Review

Simple Capacitors to Supercapacitors - An Overview

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The renaissance of electrical/electrochemical double layer capacitors is occurring at a phenomenally high rate as the significant role of these power storage devices in traction, space flight technology, power electronics and other related fields is recognized. The needs of to-day's computer world cannot be fulfilled by the conventional capacitors such as electrostatic and electrolytic capacitors as their utility is limited to certain specific applications. Electric double layer capacitor (EDLC) uses carbon as the electrodes and stores charge in the electric field at the interface. It uses either aqueous or non-aqueous electrolyte. It gives high power density but low energy density. So the next generation electrochemical double layer capacitor or super capacitor which uses transition metal oxide as the electrode material along with carbon has been under innovation which is expected to deliver both desirable power and energy densities. In this overview, an attempt to provide information on the chronological order of development of capacitors and the related research work is made.

1. INTRODUCTION

This paper offers a concise review on the renaissance of a conventional capacitor to electrochemical double layer capacitor or super capacitor. Capacitors are fundamental electrical circuit elements that store electrical energy in the order of microfarads and assist in filtering. Capacitors have two main applications; one of which is a function to charge or discharge electricity. This function is applied to smoothing circuits of power supplies, backup circuits of microcomputers, and timer circuits that make use of the periods to charge or discharge electricity. The other is a function to block the flow of DC. This function is applied to filters that extract or eliminate particular frequencies. This is indispensable to circuits where excellent frequency characteristics are required. Electrolytic capacitors are next generation capacitors which are commercialized in full scale. They are similar to batteries in

cell construction but the anode and cathode materials remain the same. They are aluminum, tantalum and ceramic capacitors where they use solid/liquid electrolytes with a separator between two symmetrical electrodes.

The third generation evolution is the electric double layer capacitor, where the electrical charge stored at a metal/electrolyte interface is exploited to construct a storage device. The interface can store electrical charge in the order of $\sim 10^6$ Farad. The main component in the electrode construction is activated carbon. Though this concept was initialized and industrialized some 40 years ago, there was a stagnancy in research until recent times; the need for this revival of interest arises due to the increasing demands for electrical energy storage in certain current applications like digital electronic devices, implantable medical devices and stop/start operation in vehicle traction which need very short high power pulses that could be fulfilled by electric double layer capacitors (EDLCs). They are complementary to batteries as they deliver high power density and low energy density. They also have longer cycle life than batteries and possess higher energy density as compared to conventional capacitors. This has led to new concepts of the so-called hybrid charge storage devices in which electrochemical capacitor is interfaced with a fuel cell or a battery. These capacitors using carbon as the main electrode material for both anode and cathode with organic and aqueous electrolytes are commercialized and used in day to-day applications. Fig. 1 presents the three types of capacitors depicting the basic differences in their design and construction.
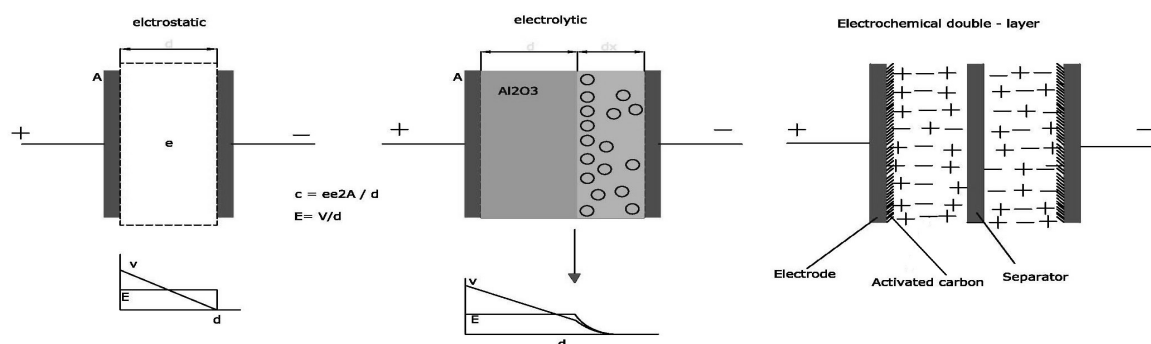

Figure 1. Schematic presentation of electrostatic capacitor, electrolytic capacitor and electrical double layer capacitor.

EDLCs, however suffer from low energy density. To rectify these problems, recently researchers try to incorporate transition metal oxides along with carbon in the electrode materials. When the electrode materials consist of transition metal oxides, then the electrosorption or redox processes enhance the value of specific capacitance ca. 10 -100 times depending on the nature of oxides. In such a situation, the EDLC is called as supercapacitor or pseudocapacitor. This is the fourth generation capacitor. Performance of a supercapacitor combines simultaneously two kinds of energy storage, i.e. non-faradic charge as in EDLC capacitors and faradaic charge similar to processes proceeding in batteries. The market for EC devices used for memory protection in electronic circuitry

is about \$150-200 million annually. New potential applications for ECs include the portable electronic device market, the power quality market, due particularly to distributed generation and low-emission hybrid cars, buses and trucks. There are some published reviews on capacitors and supercapacitors [1-11]. In the present overview, the evolution of electrochemical double layer capacitors starting from simple electrostatic capacitors is summarized.

2. EXPERIMENTAL PART

The invention of Leiden jar in 1745 started the capacitor technology; since then, there has been tremendous progress in this field. In the beginning, capacitors are used primarily in electrical and electronic products, but today they are used in fields ranging from industrial application to automobiles, aircraft and space, medicine, computers, games and power supply circuits. Capacitors are made from two metallic electrodes (mainly Si) placed in mutual opposition with an insulating material (dielectric) between the electrodes for accumulating an electrical charge. The basic equation relating to the capacitors is:

$$C = \epsilon \ S/d \tag{1}$$

where C (μF) is the electrostatic capacity, ϵ the dielectric constant of the dielectric, S (cm^2) the surface area of the electrode and d (cm) the thickness of the dielectric. The charge accumulating principle can be described as follows: when a battery is connected to the capacitor, flow of current induces the flow of electrons so that electrons are attracted to the positive terminal of the battery and so they flow towards the power source. As a result, an electron deficiency develops at the positive side, which becomes positively charged and an electron surplus develops at the negative side, which becomes negatively charged. This electron flow continues until the potential difference between the two electrodes becomes equal to the battery voltage. Thus the capacitor gets charged. Once the battery is removed, the electrons flow from the negative side to the side with an electron deficiency; this process leads to discharging. The conventional capacitors yield capacitance in the range of 0.1 to 1 μF with a voltage range of 50 to 400 V. Various materials such as paper (ϵ, 1.2-2.6), paraffin (ϵ, 1.9-2.4), polyethylene (ϵ, 2.2-2.4), polystyrene (ϵ, 2.5-2.7), ebonite (ϵ, 2-3.5), polyethylene tetraphtharate (ϵ, 3.1-3.2), water (ϵ, 80) sulfur (ϵ, 2-4.2), steatite porcelain (ϵ, 6-7), Al porcelain (ϵ, 8-10), mica (ϵ, 5-7) and insulated mineral oil (ϵ, 2.2-2.4) are used as dielectrics in capacitors [1].

The capacitance output of these silicon based capacitors is limited and has to cope with low surface-to volume ratios of these electrodes. To increase the capacitance, as per eq. (1), one has to increase to ϵ or S and decrease δ; however the δ value is largely determined by the working voltage and cannot be tampered. When aiming at high capacitance densities, it is necessary to combine the mutual benefits achieved with a high permittivity insulator material and an increased effective surface area. With Si as the substrate material, electrochemical etching produces effective surface area. The surface area of this material gets enlarged by two orders of magnitude compared to unetched surface. Electrochemically formed macroporous Si has been used for the preparation of high aspect ratio

capacitors with layered $SiO_2/Si_3N_4/SiO_2$ insulators. [12, 13]. Research work on the modification of conventional capacitors to increase the specific capacitance is also in progress. Approximately 30 times higher capacitance densities are reported recently for $Si/Al_2O_3/ZnO$: Al capacitor where Si is electrochemically etched porous one [14]. Another way identified to increase the surface area of the electrodes is to form anodically formed oxides (Al, Ta); however, ceramic capacitors are based on the high dielectric constant rather than the electrode area.

3. ELECTROLYTIC CAPACITORS

The next generation capacitors are the electrolytic capacitors; they are of Ta, Al and ceramic electrolytic capacitors. Electrolytic capacitors use an electrolyte as conductor between the dielectrics and an electrode. A typical aluminum electrolytic capacitor includes an anode foil and a cathode foil processed by surface enlargement and or formation treatments. Usually, the dielectric film is fabricated by anodizing high purity Al foil for high voltage applications in boric acid solutions. The thickness of the dielectric film is related to the working voltage of the aluminum electrolytic capacitor. After cutting to a specific size according to the design specification, a laminate made up of an anode foil, a cathode foil which is opposed to the dielectric film of the anode foil and a separator interposed between the anode and cathode foils, is wound to provide an element. The wound element does not have any electrical characteristics of electrolytic capacitor yet until completely dipped in an electrolyte for driving and housed in a metallic sheathed package in cylindrical form with a closed-end equipping a releaser. Furthermore, a sealing material made of elastic rubber is inserted into an open-end section of the sheathed package and the open-end section of the sheathed package by drawing, whereby an aluminum electrolytic capacitor is constituted [15]. Electrolytic aluminum capacitors are mainly used as power supplies for automobiles, aircraft, space vehicles, computers, monitors, motherboards of personal computers and other electronics.

There are two types of tantalum capacitors commercially available in the market; wet electrolytic capacitors which use sulfuric acid as the electrolyte and solid electrolytic capacitors which use MnO_2 as the solid electrolyte. Though the capacitances derived from both Ta and Al capacitors are the same, Ta capacitors are superior to Al capacitors in temperature and frequency characteristics. For analog signal systems, Al capacitors produce a current-spike noise which does not happen in Ta capacitors. In other words, Ta capacitors are preferred for circuits which need high stability characteristics. The total world wide production of Al electrolytic capacitors amounts to US$ 3.8 billion, 99% of which are of the wet type. Unlike Ta solid electrolytic capacitors, the solid electrolyte materials used are of organic origin; polypyrrole, a functional polymer and TCNQ (7,7, 8, 8-tetracyanoquniodimethane) an organic semiconductor. Next, MnO_2 solid electrolyte material is formed on the surface of that dielectric layer and on top of that a layer of polypyrrole organic solid electrolyte material is formed by electrolytic synthesis. Following this, the positive and negative electrodes are mounted to complete the electronic component. However, the capacitances of these electrolytic capacitors are in the range 0.1 to 10 μF with a voltage profile of 25 to 50 V [1].

The history of development of electrolytic capacitors which were mass produced in the past as well as to-day is presented by S. Niwa and Y. Taketani [16]. Many researchers try to improve the performance of these electrolytic capacitors by modifying the electrode or electrolyte. Generally, the increases in effective surface area (S) are achieved by electrolytic etching of aluminum substrate before anodization, but now it faces with the limit. It is also very difficult to decrease d because the d value is largely decided when the working voltages are decided. Increase in ϵ may be a possible routine to form composite dielectric layers by incorporating relatively large ϵ value compounds. Replacement of MnO_2 by polypyrrole solid electrolyte was reported to reduce electrostatic resistance due to its higher conductivity; aromatic sulfonate ions were used as charge compensating dopant ions [17]. A tantalum capacitor with Ta metal as anode, polypyrrole as cathode and Ta_2O_5 dielectric layer was also reported [18]. In the Al solid electrolytic capacitors, polyaniline doped with inorganic and organic acids was also studied as counter electrode [19]. In yet another work, Al solid electrolytic capacitor with etched Al foil as anode, polyaniline/polypyrrole as cathode and Al_2O_3 as dielectric was developed [20]. Ethylene carbonate based organic electrolytes and γ-butyrolactone based electrolytes have been tried as operating electrolytes in Al electrolytic capacitors [21, 22]. Masuda et al. have obtained high capacitance by electrochemically anodizing rapidly quenching Al-Ti alloy foil [23, 24]. Many researchers have tried the other combination of alloys such as Al-Zr, Al-Si, Al-Ti, Al-Nb and Al-Ta composite oxide films [25-31]. Composite oxide films of Al_2O_3-$(Ba_{0.5}Sr_{0.5}TiO_3)$ and Al_2O_3-$Bi_4Ti_3O_{12}$ on low-voltage etched aluminum foil were also studied [32, 33]. Nb-Ta-Al for Ta electrolytic capacitors was also tried as anode material [34].

A ceramic capacitor is a capacitor constructed of alternating layers of metal and ceramic, with the ceramic material acting as the dielectric. Multilayer ceramic capacitors (MLCs) typically consist of ~100 alternate layers of electrode and dielectric ceramics sandwiched between two ceramic cover layers. They are fabricated by screen-printing of electrode layers on dielectric layers and co-sintering of the laminate. Conventionally, Ag-Pd is used as the electrode material and $BaTiO_3$ is used as the dielectric ceramics [35, 36]. From 2000 onwards, the MLCs market has been growing in pace with the exponential development of communications. They are produced in the capacitance range of 10 μF (normally the range of Ta and Al electrolytic capacitors); they are highly useful in high frequency applications. Historically, a ceramic capacitor is a two-terminal non-polar device. The classical ceramic capacitor is the disc capacitor. This device predates the transistor and was used extensively in vacuum-tube equipment (e.g radio receivers) from c. a. 1930 through the 1950s and in discrete transistor equipment from the 1950s through the 1980s. As of 2007, ceramic disc capacitors are in widespread use in electronic equipment, providing high capacity and small size at low price compared to the other types.

The other ceramic materials that have been identified and used are $CaZrO_3$, $MgTiO_3$, $SrTiO_3$ etc. A typical 10 μF MLC is a chip of size (3.2 x 1.6 x 1.5 mm). Mn, Ca, Pd , Ag etc are some of the other internal electrodes used. Linear dielectrics and antiferroelectrics based o strontium titante have been developed for high voltage disk capacitors. These are applicable for MLCs with thinner layers because of their high coercive fields. One of the most critical material processing parameters is the degree of homogeneous mixing of additive in the slurry. The binder distribution in the green ceramic sheet, the degree of surface roughness, fine size nickel powder, formation of green sheet, electrode

deposition ad sheet stacking etc play a crucial role in the process technology. Any one of these facts if mishandled would result in the failure of the device. For instance, providing a roughess of 5 μm thick green sheet to 0.5 μm is mandatory so that a smooth contact surface with the inner nickel electrode can be established. This is a very important factor in avoiding the concentration of electric filed at asperities, where the charge emission from the electrode is accelerated, resulting in short failure. Conventional sheet/printing method has a technical limit of producing a thickness around 1 μm dielectric; in order to decrease the thickness further, thin film technologies like CVD, sputtering, plasma-spray etc has to be used [37].

The other types of capacitors are film capacitors which use thin polyester film and polypropylene film as dielectrics and meta-glazed capacitors which incorporate electrode plates made of film vacuum evaporated with metal such as Al. Films can be of polyester, polypropylene or polycarbonate make. Also capacitors are specified depending on the dielectric used such as polyester film capacitor, polypropylene capacitor, mica capacitor, metallized polyester film capacitor etc.
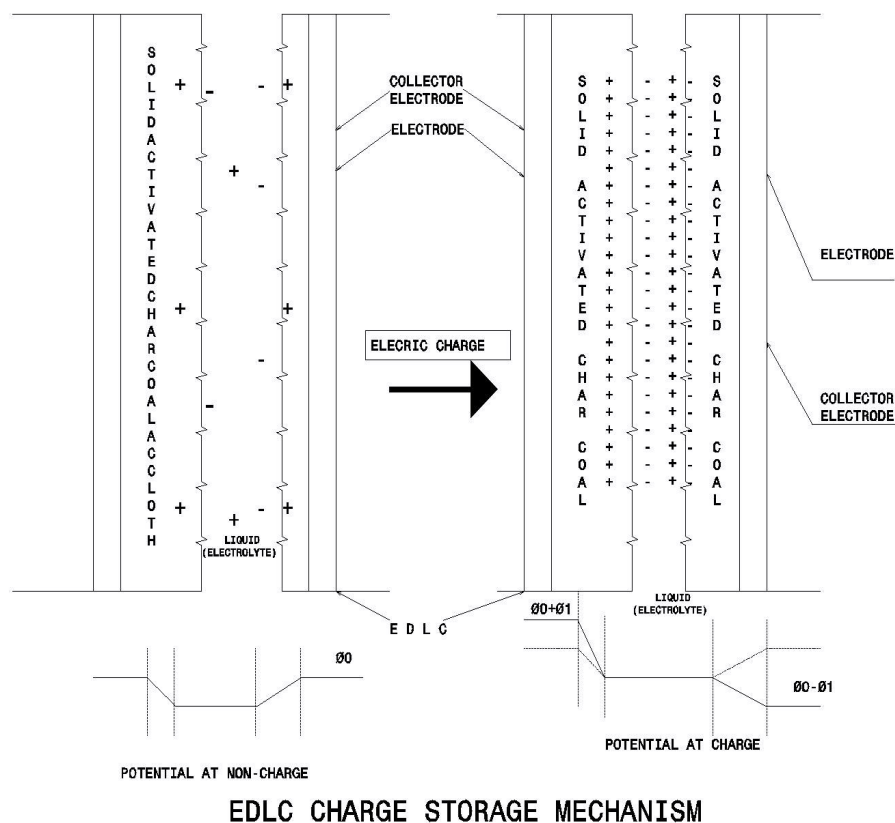

Figure 2. Charge storage mechanism of an EDLC cell under idle and charged conditions.

4. DOUBLE LAYER CAPACITORS

Electric/electrochemical double layer capacitor (EDLC) is a unique electrical storage device, which can store much more energy than conventional capacitors and offer much higher power density

than batteries. EDLCs fill up the gap between the batteries and the conventional capacitor, allowing applications for various power and energy requirements i.e., back up power sources for electronic devices, load-leveling, engine start or acceleration for hybrid vehicles and electricity storage generated from solar or wind energy. EDLC works on the principle of double-layer capacitance at the electrode/electrolyte interface where electric charges are accumulated on the electrode surfaces and ions of opposite charge are arranged on the electrolyte side. Fig. 2 shows the mechanism of charge storage in an EDLC cell and Fig. 3 shows the configuration of an typical EDLC cell.   There are two main types of double layer capacitors as classified by the charge storage mechanism: (1) electrical double-layer capacitor; (ii) electrochemical double layer capacitor or super/pseudo-capacitor [5, 7]. An EDLC stores energy in the double-layer at the electrode/electrolyte interface, whereas the supercapacitor sustains a Faradic reaction between the electrode and the electrolyte in a suitable potential window. Thus the electrode material used for the construction of the cell for the former is mainly carbon material while for the latter, the electrode material consist of either transition metal oxides or mixtures of carbon and metal oxides/polymers. The electrolytes can be either aqueous or non-aqueous depending on the mode of construction of EDLC cell.
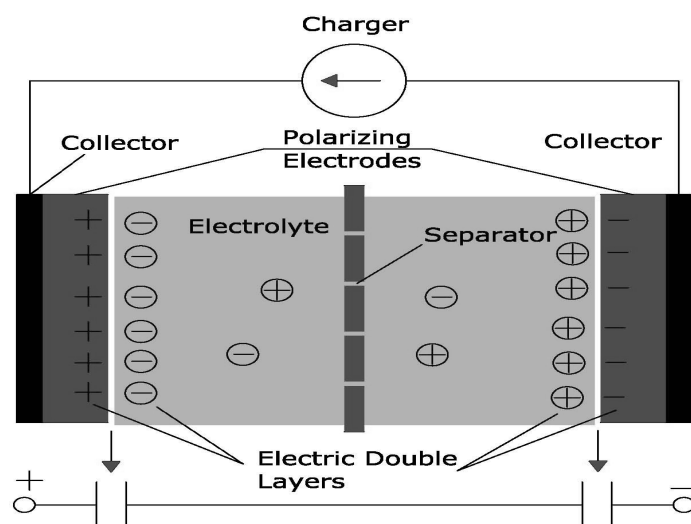

Figure 3. Typical configuration of an EDLC cell

There are two general directions of interest. One is the long term goal of the development of electrical propulsion for vehicles, and the other is the rapid growth of portable electronic devices that require power sources with maximum energy content and the lowest possible size and weight [9].

4.1. Electric double layer capacitor

Electric double layer capacitors (EDLCs) are defined as a sort of physical battery [38]. The EDLC has a pair of polarizable electrodes with collector electrodes, a separator, and an electrolyte

solution. Fig. 4 shows the ideal lab-scale construction of an EDLC cell. The capacitor is charged and the electrical energy stored in the capacitor is discharged at loads. An outline on the development, history and EDLC characteristics developed for power uses "UP-Cap" is described in brief in a review paper by S. Nomoto et al [11]. EDLCs based on carbon electrodes has been used for memory back-up device since 1978 for many electrical appliances like VCRs, camera etc. In 1980s, the EDLCs were used for the energy source to drive wrist watches with solar cells. In 1990s, they were used as actuator back-up sources for toys, electric appliances, home equipment etc. Recently, EDLCs with higher capacitances are under development for higher electric power sources in electric vehicle systems and electric power storage systems. Another interesting review on carbon materials that are used as electrodes in EDLCs is written by E. Frackowiak and F. Béguin; they have discussed about the different forms of carbon such as carbon aerogels, activated carbon and carbon nanotubes being used as the electrodes in EDLCs [10]. Typical electrochemical response of carbon nanotube in aqueous electrolyte is shown in Fig. 5 where the symmetrical and rectangular cyclic voltammetric curve is a trademark for double layer capacitance [39]. Theoretically, specific capacitance of an activated carbon is directly proportional to the specific surface area. However, in reality it does not happen. It was reported that the some activated carbons with smaller surface area give a larger specific capacitance than those with a larger surface area; for instance, M-30 with a BET surface area of 2571 m^2/g gave the specific capacity of 62.9 Fg^{-1} while M-30 with a BET surface area of 2130 m^2/g gave a specific capacity of 100 Fg^{-1} [40]. The relation between the surface area of the activated carbons and their electrochemical performance has been discussed by Shi et al [40, 41].
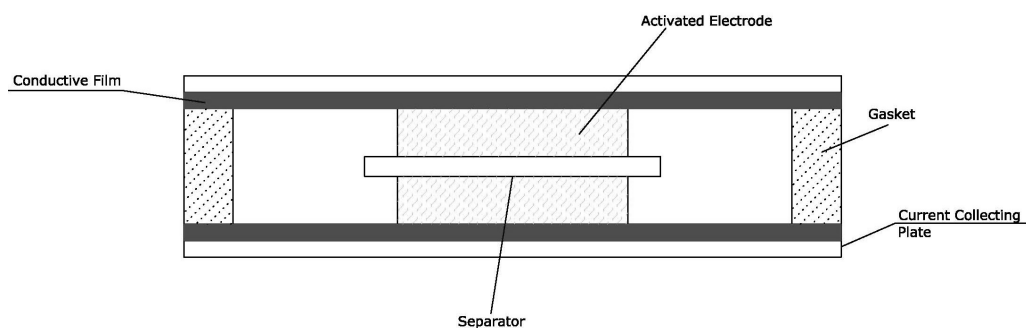
Figure 4. Typical lab-scale design and construction of EDLC.

On the influence of physical properties of activated carbons on the behavior of EDLCs, it was reported by M. Nakamura et al that the rest potential was not influenced by the precursors (phenolic resin, mineral oil, coconut shell and coal) or manufacturing methods and the electrochemical characteristics of the activated carbons depend on the oxygen content and the concentration of acidic surface functional groups [42]. For a series of nanopororus activated carbons prepared from bituminous coal, it was found that the gravimetric capacitance in KOH electrolyte depended not only

on the surface area of the activated carbons but also on the higher oxygen content [43]. However, it was shown that the electrochemical capacitance of nanoporous carbons also depends on the electrolyte; carbon nanotubes with micropores have higher capacitance in aqueous electrolytes while carbon aerogel with macropores have higher capacitance in ionic liquids. This fact implies that the specific capacitance of porous carbon depends on its matching degree to the applied electrolytes rather than its overall pore volume [44]. In another singularly interesting work, 25 samples of porous carbon materials were prepared from three different precursors and activated in alkali solution. The samples chemically activated with KOH were found to have higher oxygen content than the NaOH; a very good correlation between specific capacitance and CO-type oxygen groups has been found [45]. An elaborate review on carbon properties and their role in supercapacitors was published by A. G. Pandolfo and A. F. Hollenkamp; they concluded that factors like carbon structure, pore size, particle size, electrical conductivity and surface functionalities also influence the capacitance other than the surface area [46]. Twelve activated carbons were well-characterized for the variation of specific capacitance with current density and oxygen content and it decreases with increasing current density because of the resistance in pores due to the hindering of ion transfer in the randomly connected micropores [47].
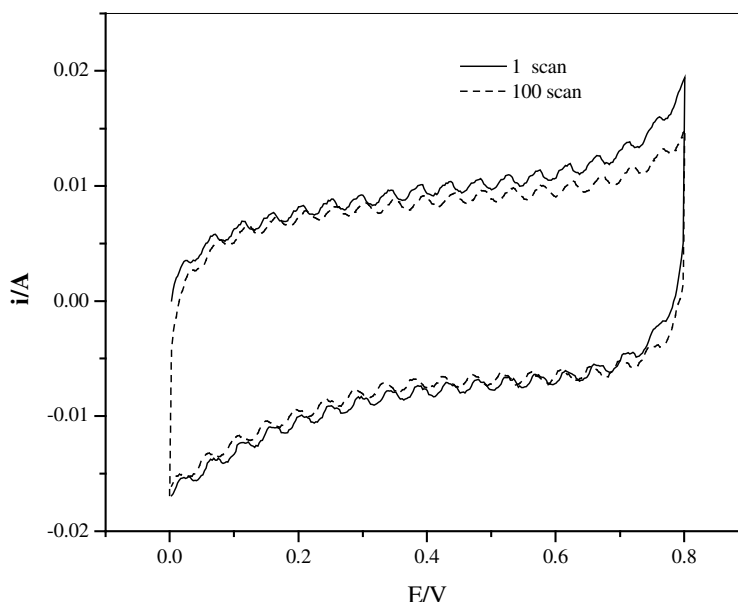
Figure 5. Cyclic voltammograms of CNT (carbon nanotubes) immobilized on paraffin impregnated graphite electrode and recorded in 0.1 M KCl solutions; Scan rate = 0.1 Vs^{-1} (Reproduced from ref. 41).

Various types of carbons that have been tried as electrodes in EDLCs can be summarized as: halloysite templated porous carbon [48], multi-branched porous carbon nanofibers [49], nano-structured graphite [50], bamboo-based activated carbon [51], woven C-cloth [52], carbon nanotubes

[53], nanostructured mesoporous carbon [5448], carbon nanotube/felt composite electrode [55], cresol-formaldehyde based carbon aerogel [56], mesoporous carbon composite (carbon nanofibres/porous carbon) [57], porous carbon from thermoplastic and MgO precursors [58], sodium oleate modified activated carbon aerogel [59,60], TiC-derived nanoporous carbon [61], silica MCM-48 templated mesoporous carbon [62], electrospun activated carbon nanofibres [63], silica MCM-48 and SBA-15 templated mesoporous carbon [64], carbon nanofiber and PEDOT-PSS bilayer systems [65], carbon blacks, vegetable/wood based activated carbons, activated novoloid fibres [66], activated needle coke from coal tar pitch [67], fullerene-soot [68], Nomex-derived activated carbon fibers [69], activated carbon nanotubes [70], polypyrrole and graphite composite [71], MSP 20 activated carbon: carbon black: PTFE [72], activated carbon-carbon nanotube composite porous film [73], polymer/carbon composites [74], mesoporous carbon spheres [75], pyrolized carbons from graphite oxides [76] and ketjen black/ carbon nanotube [77], Multi-walled and single-walled carbon nanotubes [78], exfoliated carbon fibers [79], carbon nanotubes /activated carbon [80], CNT array [81] and double walled CNT/activated carbon [82]. A comprehensive review on electrodes based on carbon nanotubes and activated crbon materials for supercapacitor application has been published recently by V. V. N. Obreja [8]. The capacitance values reported by each author depend on the origin and synthesis of carbon as well the type of electrolyte used to assimilate the electrode material.

4.2. Electrochemical double layer capacitor

Electrochemical double layer capacitor is also designated as supercapacitor or ultracapacitor or pseudocapacitor. When metal oxides/ metal oxide and carbon composite/conducting polymer and carbon composite are used as electrodes for the construction of EDLCs, the charge storage mechanism includes both double layer capacitance and pseudo capacitance which result in higher capacitance output and the EDLCs are termed as supercapacitors (SCs). One major disadvantage of carbon based EDLC is the lower specific stored energy. Most of available commercial products have a specific energy below 10 Wh/kg, whereas the lowest figure for batteries is 35-40 Wh/kg, in the case of lead-acid ones, but value as high as 150 Wh/kg is available for rocking chair lithium ion batteries.

Metal oxides present an attractive alternative as an electrode material because of high specific capacitance at low resistance, possibly making it easier to construct high energy, high power supercapacitors. The most beneficial metal oxide known to give very high capacitance is RuO_2. Pure RuO_xH_y is a mixed electron-proton conductor with a high specific capacitance from 720 to 900 F/g. Extensive research into ruthenium oxide has conducted for military applications, where cost is presumably less of an issue than it is for commercial ventures. Academic institutions have focused on searching for other cheaper materials instead of RuO_2. The rarity of this oxide is also main factor which diverted the researchers towards other transition metal oxides [7].

Some of the oxides which have been studied as SC electrode material are NiO, $Ni(OH)_2$, MnO_2, Co_2O_3, IrO_2, FeO, TiO_2, SnO_2, V_2O_5 and MoO. None of these oxides are used in commercial production of EDLCs and they are still in lab-scale research. There are reports on composite electrode materials which use mixture of one or two oxides along with carbon or polymer and investigated for

EDLC application. Combination of ruthenium oxide with other metal oxides in the form of thin foils is the initial attempt by many authors to fortify the research goal. TiO_2, MoO_3, VO_x, SnO_2, WO_3 and CaO are some of the oxides studied by this route [83-89]. In addition, there are many metal oxides and mixed metal oxides have been prepared and characterized for supercapacitor application by several authors. It is one of the most significant ongoing researches in the field of energy conservation systems in recent times. Vanadium pentaoxide (V_2O_5), in particular, has been widely examined as an electrode material for ECs that use organic electrolytes [90-92]. Since V_2O_5 has a modest electronic conductivity, composites with metal fibres or carbonaceous materials have been prepared in an attempt to improve electrode performance [93-98]. Amorphous, nanoporous and mesoporous forms of V_2O_5 have been synthesized in order to enhance the specific capacitance of the oxide and the performance was evaluated in KCl electrolytes; to a certain extent, these efforts were successful [99-101]. Composite electrodes of V_2O_5 thin layer on conductive materials, such as metal fibers or carbonaceous materials have recently attracted much attention as high rate intercalation electrodes for pseudocapacitor applications [102-107]. Analysis of recent reports on the transition metal oxides for pseudocapacitor applications indicates that high specific capacitance and rate capability could be obtained, especially when a small amount of metal oxide is uniformly dispersed on the conductive and porous carbonaceous materials with a very high surface area, due to the increased electrochemical utilization of the metal oxide and low concentration polarization of the electrolyte [108-113]. Vanadium oxide electrochemically deposited on carbon nanotubes has been elaborately studied in organic electrolytes for supercapacitor application by K.B. Kim research group [114, 115].
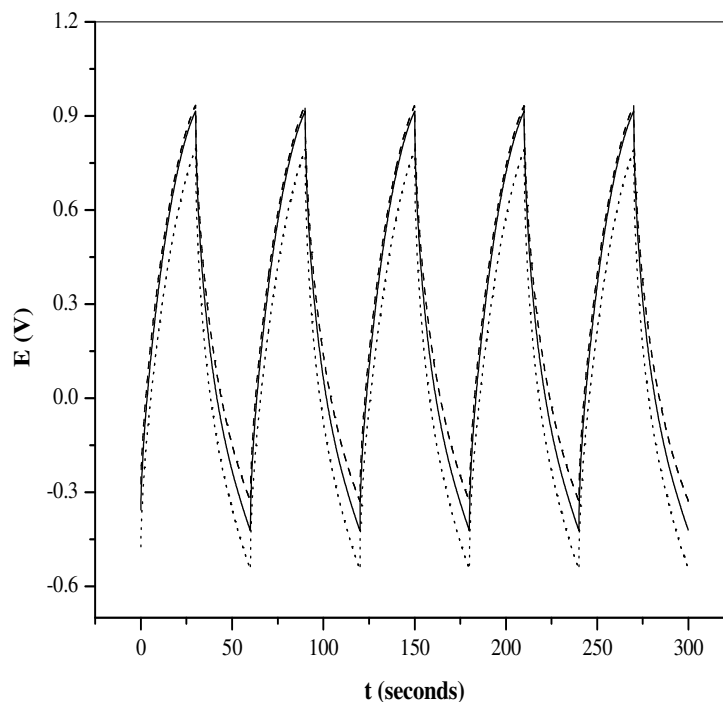

Figure 6. Galvanostatic charge-discharge curves of SnO_2-Al_2O_3 sample at different cycles; ....cycle 1; —— cycle 250; - - - - cycle 1000 (Reproduced from ref.123).

Other less studied oxide is tin oxide. There are relatively few publications available on this oxide. They are: tin oxide/carbon aerogel composite [116], Nano SnO [117], Sb-doped SnO_2, SnO_2–Fe_3O_4, SnO_2–RuO_2 [118], $30RuO_2$-$70SnO_2$ composite [119], amorhous nanostructured potentiodynamically deposited tin oxide [120], RuO_2-imprenated SnO_2 xerogel [121], SnO_2-V_2O_5, SnO_2-V_2O_5-CNT [122], SnO_2- Al_2O_3 and SnO_2- Al_2O_3-Carbon [123]. Typical galvanostatic charge-discharge curves obtained for SnO_2- Al_2O_3 electrode are shown in Fig. 6. Nickel oxide is the most copiously studied oxide; the reason being its use as anode in Ni-Cd, Ni-Fe, Ni-air secondary batteries and in fuel cells. It is a well studied oxide in view of its technologically important application in power sources. For super-capacitor application, it is been studied by several authors. Some examples are: mesoporous nickel oxide [124], nickel oxide/CNT nanocomposite [125], multiwalled CNT/nickel oxide porous composite [126], activated carbon/nickel oxide [127], nickel hydroxide/activated carbon composite [128], nanocrystalline NiO [129], activated carbon/nickel hydroxide with polymer hydrogel electrolyte [130], nickel oxide embedded titania nanotubes [131], Co_xNi_{1-x} layered double hydroxides [132], cobalt-nickel oxides/CNT composites [133], porous nickel/activated carbon [134], nickel-based mixed rare-earth oxide/ activated carbon [135], electrochemically deposited nickel hydroxide [136], nanoporous electrodeposited nickel oxide films [137], hexagonal nanoporous nickel hydroxide [138], spherical $Ni(OH)_2$/CNTs composite [139], nickel oxide/hydroxide nanoplatelets [140], ordered mesoporous nickel oxide [141], Me/Al layered double hydroxides (Me = Ni, co) [142], nickel oxide films on different substrates [143], urchin-like NiO nanostructures [144], porous carbon with impregnated nickel oxide [145], NiO_x xerogels [146], sol-gel derived nickel oxide films [147], electrodeposited $Ni(OH)_2$ films [148-152], NiO electrode via electrochemical route [153], NiO/CNT nanocomposite [154], nanosized NiO [155], aerogel-like mesoporous nickel oxide [156], nickel oxide porous electrode [157], nano-whiskers of nickel oxide [158] and nickel oxide /CNT [159].

Research work is channeled in this direction mainly because of the high specific capacitance obtained by using oxides like RuO_2 and IrO_2. These oxides are very expensive and available in scarce quantities. However, US military is using supercapacitors made of these oxides are used in missile and aerospace applications where cost is not the deciding factor. Many papers are published on this topic by several authors. It is been studied extensively as electrode material for supercapacitor application either as single oxide or mixed oxide; both with and without carbon as additive. Exclusive examples of relevant work are: Co_3O_4/$RuO_2.xH_2O$ [160], anodically deposited hydrous RuO_2 [161], anodically deposited porous RuO_2 [162], carbon/nanostructured Ru compoistes [163], Ru/multiwalled carbon nanotubes [164], hydrous ruthenium oxide [165], RuO_2-coated titanium electrodes [166], hydrous ruthenium oxide/ordered mesoporous carbon composites [167], carbon nanofibre/hydrous RuO_2 nanocompoiste [168], RuO_2/activated carbon composites [169], Ru-Sn oxide composites [170], spray deposited amorphous RuO_2 [171], RuO_2/ activated carbon composites [172], arrayed CN_xNT-RuO_2 nanocomposites [173], anodically deposited hydrous ruthenium oxide [174], binary Ru-Ti oxides [175], highly dispersed hydrous ruthenium oxide in polyacids [176], nanoparticulate rutile-type $Ru_{1-x}V_xO_2$ [177], nanocomposite films formed by loading carbon nanotubes with ruthenium oxide [178], RuO_2 in a proton exchange ionic liqud [179], RuO_2 film electrodes [180], $RuO_2. xH_2O$/NiO composite [181], RuO_2/TiO_2 nanotube composite [182, 183], $RuO_2. xH_2O$/carbon nanotube composite [184, 185], MnO_2 and RuO_2 [186], mesoporous anhydrous RuO_2 [187], activated carbon-semi-conducting oxide

composite [188], NiO-based composite electrode with RuO_2 [189], RuO_2/GC thin film electrode [190], Lead ruthenium oxide $Pb_2Ru_2O_{6.5}$ [191], cyclic voltammetrically deposited hydrous ruthenium oxide [192], polyaniline/Nafion/hydrous RuO_2 [193], Ru/carbon nanocomposite [194], catalytic modification of activated carbon fabrics by ruthenium chloride [195], layered lithium ruthenate [196], activated carbon based ruthenium oxide [197], hydrous ruthenium oxide [198], anodically deposited hydrous ruthenium oxide [199], electrochemically deposited nanograin ruthenium oxide [200], ruthenium oxide thin film electrode [201], ruthenium oxide-carbon composite [202], hydrous ruthenium oxide and hydrogen inserted ruthenium oxide [203], ruthenium oxide nanoparticles on carboxylated carbon nanotubes [204], electrodeposited RuO_2 on electrospun TiO_2 nanorods [205], electrodeposited ruthenium oxide film electrode [206], activated carbon-ruthenium oxide composite [207], coconut-shell based activated carbon-hydrous ruthenium oxide [208], Lead Pb/Ru pyrochlore ($Pb_2Ru_2O_{6.5}$) [209] and $SrRuO_3$ [210]. In most of the studies, H_2SO_4 is used as the electrolyte but the molarity remained a variable in each report.

Manganese oxide is yet another transition metal oxide studied as an electrode material for supercapacitor application. Manganese can be present in three different valence states and its oxides are highly complex. The theoretical capacitance of manganese oxides reaches to 1100 Cg^{-1} (from Mn (IV) to Mn (III)) but the electrochemical reversibility of redox transition of manganese dioxide is usually too low to be applicable and the pure manganese dioxide possess poor capacitive response due to its high resistance of bulk manganese oxide. In spite of this, manganese oxides are seen to be potential useful materials for pseudocapacitors not only due to their low cost but also to their environmental friendliness [211, 212]. Most of the manganese oxides reported in the literature showed specific capacitances as high as 600 F g^{-1} for thin films [213, 214] and 150-300 F g^{-1} [215-219] for powder based electrodes in aqueous electrolytes. Potentiodynamically co-deposited manganese oxide/carbon composite gave 410 F g^{-1} in 1.0 M Na_2SO_4 electrolyte [220]. At a loading level of 0.4-0.5 mg cm^{-2}, the specific capacitance of manganese oxide is reported to be between 150 and 250 F g^{-1} [221]. Prasad and Miura reported a capacitance value between 400 and 621 F g^{-1} for amorphous electrolytic manganese dioxide and MnO_2-based mixed oxides [219, 222]. A higher capacitance is expected for MnO_2-based supercapacitor electrodes [223]. In order to increase the material utilization, direct deposition of manganese oxide on a carbon host, such as active carbon, carbon nanotubes and mesoporous caron has been also studied [224-226]. Carbon-supported MnO_2 nanorods as the composite electrode gave a specific capacitance of 165 F g^{-1} while MnO_2 gave a higher value of 458 Fg^{-1} [227]. In another work on $MnO_2.xH_2O$/carbon aerogel composite electrode, the specific capacitance was reported to be 226 F g^{-1} when the loading amount of $MnO_2.xH_2O$ was 60% and the capacitance of carbon aerogel electrode alone was of lesser value i.e 112 F g^{-1} [228]. During the electro-oxidation of Mn/MnO starting films, it was found that the undisturbed base layer and the dense disturbed layer oxidize to Mn_3O_4 while the porous surface layer consisting of amorphous MnO_2 accounts for the pseudocapacitance behavior [229]. There are reports on manganese oxide/MWNTs composite electrode [230], manganese oxide coated on CNTs [231], polyaniline and manganese oxide in nanofibrous structures [232], cobalt-manganese oxide [233], polyaniline intercalated layered manganese oxide nanocomposite [234], CNT/polypyrrole/MnO_2 [235], hydrated Mn(IV)oxide-exfoliated graphite composite [236], cobalt-manganese oxide nanowire array thin film on Ti/Si

substrate [237], poly(3-methylthiophene)/MnO_2 composite [238], manganese oxide film electrodes prepared by electrostatic spray deposition [239], hydrothermally synthesized nanostructured MnO_2-based electrode [240], thin sputtered Mn films [241], manganese oxide/carbon composite [242], Co, Al substituted manganese oxides [243], manganese oxide/CNT composite [244], manganese oxide and polyaniline composite thin film [245], cathodically deposited manganese oxide films [246, 247] and manganese oxide films prepared by sol-gel process [248].

It was shown that manganese oxide can be used as positive electrode in EDLC construction but not as both positive and negative electrodes. The performance of capacitors based on manganese oxide is limited by the two irreversible reactions Mn(IV) to Mn(II) at the negative electrode and Mn(IV) to Mn(VII) at the positive electrode. An asymmetric manganese oxide/activated carbon capacitor working at 2 V in 2 M KNO_3 electrolyte was shown to give specific capacitances in the range of 170-230 F g^{-1} [249]. All solid state electrochemical capacitor fabricated with MnO_2 thin film electrode ad Cs HSO_4 proton-conductive electrolyte is reported for 150-180 ºC operation range [250]. Pseudocapacitive nature of $Ir_{0.3}Mn_{0.7}O_2$ electrode and manganese oxide prepared by anodic deposition is also established [251, 252].

Among the transition metal oxides, TiO_2 is non-toxic, inexpensive and available in abundance. It being an n-type semiconductor, the charges on the surface are more than the other regions due to the attractive contribution of the positively charged depletion region [253]. It has been tried as EDLC electrode material as an alternative or co-material for other metal oxides. Some examples are: tin oxide/carbon aerogel composite electrode [254], nanosize TiO_2 and activated carbon [255], hydrothermally synthesized Ru-Ti oxides [256], amorphous $Ru_{1-y}Cr_yO_2$ loaded on TiO_2 nanotubes [257], TiO_2(B)/activated carbon [258], metal double hydroxides (Co, Ni)/TiO_2 nanotubes composite electrode [259], RuO_2/TiO_2 nanotube composite [260,261], polythiophene and TiO_2 nanocomposite [262], Ti/RhO_x + Co_3O_4 [263], amorphous potentiodynamically deposited nanostructured tin oxide [264], RuO_2 impregnated SnO_2 xerogel [265] and Ru-Sn oxide composite [266].

Cobalt oxide is another battery electrode material that has been studied for supercapacitor application. These class of materials, which exhibit a current-voltage response similar to a double layer albeit with charge transfer process similar to batteries. There are three forms of cobalt oxide; cobaltous oxide (CoO), cobaltic oxide (Co_2O_3) and cobalt cobaltite (Co_3O_4). The most widely studied oxide for electrochemical capacitor application is the spinel Co_3O_4. Some of the publications based on this oxide are: cobalt metal coated with oxide film [267], radio-frequency sputtered cobalt oxide thin film [268], electrochemically precipitated cobalt oxide film [269], cobalt oxide xerogels [270], Co_3O_4 thin film by spray pyrolysis [271], cobalt-nickel oxide/CNT composite [272], amorphous cobalt oxide films [273], Mn-Co oxide [274], MWCNT/ Co_3O_4 [275], Co_xNi_{1-x}layered double hydroxides [276], Co(OH)$_2$ [277], chemically formed cobalt oxyhydroxide thin films [278], Mn-Co binary oxide [279], cobalt based layered double hydroxide nanosheet thin film electrodes [280], Co(OH)$_2$/USY composite and activated carbon electrodes [281], Co-Mn oxide [282], γ-Mo_2N/Co_3Mo_3N composite [283] and binary cobaltous nickel oxide [284]. In-situ synthesized ZnO/carbon [285] and chemically precipitated ZnO/carbon aerogel [286] are also tried as EDLC electrodes. Fig. 7 shows the cyclic voltammetric behavior of ZnO with and without carbon in aqueous electrolyte. Hydrous IrO_2 has also been studied as electrochemical capacitor electrode in aqueous electrolytes [287, 288].
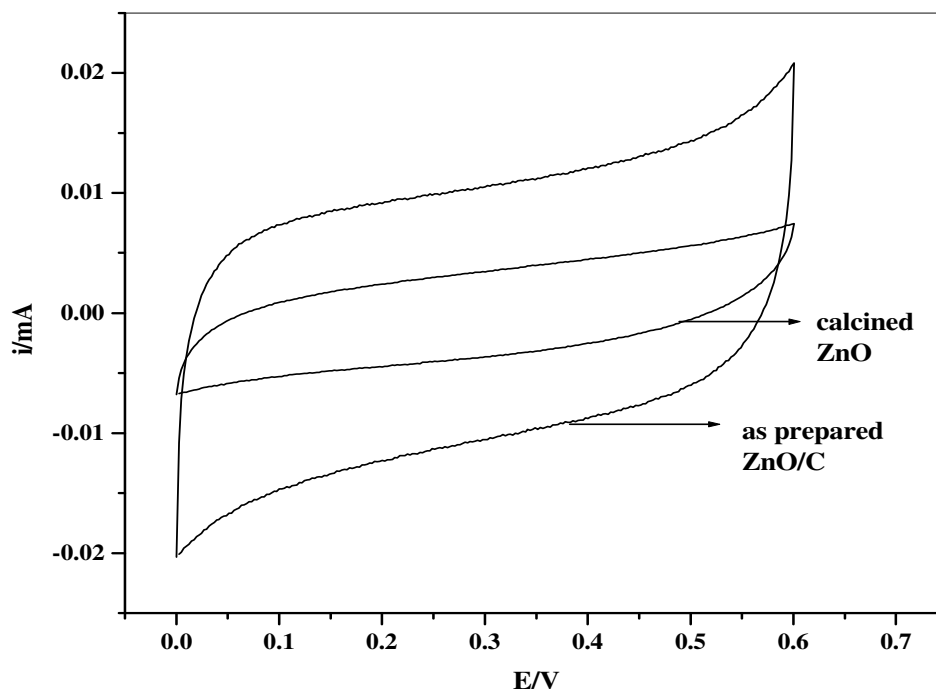
Figure 7. Cyclic voltammgorams of ZnO (with and without carbon) synthesized by combustion method using dextrose as carbon source and fuel (Reproduced from ref. 285).

5. CONCLUSIONS

According to a market survey by Montana, super capacitors are becoming a promising solution for brake energy storage in rail vehicles. The expected technological development outside railway sector is also shown to be highly dynamic: diesel electric vehicles, catenary-free operation of city light rail, starting system for diesel engines, hybrid-electric cars, industrial applications, elevators, pallet trucks etc. The time horizon expected for development is next 5 to 10 years. The main development goals will be,

- long life time
- increase of the rated voltage
- improvements of the range of operating temperature
- increase of the energy and power densities

Very recently, hybrid car is introduced in the market but it is turned to be very expensive and out of common man's reach. Shortage and cost of fossil fuels already instigated alternate technologies viable for traction purposes. In such a situation, EDLCs are also useful to store energy generated from non-conventional energy sources. A future possibility of service centers set up for EDLC supply similar to petrol (as on date) is not far as the main setbacks in technology development may take a decade for fruitful results.

References

1. A. Nishino, *J. Power Sources,* 60 (1996) 137.
2. S. Niwa, Y. Taketani, *J. Power Sources,* 60 (1996) 165.
3. B. E. Conway, Electrochemical Supercapacitors, Plenum/Kluwer publication, N. Y. 1999.
4. S. Sarangapani, B. V. Tilak, C. P. Chen, *J. Electrochem. Soc*. 143 (1996) 3791.
5. R. Kotz, M. Carlen, *Electrochim. Acta*, 45 (2000) 2483.
6. A. G. Pandolfo, A. F. Hollenkamp, *J. Power Sources* 157 (2006) 11.
7. A. Burke, *J. Power Sources*, 91 (2000) 37.
8. V. V. N. Obreja, *Physica E* (2007), doi:10.1016/j.physe.2007.09.044.
9. R. A. Huggins, *Solid State Ionics*, 134 (2000) 179.
10. E. Frackowiak, F. Béguin, *Carbon,* 39 (2001) 937.
11. S. Nomoto, H. Nakatu, K. Yoshioka, A. Yoshida**,** H. Yoneda, *J. Power Source,s* 97-98 (2001) 807.
12. V. Lehmann, W. Hönlein, H. reisinger, A. Spitzer, H. Wendt, J. Willer, *Thin Solid Films,* 276 (1996) 138.
13. F. Roozeboom, R. Elfrink, J. Verhoeven, J. van den Meerakker, F. Holthuysen, *Microelectron. Eng*. 53 (2000) 581.
14. M. Kemell, M. Ritala, M. Leskelä, E. Ossei-Wusu, J. Carstensen, H. Föll, *Microelectron. Eng* . 84 (2007) 313.
15. I. Nagata, Aluminum Dry Electrolytic Capacitors, Japan Capacitor Industry, Tokyo, 1983.
16. S. Niwa, Y. Taketani, *J. Power Sources*, 60 (1996) 165.
17. F. Larmat, J. R. Reynolds, Y. Qiu, *Syn. Metals*, 79 (1996) 229.
18. M. Satoh, H. Ishikawa, K. Amane, E. Hassegawa, K. Yoshino, *Syn. Metals,* 71 (1995)2259.
19. J. Li, J. -Z. Zhang, Y.-H. Geng, L.-X. Wang, X. -B. Jing, F.-S. Wang, *Syn. Metals*, 69 (1995) 245.
20. H. Yamamoto, M. Oshima, M. Fukuda, I. Isa, K. Yoshino, *J. Power Sources*, 60 (1996) 173.
21. M. Morita, Y. Matsuda, *J. Power Sources*, 60 (1996) 179.
22. M. Ue, M. Takeda, Y. Suzuki, S. Mori, *J. Power Sources*, 60 (1996) 185.
23. M. Masuda, S. Nanao, N. Masuko, T. Mochizuki, Keikinzoku/J. Jpn.Inst. *Light Metals*, 36 (10) (1986) 633.
24. M. Masuda, Y. Tanaka, Y. Watanabe, S. Nanao, T. Mochizuki, *Nippon Kinzoku Gakki*-si/J. Jpn. Inst. Metals, 52 (3) (1988) 336.
25. K. Watanabe, M. Sakairi, H. Takahashi, S. Hirai, S. Yamaguchi, *J. Electroanal*. *Chem*. 473 (1999) 250.
26. K. Watanabe, M. Sakairi, H. Takahashi, S. Hirai, S. Yamaguchi, *Electrochemistry*, 69(6) (2001) 407.
27. K. Watanabe, M. Sakairi, H. Takahashi, K. Takahiro, S. Nagata, S. Hirai, *J. Electrochem. Soc.* 148 (11) (2001) B473.
28. G. Lai*, J. Ceram. Soc. Jpn., Int. Ed*. 107 (12)(1999) 1221.
29. S. Park, B. Lee, *J. Electroceram*. 13 (2004) 111.
30. M. Shikanai, M. Sakari, H. Takashashi, M. Seo, *J. Electrochem. Soc*. 144 (8) (1997)2756.
31. H. Yamamoto, M. Oshima, T. Hisaka, I. Isa, *Syn. Metals* 104 (1999) 33.
32. Y. Xu, *Ceram. Int*. 30 (7) (2004) 1741.
33. X. Du, Y. Xu, *Surf. Coat. Technol*. (2007), doi:10.1016/j.surfcoat.2007.08.020
34. J. N. F. Holanda, U. U. Gomes, K. Strecker, *Mater. Character*. 43 (1999) 235.
35. Chun-Hway Hsueh, M. K. Ferber, *Composites Part A*, 33 (2002) 1115.
36. M. Pollet, S. Marinel, G. Desgardin, *J. Euro. Cera. Soc*. 24 (2004) 119.
37. Y. Sakabe, *Current Opinion in Solid State & Materials Science*, 2 (1997) 584.
38. B. E. Conway, Electrochemical Supercapacitors, NTS, 2001.
39. M. Jayalakshmi, M. Mohan Rao, N. Venugopal, Kwang-Bum Kim, *J. Power Sources*, 166 (2007) 578.

40. H. Shi, *Electrochim. Acta*, 41 (1996) 1633.
41. D. Qu, H. Shi, *J. Power Sources*, 74 (1998) 99.
42. M. Nakamura, M. Nakanishi, K. Yamamoto, *J. Power Sources*, 60 (1996) 225.
43. E. Raymundo-Piñero, K. Kierzek, J. Machnikowski, F. Béguin, *Carbon*, 44 (2006) 2498.
44. H. Liu, G. Zhu, *J. Power Sources*, 171 (2007) 1054.
45. M. J. Bleda-Martínez, J. A. Maciá-Agulló, D. Lozano-Castelló, E. Morallón, D.Cazorla-Amorós, A. Linares-Solano, *Carbon*, 43 (2005) 2677.
46. A. G. Pandolfo and A. F. Hollenkamp, *J. Power Sources*, 157 (2006) 11.
47. T. A. Centeno, F. Stoeckli, *J. Power Sources*, 154 (2006) 314.
48. G. Liu, F. Kang, B. Li, Z. Huang, X. Chuan, *J. Phys. Chem. Solids*, 67 (2006) 1186.
49. X. Y. Tao, X. B. Zhang, L. Zhang, J. P. Cheng, F. Liu, J. H. Luo, Z. Q. Luo, H. J. Geise, *Carbon*, 44 (2006) 1425.
50. E. Gomibuchi, T. Ichikawa, K. Kimura, S. Isobe, K. Nabeta, H. Fujii, *Carbon*, 44(2006) 983.
51. Y. J. Kim, B. J. Lee, H. Suezaki, T. Chino, Y. Abe, T. Yanagiura, K. C. Park, M. Endo, *Carbon*, 44 (2006) 1581.
52. J. Niu, W. G. Pell, B. E. Conway, *J. Power Sources*, 156 (2006) 725.
53. Y. T. Kim, T. Mitani, *J. Power Sources*, 158 (2006) 1517.
54. S. R. S. Prabaharan, R. Vimala, Z. Zainal, *J. Power Sources*, 161 (2006) 730.
55. J. M. Rosolen, E. Y. Matsubara, M. S. Marchesin, S. M. Lala, L. A. Montoro, S. Tronto, *J. Power Sources*, 162 (2006) 620.
56. Y. Zhu, H. Hu, W. C. Li, X. Zhang, *J. Power Sources*, 162 (2006) 738.
57. C. Hsieh, Y. Lin, *Micropor. Mesopor. Mater.* 93 (2006) 232.
58. T. Morishita, Y. Soneda, T. Tsumura, M. Inagaki, *Carbon*, 44 (2006) 2360.
59. Y. -Z. Wei, B. Fang, S. Iwasa, M. Kumagai, *J. Power Sources*, 141 (2005) 386.
60. Y. -Z. Wei, B. Fang, S. Iwasa, M. Kumagai, *J. Power Sources*, 155 (2006) 487.
61. M. Arulepp, J. Leis, M. Lätt, F. Miller, K. Rumma, E. Lust, A. F. Burke, *J. Power Sources,* 162 (2006) 1460.
62. C. Vix-Guterl, S. Saadallah, K. Jurewicz, E. Frackowiak, M. Reda, J. Parmentier, J. Patarin, F. Beguin, *Mater. Sci. Eng. B* 108 (2004) 148.
63. C. Kim, *J. Power Sources*, 142 (2005) 382.
64. W. Xing, S. Z. Qiao, R. G. Ding, F. Li, G. Q. Lu, Z. F. Yan, H. M. Cheng, *Carbon*, 44 (2006) 216.
65. A. K. C. Gallegos, M. E. Rincón, *J. Power Sources,* 162 (2006) 743.
66. O. Barbieri, M. Hahn, A. Herzog, R. Kötz, *Carbon*, 43 (2005) 1303.
67. S. Mitani, S. I. Lee, K. Saito, S. -H. Yoon, Y. Korai, I. Mochida, Carbon, 43 (2005) 2960.
68. M. Egashira, S. Okada, Y. Korai, J. -I. Yamaki, I. Mochida, *J. Power Sources*, 148 (2005) 116.
69. K. Leitner, A. Lerf, M. Winter, J. O. Besenhard, S. Viller-Rodil, S. Suárez-García, A. Martínez-alonso, J. M. D. Tasón, *J. Power Sources*, 153 (2006) 419.
70. Q. Jiang, M. Z. Qu, G. M. Zhou, B. L. Zhang, Z. L. Yu, *Mater. Lett*. 57 (2002) 988.
71. G. Dione, M. M. Dieng, J. J. Aaron, H. Cachet, C. Cachet, *J. Power Sources*, 170 (2007) 441.
72. I. Kim, S. Yang, S. Moon, H. Kim, *J. Power Sources*, 164 (2007) 964.
73. P. Taberna, G. Chevallier, P. Simon, D. Plée, T. Aubert, *Mater. Res. Bull*. 41 (2006) 478.
74. J. M. Pernaut, G. Goulart, *J. Power Sources*, 55 (1995) 93.
75. W. Li, D. Chen, Z. Li, Y. Shi, Y. Wan, G. Wang, Z. Jiang, D. Zhao, *Carbon*, 45 (2007) 1757.
76. I. Kim, S. Yang, M. Jeon, H. Kim, Y. Lee, K. An, Y. Lee, J. Power Sources, 173(2007) 621.
77. D. Tashima, K. Kurosawatsu, M. Uota, T. Karashima, M. Otsubo, C. Honda, Y. M. Sung, *Thin Solid Films*, 515 (2007) 4234.
78. E. Frackowiak, K. Jurewicz, S. Delpeux, F. Béguin, *J. Power Sources*, 97-98 (2001) 822.
79. Y. Soneda, M. toyoda, K. Hashiya, I. Yamashita, M. Kodama, H. Hatori, M. Inagaki, *Carbon*, 41 (2003) 2680.

80. Ch. Emmenegger, Ph. Mauron, P. Sudan, P. Wenger, V. Hermann, R. Gallay, A. Züttel, *J. Power Sources*, 124 (2003) 321.
81. Q. Chen, K. Xue, W. Shen, F. Tao, S. Yin, W. Xu, *Electrochim. Acta*, 49 (2004)4157.
82. C. Portet, P. L. Taberna, P. Simon, E. Flahaut, *J. Power Sources*, 139 (2005) 371.
83. H.K. Kim, O.W. Ok, T.Y. Seong, Y.S. Yoon, *J. Vac. Sci. Technol*. B 21(2003) 949.
84. W. Sugimoto, T. Shibutani, Y. Murakami, Y. Takasu, *Electrochem. Solid- State Lett*. 5 (2002) A170.
85. Y. Takasu, Y. Murakami, *Electrochim. Acta*, 45 (2000) 4135.
86. C. Angelinetta, S. Trasatti, L.D. Atanasoska, R.T. Atanasoski, *J. Electroanal.Chem*. 214 (1986) 535.
87. S. Trasatti, *Electrochim. Acta*, 36 (1991) 225.
88. S.L. Kuo, N.L. Wu, *Electrochem. Solid-Sate Lett*. 6 (2003) A85.
89. H.K. Kim, S.H. Choi, Y.S. Yoon, S.Y. Chang, Y.W. Ok, T.Y. Seong, *Thin Solid Films*, 475 (2005) 54.
90. W. Dong, D.R. Rolison, B. Dunn, *Electrochem. Solid-State Lett*. 3 (2000) 457.
91. T. Kudo, Y. Ikeda, T. Watanabe, M. Hibino, M. Miyayama, H. Abe, K. Kajita, *Solid State Ionics*, 152 (2002) 833.
92. G.X. Wang, B.L. Zhang, Z.L. Yu, M.Z. Qu, *Solid State Ionics*, 176 (2005) 1169.
93. H.P.Wong, B.C. Dave, F. Leroux, J. Harreld, B. Dunn, L.F. Nazar, *J. Mater. Chem*. 8 (1998) 1019.
94. M.J. Parent, S. Passerini, B.B. Owens, W.H. Smyrl, *J. Electrochem. Soc*. 146 (1999)1346.
95. S. Passerini, J.J. Ressler, D.B. Le, B.B. Owens, W.H. Smyrl, *Electrochim. Acta*, 44 (1999) 2209.
96. S. Suzuki, M. Hibino, M. Miyayama, *J. Power Sources*, 124 (2003) 513.
97. A. Dobley, K. Ngala, S. Yang, P.Y. Zavalij, M.S. Whittingham, *Chem. Mater*. 13 (2001) 4382.
98. J.S. Sakamoto, B. Dunn, *J. Electrochem. Soc*. 149 (2002) A26–A30.
99. H.Y. Lee, J.B. Goodenough, *J. Solid State Chem*. 148 (1999) 81.
100. Ravinder N. Reddy, Ramana G. Reddy, *J. Power Sources*, 156 (2006) 700.
101. Ravinder N. Reddy, Ramana G. Reddy, *J. Power Sources*, 132 (1–2) (2004) 315.
102. T. Kudo, Y. Ikeda, T. Watanabe, M. Hibino, M. Miyayama, H. Abe, K. Kajita, *Solid State Ionics*, 152 (2002) 833.
103. T. Watanabe, Y. Ikeda, T. Ono, M. Hibino, M. Hosoda, K. Sakai, T. Kudo, *Solid State Ionics*, 151 (2002) 313.
104. S. Suzuki, M. Hibino, M. Miyayama, *J. Power Sources*, 124 (2003) 513.
105. S. Passerini, J. J. Ressler, D. B. Le, B. B. Owens, and W. H. Smyrl, *Electrochim. Acta*, 44 (1999) 2209.
106. M. J. Parent, S. Passerini, B. B. Owens, W. H. Smyrl, *J. Electrochem. Soc*.146 (1999)1999.
107. W. Dong, J. Sakamoto, B. Dunn, *J. Sol-Gel Sci. Technol.*, 26 (2003) 641.
108. H. Kim, B. N. Popov, *J. Power Sources*, 104 (2002) 52.
109. J. H. Park, J. M. Ko, O. O. Park, *J. Electrochem. Soc.*, 150 (2003) A864.
110. K.-W. Nam, E.-S. Lee, J.-H. Kim, Y.-H. Lee, K.-B. Kim, *J. Electrochem. Soc.*, 152 (2005) A2123.
111. C.-C. Hu, W.-C. Chen, K.-H. Chang, *J. Electrochem. Soc.*, 151 (2004) A281.
112. I.-H. Kim, J.-H. Kim, K.-B. Kim, *Electrochem. Solid-State Lett*., 8 (2005) A369.
113. I.-H. Kim, J.-H. Kim, Y.-H. Lee, K.-B. Kim, *J. Electrochem. Soc.*, 152(2005)A2170.
114. Il-Hwan Kim, Jae-Hong Kim, Byung-Won Cho, Young-Ho Lee, Kwang-Bum Kim, *J. Electrochem. Soc*. 153 (2006) A989.
115. Il-Hwan Kim, Jae-Hong Kim, Byung-Won Cho, Kwang-Bum Kim, *J. Electrochem. Soc*. 153 (2006) A1451.
116. S.-W. Hwang, S.-H. Hyun, *J. Power Sources*, 172 (2007) 451.
117. M. Mohan Rao, M. Jayalaksmi, B. Ramachandra Reddy, S. S. Madhavendra, and M.

Lakshmi Kantam, *Chem. Lett*. 34 (2005) 712.

118. N.-L. Wu, *Mater. Chem. Phys*. 75 (2002) 6.

119. C.-C. Hu, K. -H. Chang, C.-C. Wang, *Electrochim. Acta*. 52 (2007) 4411.

120. K. R. Prasad, N. Miura, *Electrochem. Commun*. 6 (2004) 849.

121. N. L. Wu, S. L. Kuo, M. H. Lee, *J. Power Sources*, 104 (2002) 62.

122. M. Jayalakshmi, M. Mohan Rao, N. Venugopal, Kwang-Bum Kim, *J. Power Sources,* 166 (2007) 578.

123. M. Jayalakshmi, N. Venugopal, K. Phani Raja, M. Mohan Rao, *J. Power Sources,* 158 (2006) 1538

124. W. Xing, F. Li, Z. Yan, G. Q. Lu, *J. Power Sources*, 134 (2004) 324.

125. J. Y. Lee, K. Liang, K. H. An, Y. H. Lee, *Syn. Metals*, 150 (2005) 153.

126. Y. Zheng, M. Zhang, P. Gao, *Mater. Res. Bull*. 42 (2007) 1740.

127. G. Yuan, Z. Jiang, A. Aramata, Y. Gao, *Carbon*, 43 (2005) 2913.

128. Q. Huang, X. Wang, J. Li, C. Dai, S. Gamboa, P. J. Sebastian, *J. Power Sources*, 164 (2007) 425.

129. F. Zhang, Y. Zhou, H. Li, *Mater. Chem. Phys*. 83 (2004) 260.

130. S. Nohara, T. Asahina, H. Wada, N. Furukawa, H. Inoue, N. Sugoh, H. Iwasaki, C. Iwakura, *J. Power Sources*, 157 (2006) 605.

131. Y. Xie, L. Zhou, C. Huang, H. Huang, J. Lu, *Electrochim. Acta*, 53 (2008) 3643.

132. V. Gupta, S. Gupta, N. Miura, *J. Power Sources*, 175 (2008) 680.

133. Z. Fan, J. Chen, K. Cui, F. Sun, Y. Xu, Y. Kuang, *Electrochim. Acta*, 52 (2007) 2959.

134. V. Ganesh, S. Pitchumani, V. Lakshminarayanan, *J. Power Sources*, 158 (2008)1523.

135. H. Liu, P. He, Z. Li, Y. Liu, J. Li, *Electrochim. Acta*, 51 (2006) 1925.

136. E. E. Kalu, T. T. Nwoga, V. Srinivasan, J. W. Weidner, *J. Power Sources*, 92(2001) 163.

137. M. S. Wu, Y. A. Huang, C. H. Yang, J. J. Jow, *Int. J. Hyd. Energy*, 32 (2007) 4153.

138. D. D. Zhao, S. J. Bao, W. J. Zhou, H. L. Li, *Electrochem. Commun*. 9 (2007) 869.

139. X. F. Wang, D. B. Ruan, Z. You, *Trans. Non-ferrous Metal Soc. China*, 16 (2006) 1129.

140. M. S. Wu, H. H. Hsieh, *Electrochim. Acta*, 53 (2008) 3427.

141. D. D. Zhao, M. W. Xu, W. J. Zhou, J. Zhang, H. L. Li, *Electrochim. Acta*, 53 (2008)2699.

142. X. M. Li, Y. H. Zhang, X. G. Zhang, S. Y. Fu, *Electrochim. Acta*, 49 (2004) 3137.

143. M. Wu, J. Gao, S. Zhang, A. Chen, *J. Power Sources*, 159 (2006) 365.

144. X. Liu, X. Zhang, S. Fu, *Mater. Reser. Bull*. 41 (2006) 620.

145. Y. L. Tai, H. Teng, *Carbon*, 42 (2004) 2335.

146. J. Cheng, G. P. Cao, Y. S. Yang, *J. Power Sources*, 159 (2006) 734.

147. K. C. Liu, M. A. Anderson, *J. Electrochem. Soc*. 143 (1996) 124.

148. V. Srinivasan, J.W. Weidner, *J. Electrochem. Soc*. 144 (1997) L210.

149. V. Srinivasan, J.W. Weidner, *J. Electrochem. Soc*. 147 (2000) 880.

150. A.A.F. Grupioni, T.A.F. Lassali, *J. Electrochem. Soc*. 148 (2001) A1015.

151. V. Srinivasan, J.W. Weidner, *J. Power Sources* 108 (2002) 15.

152. K. Liang, A.Chen, L. He, W. Wang, *J. Mater. Sci. & Tech*. 18 (2002) 383.

153. K. W. Nam, K. B. Kim, *J. Electrochem. Soc*. 149 (2002) A 346.

154. K. W. Nam, C. W. Lee, K. B. Kim, *ESC 210th Meeting*, Abstract 1771.

155. M. G. Deng, B. C. Yang, Y. D. Hu, C. Gongcheng, *J. Mater. Eng*. 26 (2005) 319.

156. M. Wu, J. Gao, S. Zhang, A. Chen, *J. Porous Mater*. 13 (2006) 407.

157. M. A. Anderson, K. C. Liu, C. M. Mohr, *US Patent*, 5963417, 1999.

158. K. Rajendra Prasad, N. Miura, *Appl. Phys. Lett*. 85 (2004) 4199.

159. X. F. Wang, D. Z. Wang, L. Liang, *J. Inorg. Mater*. 18 (2003) 331.

160. Y. Liu, W. Zhao, X. Zhang, *Electrochim. Acta*, 53 (2008) 3296.

161 C. C. Hu, M. J. Liu, K. H. Chang, *Electrochim. Acta*, 53 (2008) 2679.

162. S. Mondal, N. Munichandraiah, *J. Power Sources*, 175 (2008) 657.

163. G. Cui, X. Zhou, L. Zhi, A. Thomas, K. Müllen, *New Carbon Mater*. 22 (2007) 302.
164. S. Yan, P. Qu, H. Wang, T. Tian, Z. Xiao, *Mater. Res. Bull*. (2007)- in press.
165. Y.Y. Liang, H. L. Li, X. G. Zhang, J. Power Sources, 173 (2007) 599.
166. V. V. Panić, T. R. Vidaković, A. B. Dekanski, V. B. Mišković-Stanković, B. Ž. Nikolić, *J. Electroanal. Chem*. 609 (2007) 120.
167. H. Li, R. Wang, R. Cao, *Micro. & Meso. Mater*. (2007)- in press.
168. B. J. Lee, S. R. Sivakkumar, J. M. Ko, J. H. Kim, S. M. Jo, D. Y. Kim, *J. Power Sources*, 168 (2007) 546.
169. Y. F. Su, F. Wu, L. Y. Bao, Z. H. Yang, *Carbon*, 45 (2007) 1378.
170. C. C. Hu, K. H. Chang, C. C. Wang, *Electrochim. Acta*, 52 (2007) 4411.
171. T. P. Gujar, V. R. Shinde, C. D. Lokhande, Woo-Young Kim, Kwang-Deog Jung, Oh-Shim Joo, *Electrochem. Commun*. 9 (2007) 504.
172. Y. F. Su, F. Wu, L. Y. Bao, Z. H. Yang, *New Carbon Mater*. 22 (2007) 53.
173. W. C. Fang, O. Chyan, C. L. Sun, C. T. Wu, C. P. Chen, K. H. Chen, L. C. Chen, J. H. Huang, *Electrochem. Commun*. 9 (2007) 239.
174. C. C. Hu, M. J. Liu, K. H. Chang, *J. Power Sources*, 163 (2007) 1126.
175. K. H. Chang, C. C. Hu, *Electrochim. Acta*, 52 (2006) 1749.
176. L. M. Huang, H. Z. Lin, T. C. Wen, A. Gopalan, Electrochim. Acta, 52 (2006) 1058.
177. K. Yokoshima, T. Shibutani, M. Hirota, W. Sugimoto, Y. Murakami, Y. Takasu, *J. Power Sources*, 160 (2006) 1480.
178. J. K. Lee, H. M. Pathan, K. W. Jung, O. S. Joo, *J. Power Sources*, 159 (2006) 1527.
179. D. Rochefort, A. L. Pont, *Electrochem. Commun*. 8 (2006) 1539.
180. A. V. Rosario, L.O. S. Bulhöes, E. C. Pereira, *J. Power Sources*, 158 (2006) 795.
181. F. Pico, J. Ibañez, T. A. Centeno, C. Pecharroman, R. M. Rojas, J. M. Amarilla, J. M. Rojo, *Electrochim. Acta*, 51 (2006) 4693.
182. Y. -G. Wang, Z. -D. Wang, Y. Y. Xia, *Electrochim. Acta*, 50 (2005) 5641.
183. W.Yong-gang, Z. Xiao-gang, *Electrochim. Acta*, 49 (2004) 1957.
184. G. H. Deng, X. Xiao, J. H. Chen, X. B. Zeng, D. L. He, X. F. Kuang, *Carbon*, 43 (2005) 1566.
185. X. Qin, S. Durbach, G. T. Wu, *Carbon*, 42 (2004) 451.
186. S. Wen, J.-W. Lee, I.-H.Yeo, J. Park, S.-I. Mho, Electrochim. Acta, 50 (2004) 849.
187. V. Subramanian, S. C. Hall, P. H. Smith, B. Rambabu, *Solid State Ionics*, 175 (2004)511.
188. H. Liang, F. Chen, R. Li, L. Wang, Z. Deng, *Electrochim. Acta*, 49 (2004) 3463.
189. X. M. Liu, X. G. Zhang, *Electrochim. Acta*, 49 (2004) 229.
190. W. Sugimoto, T. Kizaki, K. Yokoshima, Y. Murakami, Y. Takasu, *Electrochim. Acta*, 49 (2004) 313.
191. B. -O. Park, C. D. Lokhande, H. -S. Park, K.-D. Jung, O.-S. Joo, *Mater. Sci. commun*. 86 (2004) 239.
192. J. Wen, Z. Zhou, *Mater. Chem. Phys*. 98 (2006) 442.
193. R. K. Song, J. H. Park, S. R. Sivakkumar, S. H. Kim, J. M. Ko, D. Y. Park, S. M. Jo, D. J. Kim, *J. Power Sources*, 166 (2007) 297.
194. G.-Y. Yu, W. -X. Chen, Y. -F. Zheng, J. Zhao, X. Li, Z. -D. Xu, *Mater. Lett*. 60 (2000) 2453.
195. C. -C. Wang, C. -C. Hu, *Carbon*, 43 (2005) 1926.
196. Y. -Q. Zhao, G. -Q. Zhang, H. -L. Li, *Solid State Ionics*, 177 (2006) 1335.
197. X. F. Wang, D. Z. Wang, J. Liang, *Rare metal mater. & Eng*. 32 (2003) 424.
198. J. P. Zheng, P. J. Cygan, T. R. Jow, *J. Electrochem. Soc*. 142 (1995) 2699.
199. C. C. Hu, M. J. Liu, K. H. Chang, *Electrochim. Acta*, 53 (2008) 2679.
200. T.P. Gujar, W.Y. Kim, I. Puspitasari, K.-D. Jung, O.S. Joo, *Int. J. Electrochem. Sci*. 2(2007)666.
201. I.-H. Kim, K.-B. Kim, *Electrochem. Solid-State Lett*., 4 (2001) A62.
202. J. P. Zheng, *Electrochem. Solid-State Lett*., 2 (1999) 359.
203. T. R. Jow, J. P. Zheng, *J. Electrochem. Soc*. 145 (1998) 49.

204. Y. -T. Kim, K. Tadai, Ti Mitani, *J. Mater. Chem*. 15 (2005) 4914.
205. Y. R. Ahn, M. Y. Song, S. M. Jo, C. R. Park. D. Y. Kim, *Nanotechnology*, 17 (2006) 2865.
206. B. -O. Park, C. D. Lokhande, H. -S. Park, K.-D. Jung, O.-S. Joo, *J. Power Sources*, 134 (2004) 148.
207. C. -C. Wang, C. -C. Hu, *Mater. Chem. Phys*. 83 (2004) 289.
208. M. S. Dandekar, G. Arabale, K, Vijayamohanan, *J. Power Sources*, 141 (2005) 198.
209. F. Cao, J. Prakash, *J. Power Sources*, 92 (2001) 40.
210. P. M. Wilde, T. J. Guther, R. Oesten, J. Garche, *J. Electroanal. Chem*. 461(1999)154.
211. C. C. Hu, T. W. Tsou, *J. Power Sources*, 135 (2003) 179.
212. H. Kim, B. N. Popov, *J. Electrochem. Soc*. 150 (2003) D56.
213. S. C. Pang, M. A. Anderson, T. W. J. Chapman, *J. Electrochem. Soc*. 147 (2000)444.
214. S. F. Chin, S. C. Pang, M. A. Anderson*, J. Electrochem. Soc*. 149 (2002) A37.
215. Y. U. Jeong, A. Manthiram, *J. Electrochem. Soc.* 149 (2002) A1419.
216. M. Toupin, T. Brousse, D. Belanger, *Chem. Mater*. 14 (2002) 3946.
217. C. C. Hu, T. W. Tsou, *Electrochem. Commun*. 4 (2002) 105.
218. J. K. Chang, W. T. Tsai*, J. Electrochem. Soc*. 150 (2003) A1333.
219. K. R. Prasad, N. Miura, *J. Power Sources*, 135 (2004) 354.
220. E-H. Liu, X-Y. Meng, R. Ding, J-C. Zhou, S-T. Tan, *Mater. Lett*. 61 (2007) 3486.
221. E. R. Pinero, V. E. Khomenko, F. E. Beguin, *J. Electrochem. Soc*. 152 (2005) A229.
222. K. R. Prasad, N. Miura, *Electrochem. Commun*. 6 (2004) 1004.
223. M. Toupin, T. Brousse, D. Belanger, *Chem. Mater*. 16 (2004) 3184.
224. S. L. Kuo, N. L. Wu, *J. Power Sources*, 162 (2006) 1437.
225. X. Liu, S. Fu, C. Huang, *Powder Technol*. 154 (2005) 120.
226. Y. Xiong, Y. Xie, Z. Li, C. Wu, *Chem. Eur. J*. 9 (2003) 1645.
227. R. K. Sharma, H-S. Oh, Y-G.Shul, H. Kim, *J. Power Sources* 173 (2007) 1024.
228. J. Li, X. Wang, Q Huang, S. Gamboa, P. J. Sebeastian, *J. Power Sources,* 160 (2006) 1501.
229. B. Djurfors, J. N. Broughton, M. J. Brett, D. G, Ivey, *Acta Materialia* 53 (2005) 957.
230. G-X. Wang, B-L. Zhang, Z-L. Yu, M-Z. Qu, *Solid State Ionics*, 176 (2005) 1169.
231. S-B. Ma, K-W. Nam, W-S. Yoon, X-Q. Yang, K-Y. Ahn, K-H. Oh, K-B. Kim, *J. Power Sources*, 178 (2008) 483.
232. L-J. Sun, X-X. Liu, K.K-T. Lau, L. Chen, W-M. Gu, *Electrochim. Acta* 53 (2008)3036.
233. Q. Li, K-x Li, J-y Gu, H. Fan, *J. Phys. Chem. Solids*- in press
234. X. Zhang, L. Ji, S. Zhang, W. Yang, *J. Power Sources*, 173 (2007) 1017.
235. S. R. Sivakkumar, J. M. Ko, D. Y. Kim, B. C. Kim, G. G. Wallace, *Electrochim. Acta*, 52 (2007) 7377.
236. C. Wan, K. Azumi, H. Konno, *Electrochim. Acta,* 52 (2007) 3061.
237. G-Y. Zhao, C-L. Xu, H-L. Li, *J. Power Sources*, 163 (2007) 1132.
238. E. C. Rios, A. V. Rosario, R. M. Q. Mello, L. Micaroni, *J. Power Sources,* 163 (2007) 1137.
239. Y. Dai, K. Wang, J. Zhao, J. Xie, *J. Power Sources,* 161 (2006) 737.
240. V. Subramanian, H. Zhu, B. Wei, *J. Power Sources* 159 (2006) 361.
241. J. N. Broughton, M. Brett, *Electrochim. Acta* 49 (2004) 4439.
242. J-K Chang, Y-L Chen, W-T Tsai, *Electrochem. Commun*. 6 (2004) 666.
243. E. Machefaux, T. Brousse, D. Belanger, D. Guyomard, *J. Power Sources,* 165 (2007) 651.
244. Z. Fan, J. Chen, M. Wang, K. Cui, H. Zhou, Y. Kuang, *Diamond & Related Materials,* 15 (2006) 1478.
245. Z. Zhou, N. Cai, Y. Zhou, *Mater. Chem. Phys*. 94 (2005) 371.
246. J. Wei, N. Nagarajan, I. Zhitomirsky, *J. Mater. Process. Technol*. 186 (2007) 356.
247. N. Nagarajan, M. Cheong, I. Zhitomirsky, *Mater. Chem. Phys*. 103 (2007) 47.
248. C-K Lin, K-H Chuang, C-Y Lin, C-Y Tsay, C-Y Chen, *Surf.& Coat. Tech.*- in press.
249. V. Khomenko, E. Raymundo-Piñero, F. Béguin, J. Power Sources 153 (2006) 183.

250. Y. Kuzuoka, C-j Wen, J. Otoma, M. Ogura, T. Kobayashi, K. Yamada, H. Takahashi, *Solid State Ionics*, 175 (2004) 507.
251. A. A. F. Grupioni, E. Arashiro, T. A. F. Lassali, *Electrochim. Acta*, 48 (2002) 407.
252. J-K Chang, Y-L Chen, W-T Tsai, *J. Power Sources* 135 (2004) 344.
253. F. Fabregat-Santiago, I. Mora-Seró, G. Garcia-Belmonte, J.Bisquert, *J. Phys. Chem. B* 107 (2003) 758.
254. S-W Hwang, S-H Hyun, *J. Power Sources*, 172 (2007) 451.
255. H. Liang, F. Chen, R. Li, L. Wang, Z. Deng, *Electrochim. Acta,* 49 (2004) 3463.
256. K-H Chang, C-C Hu, Electrochim. Acta 52 (2006) 1749.
257. G. Bo, Z. Xiaogang, Y. Changzhou, L. Juan, Y. Long, *Electrochim. Acta,* 52 (2006) 1028.
258. T. Brousse, R. Marchand, R-L. Taberna, P. Simon, *J. Power Sources,* 158 (2006)571.
259. H. KuanXin, Z. Xiaogang, L. Juan, *Electrochim. Acta,* 51 (2006) 1289.
260. Y-G. Wang, Z-D Wang, Y-Y Xia, *Electrochim. Acta,* 50 (2005) 5641.
261. W. Yong-gang, Z. Xiao-gang, *Electrochim. Acta*, 49 (2004) 1957.
262. N. Hebestreit, J. Hofmann, U. Rammlt, W. Plieth, *Electrochim. Acta,* 48 (2003)1779.
263. A. R. de Souza, E. Arashiro, H. Golveia, T. A. F. Lassali, *Electrochim. Acta,* 49 (2003) 2015.
264. K. R. Prasad, N. Miura, *Electrochem. Commun*. 6 (2004) 849.
265. N. L. Wu, S. L. Kuo, M. H. Lee, *J. Power Sources,* 104 (2002) 62.
266. C-C Hu, K-H Chang, C-C Wang, *Electrochim Acta,,* 52 (2007) 4411.
267. T. -C. Liu, W. G. Pell, B. E. Conway, *Electrochim Acta,* 44 (1999) 2829.
268. H-K. Kim, T.Y. Seong, J. H. Lim, W.L. Cho, Y. S. Yoon, *J. Power Sources,* 102(2001) 167.
269. V. Srinivasan, J. W. Weidner, *J. Power Sources,* 108 (2002)15.
270. C. Lin, J. A. Ritter, B. N. Popov, *J. Electrochem. Soc*. 145 (1998) 4097.
271. V. R. Shinde, S. B. Mahadik, T. P. Gujar, C. D. Lokhande, *Appl. Surf. Sci*. 252 (2006) 7487.
272. Z. Fan, J. Chen, K. Cui, F. Sun, Y. Xu, Y. Kuang, *Electrochim Acta,* 52 (2007)2959.
273. S. G. Kandalkar, C. D. Lokhande, R. S. Mane, S-H. Han, *Appl. Surf. Sci*. 253 (2007)3952.
274. J-K. Chang, W-C. Hsieh, W-T. Tsai, *J. Alloys and Comp*.- in press
275. Y. Shan, L. Gao, *Mater. Chem. Phys*. 103 (2007) 206.
276. V. Gupta, S.Gupta, N. Miura, *J. Power Sources,* 175 (2008) 680.
277. Wang, Xiao-Feng, You Zheng, Ruan Dian-Bo, *Chinese J. Chem*. 24 (2006) 1126.
278. S. G. Kandalkar, J. L. Gunjakar, C. D. Lokhande, *Appl. Surf. Sci*. (2008),doi:10.1016/j.apsusc.2008.02.163.
279. J-K. Chang, M-T. Lee, C-H Huang, W-T. Tsai, *Mater. Chem. Phys*. 108 (2008) 124.
280. Y. Wang, W. Yang, C. Chen, D. G. Evans, *J. Power Sources*- in press.
281. Y-Y. Liang, H-L. Li, X-G. Zhang, *Mater. Sci. and Eng*. 473 (2008) 317.
282. Q. Li, K-x. Li, J-y Gu, H. Fan, *J. Phys. Chem. Solids* - in press.
283. C. Chen, D. Zhao, D. Xu, X. Wang, *Mater. Chem. Phys*. 95 (2006)84.
284. C.-C. Hu, C.-Y. Cheng, *Electrochem. Solid-State Lett*. 5 (2002) A43-A46.
285. M. Jayalakshmi, M. Palaniappa, K. Balasubramanian *Int. J. Electrochem. Sci.,* 3 (2008) 96.
286. D. Kalpana, K. S. Omkumar, S. Suresh Kumar, N. G. Renganathan, *Electrochim. Acta*, 52 (2006) 1309.
287. C. C. Hu, Y. H. Huang, K. H. Chang, *J. Power Sources*, 108 (2002) 117.
288. A. A. F. Grupioni, E. Arashiro, T. A. F Lassali, *Electrochim. Acta*. 48 (2002) 407.