous carbon asymmetric configuration using different electrochemical techniques

CHAPTER 2
LITERATURE REVIEW

2.0 Fundamental understanding

There are two major types of capacitors: fixed and variable. The fixed capacitor has a specific value of capacitance while a variable capacitor allows for a range of capacitance. Variable capacitors are designed so that capacitance can be changed through a mechanical means such as adjusting a screw or turning a shaft. Variable capacitors are used when the application requires an adjustment of capacitance such as in a radio tuner.

Figure 2.1 shows the classification of different type of commercially available capacitors. Fixed capacitors have capacitance values that cannot be physically adjusted. They can be divided into electrostatic and electrochemical categories. In the latter, electrolytic capacitors use either a solid or liquid electrolyte in their construction. They have high capacitance values and offer the highest energy densities compared to the conventional capacitors. These capacitors are inherently polar due to their construction. A polar capacitor can only handle current flow in only one direction. The electrochemical double layer capacitors are a new type of capacitors. These are also known as ultra-capacitors or super-capacitors because their capacitance values can measure as high as several hundred farads. These capacitors are used in battery-assisted applications such as cell phones and electric vehicles (Conway, 1999).

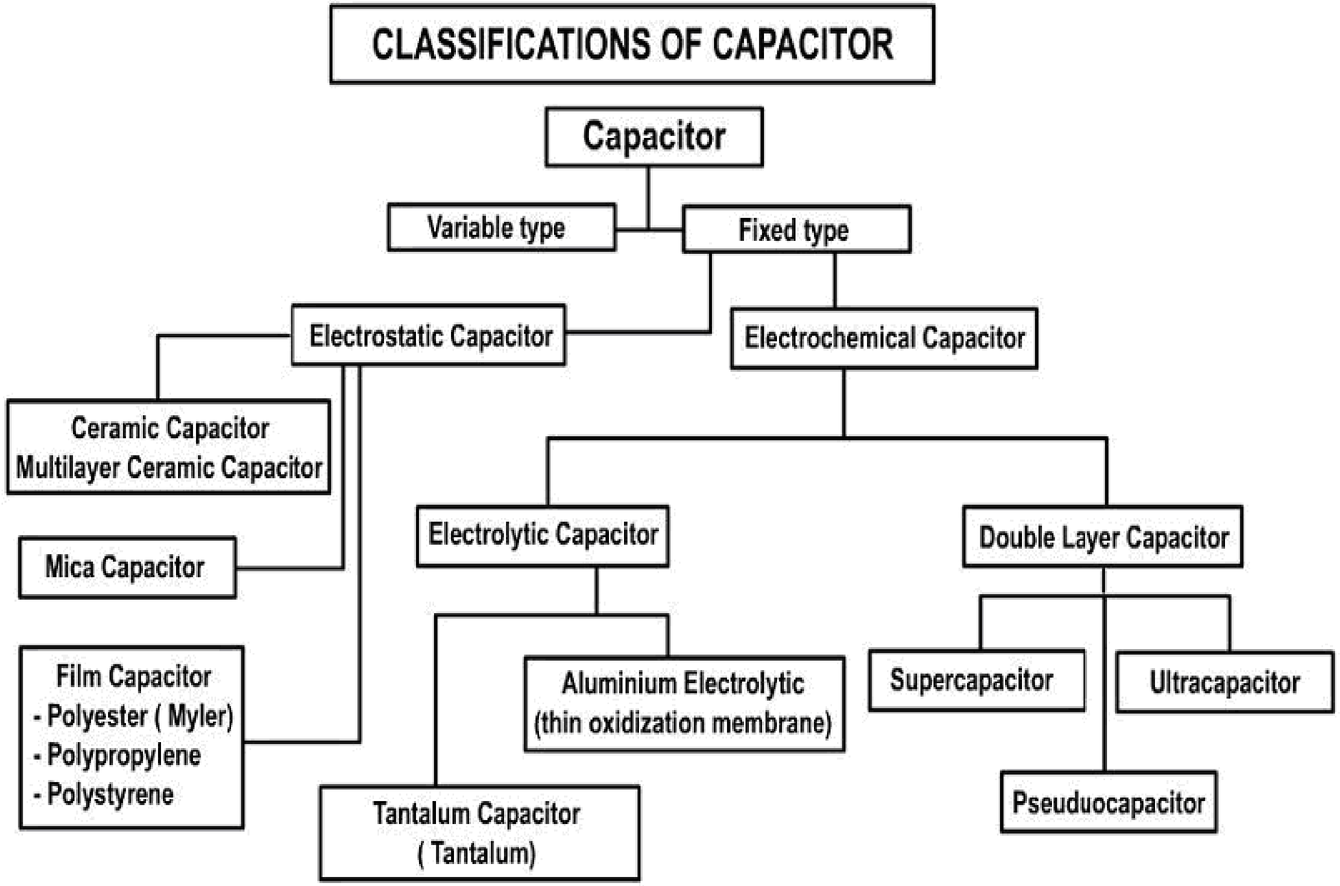

Figure 2.1: Classification of different type of commercially available capacitors. (Conway, 1999).

2.1 Current understanding of Electrochemical capacitors

2.1.1 Basic principle of a capacitor

A capacitor is commonly known as an electrical condenser. The amount of electricity which a capacitor will hold depends on the electrical pressure or voltage applied to the capacitor. The plates are charged with equal amounts of positive and negative electrical charges, respectively. This is a "physical" storage of electricity and is analogous with the "chemical" storage in a battery. A capacitor is said to be charged when there are more electron on one conductor plate than on the other. If an electric potential (voltage) is applied to the capacitor plates, the plates will become charged, one positively and one negatively. The plate with the larger number of electrons has the negative polarity. The opposite plate then has the positive polarity. When a capacitor is charged, the energy is stored in the dielectric material in the form of electrostatic field. When an electron is added to one plate of a capacitor, one electron is driven away from the opposite plate. This phenomenon is known as the principle of electrostatic induction. Figure 2.2 shows the principle of electrostatic induction in a capacitor.

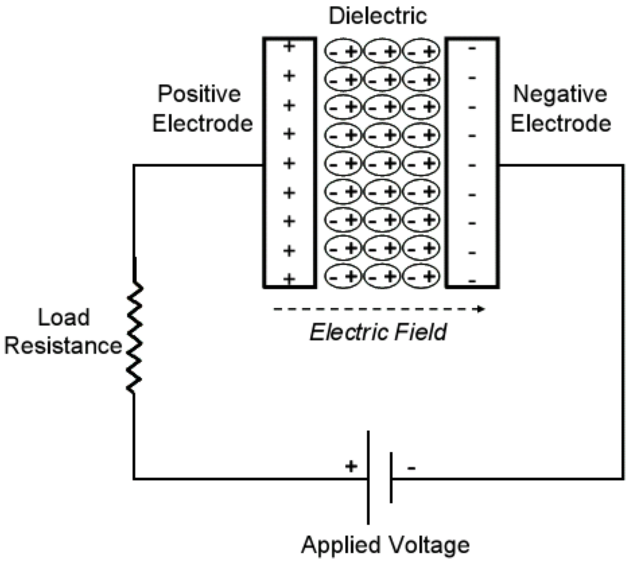

Figure 2.2: Principle of electrostatic induction (Conway, 1999).

2.1.1.2 Capacitance

Capacitors, regardless of type or kind, are all designated by their electrical size. In capacitors, this electrical size is designated as capacity. The capacity of an electrical capacitor is the ratio of the quantity of electricity and the electrical pressure or voltage. In other words the capacity of a capacitor depends on the amount of electricity it will hold at a certain electrical pressure or voltage. (Conway, 1999).

This ratio may be expressed as follows:

$$\boldsymbol{Q = CV} \text{ -------} \qquad \textit{Eq. 2.1}$$

Q = quantity of electricity

C = capacity of the capacitor

V = electrical pressure or voltage

By the same token the capacity may be expressed as follows:

$$\boldsymbol{C = Q / V} \text{ -------} \qquad \textit{Eq. 2.2}$$

Where the capacity is equal to the quantity of electricity divided by the electrical pressure or voltage. The capacity of a capacitor is dependent upon the size and spacing of the conducting plates and the type of insulating or dielectric medium between the plates. It is known as capacitance.

$$\boldsymbol{C = \varepsilon A / d} \text{ -------} \qquad \textit{Eq. 2.3}$$

C = capacitance in farads, F

ε = dielectric constant

$\varepsilon = \varepsilon_o \varepsilon_r$

ε_o is the space permittivity (8.854×10^{-12} F/m^2)

ε_r is the relative permittivity

A = area of one plate in square meters, m^2

d = distance between plates in meters, m

The capacitance is directly proportional to the surface areas of the plates, and is inversely proportional to the separation between the plates. Capacitance also depends on the dielectric constant of the substance separating the plates. The standard unit of capacitance is the farad, abbreviated F. This is a large unit; more common units are the microfarad, abbreviated μF (1 μF = 10^{-6} F) and the picofarad, abbreviated pF (1 pF = 10^{-12} F). The greater the area for storing charge, and the closer the separated charges, the greater is the capacitance.

2.1.2 Electrochemical Capacitor

2.1.2.1 The Electrochemical Double Layer Capacitor

As mentioned briefly in the earlier literature review, ELDCs or ECs store charges in the electrode/ electrolyte interface. High surface area electrodes are used in electrochemical capacitors resulting in large double layer capacitance, and much of the storage capacity which is due to the charging/discharging of the double layer. At some surface oxidation/reduction also occurs, but in contrast to reactions occurring in batteries, this is limited to a monolayer or two on the electrode surfaces. Consequently, the device behaves more like a capacitor than a battery. EDLC is also called "supercapacitor" (SCs) and "ultracapacitor" depending upon the materials and electrodes used. EDLC typically have much larger power density but much smaller energy density than batteries. Charge is stored electrostatically in polarized liquid layers between an ionically conducting electrolyte and an electrochemically-conducting electrode. This energy storage mechanism is either based on capacitive (non-faradic) or pseudocapacitive (faradic) which will be discussed later (Conway, 1999).

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2.1.2.2 Concept of Electrochemical Double Layer Capacitor

Electrochemical double layer capacitor stores energy using the double layer concept. This double layer is realized when two electrodes immersed in an electrolyte, are polarized. The polarized charges at both the positive and negative electrodes resemble two capacitors connected in series (see Figure 2.3).

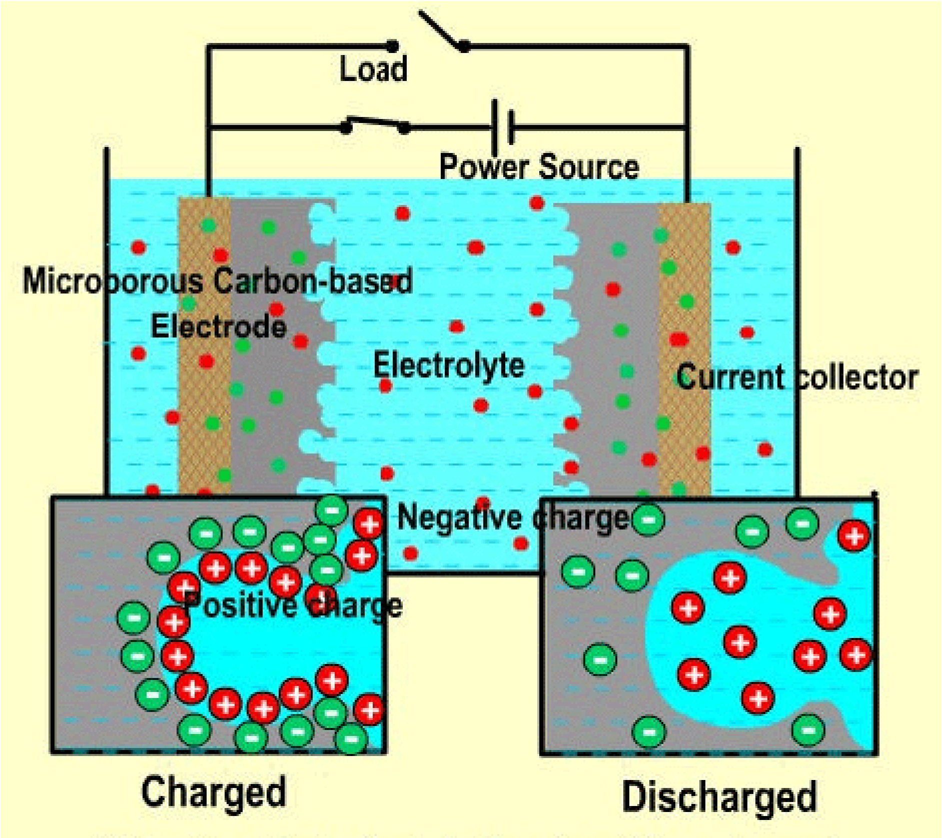

Figure 2.3: Behavior of electrolyte in ion (positive charge) in the pore when charged and discharge

Analyzing the exploded view of the individual electrode, Helmhortz has identified the existence of a 'double layer' in the electrochemical cell in 1879. And it is named after him as Helmholtz layer. There are several theoretical models that describe the structure of the double layer such as the Gouy-Chapman model, and the Gouy-Chapman-Stern model. However the most common one would be the Helmholtz model.

Helmholtz double layer is a structure of charge accumulation and charge separation that always occurs at the interface when an electrode is immersed into an electrolyte solution. This layer is formed as the solvated ions are blocked and accumulated at the electrode/electrolyte interface. This would create a charge separation between the solvated ions and the electrode material that resembles the charge storage mechanism similar to conventional capacitor, where *d* is distance between conducting plate and insulating material. Refer Equation 2.3. In general, positive and negative charges are arrayed at counter position with an extremely short distance, such as atomic distance (~ 10 Å), between both at the contact interface of two different phases where, in this case, the two phases would be the solid carbon electrode and the electrolyte. This interfacial charge distribution layer is explained as the helmholtz layer in Figure 2.4. The excess charge on the electrode surface is compensated by an accumulation of excess ions of the opposite charge in the solution. This structure behaves essentially as a capacitor as it possesses the double layer. The amount of charge is a function of the electrode potential. Figure 2.5 illustrates the electrode potential before and after charging. The charges are polarized at the interface forming the helmholtz layer. Thus creating a electrical potential which was be observed after the charging (Conway, 1999; Burke, 2000; Kotz and Carlen, 2000).

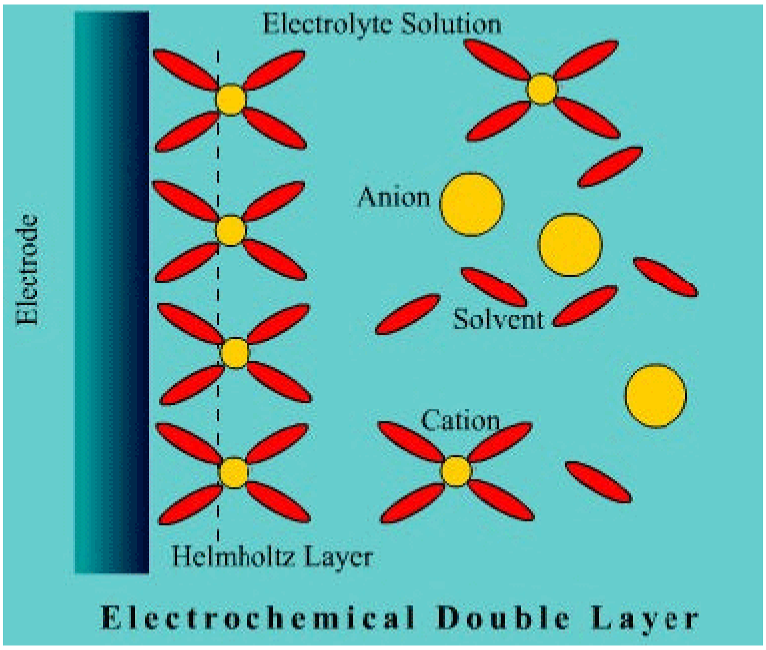

Figure 2.4: Helmholtz double layer

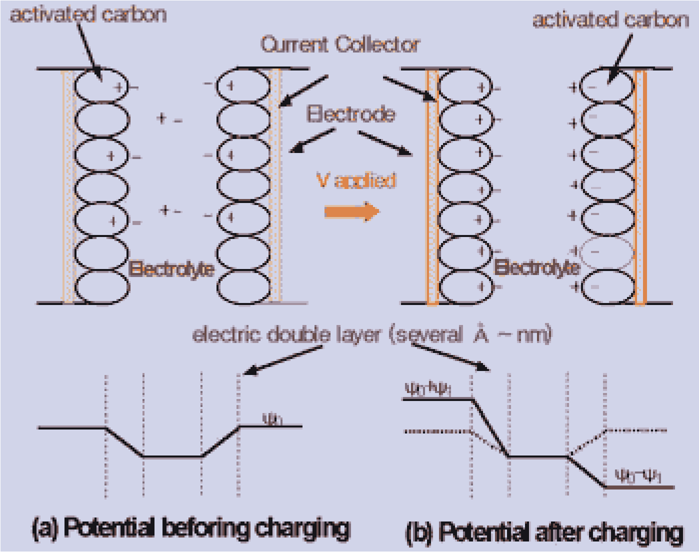

Figure 2.5: Typical distribution of charges at the interface and
its electrode potential before and after charging (Conway, 1999).

2.1.2.3 Non-Faradaic

The charge accumulation is achieved electrostatically by positive and negative charges residing on two interfaces separated by a vacuum or a molecular dielectric (the double layer or, e.g., a film of mica, a space of air or an oxide film, as in electrolytic capacitors) (Conway, 1999).

2.1.2.4 Faradaic

The charge storage is achieved by an electron transfer that produces chemical or oxidation state changes in the electroactive materials according to Faraday's laws (hence the term) related to electrode potential. This is known as pseudocapacitance in ECs. The energy storage is indirect and is analogous to that in a battery. In a battery cell, every electron charges is Faradaically neutralized by charge transfer, resulting in a charge of oxidation stage of some redox-electroactive reagent, e.g., $Ni^{3+}\ O^{2-}\ OH^{-} + e + H^{+} \rightarrow Ni^{2+}\ 2OH^{-}$ in the cathode of an Ni-Cd battery (Conway, 1999).

The electrons involved in a double-layer charging are the delocalized conduction-band electrons of the metal or carbon electrode, while the electrons involved in Faradaic battery-type processes are transferred to or from valence-electron states (orbital) of redox cathode or anode reagent, although they may arrive in or depart from the conduction-band states of the electronically conducting support material. In certain cases, the faradaically reactive battery material itself is metallically conducting (e.g., PbO_2, some sulfides, RuO_2 (Trasatti and Buzzanca, 1971) or else is a well-conducting semiconductor and a productor, e.g., NiOOH (Oliva *et al*, 1982).

2.1.2.5 Characteristics of Electrochemical Double layer Capacitor

Some of the main characteristic of EDLC (Conway, 1999);

- It employs carbon or metal oxides as the material for the electrodes
- Its capacitance values can be measured as high as several hundreds of Farads (F)
- Fast charge time up to a few seconds
- High specific power density compared to batteries (at least two order of degree) but specific energy density is one order less than batteries.
- It can be charged to any voltage within its voltage rating.
- Stores much more energy than a conventional capacitor of similar size.
- Able to deliver frequent pulses of energy without any detrimental effects unlike batteries which experience reduced life if exposed to frequent high power pulses
- Can be charged extremely fast while batteries are damaged by fast charging.
- Can be cycled hundreds of thousands of times unlike batteries which are cyclable only up to few hundred cycles.
- No charge circuit (Self charge)
- No explosion risk
- It requires no maintenance and is robust to environmental extremities such a arctic temperatures.
- Wide temperature range (operation)
- Pollution free
- No liquid leak (if properly sealed)

2.2 Classifications of Electrochemical capacitors

2.2.1 Supercapacitor , Pseudocapacitor, Hybrid Capacitor

As mentioned earlier, ultracapacitors, supercapacitors, powercapacitor and pseudocapacitors are also known as other names for double layer capacitor which are established colloquial names. They are named duly by the cell performance. The term “super” capacitor is most commonly used for carbon based double layer capacitors because of its high capacitance value. On the other hand, double layer capacitors with metal oxide electrodes are known as hybrid electrochemical capacitors / ultracapacitors for their very low equivalent series resistance value (ESR). It is also known as pseudocapacitor if it exhibits pseudocapacitance behaviour (faradaic reaction like in battery). Figure 2.1 is the summary of classification of capacitor.

2.2.2 Pseudocapacitance

There are two basic reactions, which lead to electrochemical cell. Both occur at the interface between a conductor and an electrolyte and both benefit from very high specific surface areas at the electrode. Surface areas around 2,000 m^2/g are commonly available for carbons while 140 m^2/g commonly available for ruthenium oxide (metal oxide). The first mechanism commonly referred to as charge separation, which is well documented as a non-Faradic mechanism and is the basis for EDLC. The charges are basically blocked at the electrode/electrolyte interface, preventing the charges to diffuse. The second reaction commonly referred to as an oxidation-reduction reaction (redox) due to faradic mechanism, which is the basis for pseudocapacitance. In here, the charges are partially blocked where some charges diffuse into the electrode material and intercalate. The term pseudocapacitor is commonly used to explain the pseudocapacitance behaviour of such double layer capacitors. Carbon is an example of a charge separation of non-Faradic electrode material and ruthenium oxide is an example of faradic electrode material (Conway, 1999).

Although, pseudocapacitor has electrochemical reaction similar to battery (the faradic mechanism), the distinction between a battery and an electrochemical double layer capacitor is not explicit. A battery relies on electrochemical reactions that involve active materials in the electrode, where the charges are not blocked, diffuse into the material and intercalate. In this case, active means that the materials participate in the reaction, and a transfer of electrons between the active material and ionic species in solution occurs across the solid/liquid interface. On the other hand, in an "ideal" electrochemical capacitor that utilizes carbon or metal oxides, the electrodes play passive role. That is, the electrode surface only participates by serving as sites for charged species to accumulate and no electron transfer occurs across the solid/liquidinterface. In a "practical" electrochemical capacitor there may occur some surfaceoxidation/reduction on the electrodes, that is, it operates partly as a capacitor and partly as a battery. Of course, this phenomenon is depends on the material properties. So, in order to characterize a double layer capacitor, one has to investigate the above behavior (Conway, 1999).

The metal oxide technology of the pseudocapacitor utilizes an electrochemical reaction similar to battery technology for energy storage, thus improving potential energy density. Since the pseudocapacitor uses a dense metal oxide as the electrode material, the load of the oxide is three times that of the EDLC for the same-coated area. With this advantage, pseudocapacitor cell needs to be only 60% in volume as compared to an EDLC of the same capacitance. Conversely, it also means the pseudocapacitor holds 80% more energy than the equivalent-size EDLC. Finally, the pseudocapacitor uses the same manufacturing processes and facilities as EDLC production.

2.2.3 Hybrid Capacitor

A hybrid capacitor is a double layer capacitor fabricated with one electrode purely double layer (carbon based as the negative electrode) and another electrode with pseudocapacitance (e.g., metal oxide based as the positive electrode). The energy density of these devices is found to be significantly higher than that of pure EDLCs. Like the activated carbon cathode in EDLC, an activated carbon in the cathode of the hybrid capacitor absorbs anions at the electric double-layer and linearly polarizes to positive side in the charging process. On the other hand, as shown in Figure 2.6, a Li-doped graphite in the anode of the hybrid capacitor that intercalates Li^+ ions into its interlayer in the charging process and de-intercalates Li^+ ions in the discharging process. When the anode is charged, potential of the anode becomes very negative and approaches the deposition potential of Li-metal anode as illustrated in Figure 2.6.

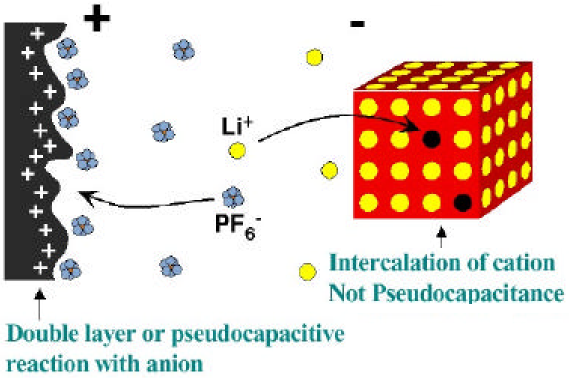

Figure 2.6: A Li-doped graphite in the anode of the hybrid capacitor that intercalates Li+ ions into its interlayer in the charging process and de-intercalates Li+ ions in the discharging process (Pasquier, A. *et al*, 2001).

The voltage is largely developed at anode but negligibly at cathode. Voltage developed in the electrolyte is due to a solution resistance the so-called ohmic drop (IR drop). The voltages developed at each electrode are made from resulting charge stored and electrode capacity. Because the cathode capacity is much larger than that of anode, voltage development occurs mostly at anode when a cell is charged. Figure. 2.7 indicates the working principle of a hybrid capacitor. The single-cell hybrid capacitor can withstand high voltages due to the nature of the anode. In contrast, the cell voltage