FUTURE ELECTRODE MATERIALS FOR SUPERCAPACITORS IN INTELLIGENT WIRELESS SENSOR SYSTEM

H. Staaf\(^1\), P. Enoksson\(^1\), P. Lundgren\(^1\)

\(^1\)Chalmers University of Technology; Gothenburg, Sweden

**Abstract** - In this paper we present how and why supercapacitors is better to use in a wireless sensor system and a theoretical model for max surface area and capacitance for supercapacitors with carbon electrode materials. The goal of the model is to see what materials are promising to gain a higher energy density for a Electrochemical double layer capacitors, this will benefit the energy storage in wireless intelligent sensor system.

**Keywords** : Carbon Electrode, Supercapacitor, intelligent wireless sensor

**Introduction**

An intelligent wireless sensor (IWS) is an autonomous device with internal computing capability and wireless communication that can be combined with harvesters that scavenge energy from the surrounding or use stored energy. Today we have battery powered or wired sensors that give us different kinds of data from our surrounding. In the near future we want to place several of these sensors in remote places or built into structures which will make it hard to maintain them [1]. The answer for these wireless sensors to be powered has so far been to rely on batteries, fuelcells or supercapacitors. These solutions give them a limited lifetime and the sensors will mostly send data if it is really necessary to save energy and by that extending their lifetime. A common sensor is wired and could be in an airplane, car or in a construction like a bridge. In a car you have many sensors and hence a great deal of wires which makes the car more expensive to produce plus that different sensors needs different wire length which add up to the pile of cables that is produced. The combination of battery and cable consumption makes the idea of using a wireless sensor system and a theoretical model for max surface area and capacitance for supercapacitors with carbon electrode materials.

**Energy storages**

For storing the harvested energy for the wireless sensor, the storage need to fulfill some properties.

- Long life cycle, because the energy storage will be charged and recharged
- A good energy density
- A low self-discharge

Possible candidates for energy storage are fuel source in a micro fuelcells, batteries and supercapacitors. Micro fuelcells have a good energy density and low self-discharge, but can’t be recharged by any harvester today. A battery has a good energy density but a limited lifecycle of in absolute best case 10000 and won't sustain for long usage. Supercapacitors have a very long cycle of their energy harvesters and the electrochemical double layer capacitors have a very long lifecycle, more than \(10^6\) times. The lifetime of an IWS depending on where it is placed e.g a bridge, could be up to 100 years or higher.

During that time the positive electrode of a battery will be depleted, while the supercapacitor still will be intact and functioning. Used over time a supercapacitor will outmatch a battery in life cycles and accumulated energy density. The energy density of a battery today is \(240\ W/kg\) and for a supercapacitor it is \(9\ W/kg\). An optimistic calculation of a battery recharge cycle will be \(10000\) which will yield a energy density of \(2,4*10^6\ W/kg\), a supercapacitor with EDLC will reach \(10^6\) and will reach \(9*10^6\ W/kg\).

**Supercapacitors**

A supercapacitor or ultracapacitor is an electrochemical capacitor with a very high capacitance. In 1957 a patent filed by General Electric explained the manufacturing of a device that used porous carbon electrodes with sulfuoric acid between the electrodes [2]. After further development supercapacitors have been used since the mid-seventies as an energy storage device in clock chips and for computer memory. Furthermore, supercapacitors have become useful for wireless communications and are used as a power devices for different applications like recovering brake energy to improve energy efficiency in a battery diesel systems [3]. The energy density of a supercapacitor defines how long the supercapacitor can deliver its energy and depends on the capacitance and voltage, if either or both are raised the energy density will be improved. Energy density (E), capacitance (C), charges (Q), voltage (V)

\[ E = \frac{CV^2}{2} = \frac{QV}{2} \quad P = \frac{V^2}{4RS} \]

The power density of a supercapacitor defines how fast it can be discharged and depends on the voltage and the
equivalent series of resistances, the latter is to be kept to a minimum for high power density. Power density (P), equivalent series of resistences (R_s)

Supercapacitors can be divided into two different types [4]: 1) electrochemical double-layer capacitors which store their energy by pure electrostatic charge at the interface between an electrode and an electrolyte. 2) supercapacitors based on pseudocapacitance which relies on adsorption of active ion or arises from a Faradaic redox reaction which takes place at a transition metal oxide surface or in a doped electrically conducting polymer. These two storage methods are more easily described one by one even though both are being used in a supercapacitor; depending on the design of the supercapacitor, one is more dominant than the other.

**Electrochemical double layer capacitors**

Electrochemical double layer capacitor (EDLC) stores their charge electrostatically[5]. Therefor it is no transfer of charge between the electrolyte and electrode. The earliest model of the electrical double layer was made by Helmholtz. He treated the EDLC as similar to a conventional capacitor, which are two layers of opposite charges that forms at the interface of the electrode and electrolyte which is separated by an atomic distance. For an EDLC an electrolyte is either an aqueous, nonaqueous liquid or a solid material like a conducting polymer. The charged ions are ordered in an array. Helmholtz model was modified by Gouy and Chapman who looked at the continuous distribution of cations and anions in the electrolyte. The distribution is driven by thermal motion and this layer is called the diffusion layer. The Gouy-Chapman model of the double layer overestimated the capacitance of the electrochemical double layer capacitor, due to the assumption of point charges at the electrode surface. Later Stern was treating this problem by suggesting the combination of the Helmholtz and Gouy-Chapman models, giving an internal Stern layer, which is a Helmholtz layer, and an outer diffuse layer. This model states that ions has a finite size, hence sets a geometrical limit to the region of adsorption in the Helmholtz layer and the total capacitance is a series of capacitances for the layers: $$\frac{1}{C_{\text{G}}} = \frac{1}{C_{\text{H}}} + \frac{1}{C_{\text{diff}}}$$

**Material requirement**

Materials used in a supercapacitor as electrodes have some important properties required. The amount of charges that can be stored and the capacitance depends on the electrode material. In order to increase those parameters a material for an electrochemical electrode in a supercapacitor, has to fulfill a number of properties:

- Long stable life cycle (>10^5)
- Resistance to electrochemical reduction or oxidation of the electrode surface
- High surface area (1000+ m² g⁻¹)
- Thermodynamic stability beyond the potential window for operation
- A mean to control the pore size and distribution of the material
- Surface wettability
- Mechanical resilience

**Pores and their impact**

The most common used electrode material is active carbon. For active carbon the surface area is dependent on pore distribution and pore size. There are three different types of pores that have distinguishable impact on the capacitance for the electrode. Macropores have a size of more than 50 nm and are to a lesser extent useful for the electrode and electrolyte. A significant disadvantage is that macropores takes up valuable volume where additional surface area would be a better option. Mesopores are 2-50 nm in size and have an important role since they provide good conductivity for the electrolyte [6]. An electrolyte with high viscosity is dependent on an ordered mesopore structure. Or if a high energy power is a priority a well ordered mesopore structure is also desired. Finally micropores have a size less than 2 nm and studies shows that micropores are important for a high surface area which leads to a higher energy density [7]. Depending on how the carbon electrode is manufactured different pores are favored, for some materials micro and mesopores get closed for the electrolyte or the micropores are too small for the electrolyte ions. The importance of pores cannot be underestimated for future electrode materials and research is to be done on an optimized pore distribution in combination with a way to control distribution.

**Electrochemical double layer electrode materials**

**Activated carbon**

Activated carbon is used as electrode material commercially today. Activated carbon has a high surface area and is easy to produce plus cost effective compared to other materials and carbon variants. Activated carbon contains all three pore sizes. It is the micro and mesopores that contributes to the capacitance. And micropores of size 0.7-0.8 nm conducts to a higher capacitance [8]. The drawback of activated carbon is its limited energy density, which today keeps supercapacitor back as a challenger against batteries. This because of limited control of pore structure and the control of pore size when manufacturing activated carbon.

**Templated carbon**

A way to control the pore size and pore distribution is to use templated carbon. By using different silicon templates, different pore structures can be manufactured and gives a better control of which pore size is domi-
nant. Since templated carbon gives better control over pore size and distribution it can be tailored to fit an electrolyte more sufficient than activated carbon. The main drawback with template carbon is that it is more costly to produce than activated carbon and needs lengthy preparations during manufacturing process [2].

**Carbon aerogels**

Carbon aerogel has a high specific surface area and good electrical conductivity. But due to a disordered structure with closed pores the carbon aerogel performance is poor and not suitable as an electrode material in an EDLC, this unless more thorough research is done resulting access to the closed pores can be made [9].

**Carbon fibres**

Carbon fibres benefit a high accessible surface area 3000 m²g⁻¹ and results shows a capacitive performance of 371 Fg⁻¹ with KOH electrolyte [10]. The drawback with a high surface area is that it suffers from local high concentration of functional groups which can lead to stability problems under prevalent cycling. And so far just poor lifecycle results have been reported.

**Carbon nanotubes (CNT)**

Carbon nanotubes can be either single walled carbon nano tubes (SWCNT) or multiwalled carbon nano tubes (MWCNT). CNT has a high electrical conductivity and very good mechanical and thermal stability which is beneficial for a high power density [11]. CNT can be combined with carbon aerogels.

**Composite electrode materials**

An alternative way to raise the capacitance is to combine materials and by that gain a larger potential gap and improve the capacitance. By coating polymers on different carbon structures the meananchile resilience is improved, which theoretically will increase the lifecycle of the polymer, alternative a transition metal can be coated on a carbon substrate. Another promising material is carbon nano tubes bundled with carbon aerogel. It has a high surface area of 1056 m²g⁻¹ and a measured capacitance of 524 F g⁻¹. This promising composite needs more research on preparation procedures since it is difficult to prepare today [19]. It is using the double layer for energy storage so its lifecycle and fast recharge ability looks promising. So far no reports on long lifecycles have been presented and more research on composite electrode materials is needed.

**Max theoretical surface area and capacitance for EDLC with carbon electrode**

The structure of activated carbon can be illustrated as a fullerene-related structure, build with rings containing 5 to 7 atoms where the ring forms a micropore. Assuming that 1 g of carbon has an amount of atoms which are put together how big would that surface area be? The bonding radii of van der Waal is 170 pm. The surface area of a carbon atom: \( A = 4\pi r^2 = 4\pi (170 \times 10^{-12})^2 = 3.63168111 \times 10^{-19} \) m². One carbon atom = 12,01115 u so: 1 g of carbon contains:

\[
\frac{6.0221367 \times 10^{23}}{12,01115} = 5,013786047 \times 10^{22} \text{ atoms}
\]

1 g of carbon has a surface area of:

\[
A_c = 5,013786047 \times 10^{22} \times 3,63168111 \times 10^{-19} = 18208 \text{ m}^2
\]

which is a theoretical max if the carbon atoms don’t have any bonds with each other. A theoretical material where one carbon atom has a bond with two other carbon atoms will half the theoretical max to 9104 m². This material will look like a long string of connected atoms, with a structure that has optimal surface area. If this material were to be used as electrode material in an EDLC we have:

\[
C = \frac{\varepsilon_r \varepsilon_0 A}{d} = \frac{9.3 \times 8.85 \times 10^{-12} \times 9104}{2 \times 10^{-10}} = 3746 \text{ F g}^{-1}
\]

\( \varepsilon_r = 9.3 \) for KOH, \( \varepsilon_0 = 8.85 \times 10^{-12} \), \( d = 2 \times 10^{-10} \text{ m} \) (distance of the double layer), \( A = 9104 \text{ m}^2 \) (theoretical max area). A theoretical max surface area of 9104 m² gives a max theoretical capacitance of 3746 F g⁻¹ if KOH is used as electrolyte. With these parameters we assume that all atoms are accessible for an electrolyte and that the electrolyte has a sufficient amount of ions. In Figure 1 measured capacitances are plotted against measured surface areas and the theoretical max material is of course the highest value. As seen different carbon electrode materials with high surface area doesn’t yield a higher capacitance. The way to get a higher capacitance hence a higher energy density seems to be more promising, looking at composite carbon materials. Which show a much higher capacitance at a fairly low surface area. An electrode for a supercapacitor used in a wireless sensor system would benefit from a well-ordered pore structure that utilizes the double layer for a higher capacitance combined with composite electrode material. The EDLC also benefits a long lifecycle and fast rechargeability.

**Carbon as electrode material from an intelligent wireless sensor point of view**

An electrode made of carbon utilizes the double layer as energy storage mechanism. Commercial EDLC today uses different carbon structures as electrode since it has good traits such as:

![Figure 1 Capacitance plotted against surface area for electrodes with carbon or composite carbon](image-url)
- Cost effective as material
- Cost effective to produce as activated carbon
- Easy to produce activated carbon
- Carbon due to the electrostatic energy storage has a long lifecycle

The shortcoming of carbon as electrode material is since it uses the double layer it has a poor energy density compared to batteries. Research shows that micropores contributes to the energy density and therefore the carbon electrode material research has been aimed towards a larger surface area to increase the capacitance and hence the energy density. Even though the theoretical and measured surface area is very high for some carbon varieties the measured capacitance is much lower than expected. A lot of today’s research on supercapacitor is aimed at getting higher energy density using so-called pseudocapacitance, while that is good it doesn’t directly profit anything for a wireless sensor system since the life cycle are significantly lower for a pseudocapacitive supercapacitor than for a double layer based one. A wireless sensor system might need to have an energy source that lasts for a reasonable amount of time, when the system can’t harvest its energy from the surrounding. Considering the last years of research on supercapacitors, results displays that one single material carbon electrode not seems to be able to yield a higher capacitance in proportion to its surface area. But a composite of carbon on carbon like carbon aerogel and CNT seems to be a good option for higher capacitance per gram. The research for supercapacitor aimed for wireless sensor system will have to look into material research on a good surface area with ordered pore structure and pore size that utilizes electrostatic energy storage.

**Supercapacitors compared with batteries in a IWS system**

An IWS system for structural health monitoring has a long lifetime and the number of recharge cycles will be high. A supercapacitor with EDLC has the ability to match the number of cycles required and also the possibility to still function after a 100 year of usage. The selfdischarge for a supercapacitor is an aspect but since a wireless system harvest energy more or less continuously, the discharge time for a supercapacitor will probably not be reached. If the system fails to harvest the selfdischarge is between 5-60% over a period of two weeks [12]. In the short run a battery will be more suitable for the IWS system but looking at a longer lifespan the supercapacitor will be a better choice.

**Conclusion**

An IWS system that will be able to operate under a long time needs a harvester and an energy storage that can be charged and recharged many times over a long period of time. A supercapacitor with its formidable cycle life will deliver a higher energy density over time and will have a longer lifespan than a battery. The research on supercapacitors from a IWS point of view shows that a higher energy density will be gained from using composite electrodes with a well ordered structure to raise the capacitance and hence the energy density. We believe EDLC with composite carbon electrodes is a most promising candidate to be developed for IWS. For Future IWS systems, energy harvesters and supercapacitors can be miniaturized, a future prospect would be do develop a MEMS method to implement all components in a small microsystem.

**References**