Electrical Double Layer Capacitors

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Abstract

A brief survey of electrical double layer capacitors (EDLC's) was conducted. The basic theory and supporting mathematics are discussed, along with modern challenges in research and development. Fundamentally, EDLC's replace a typical dielectric with a charged (electrolytic) chemical solution. They achieve higher capacitance by maximizing surface area and minimizing dielectric thickness, resulting in hundreds, and sometimes even thousands of farads. Of note are recent advancements that not only increase capacitance but maximize the charge that can be stored before detrimental breakdown effects occur (therefore maximizing energy storage). These efforts range from developing new electrolytic solutions to utilizing new types of nano-material for the conductive electrodes. Afterwards, the scope is broadened to describe the other types of supercapacitors that make up the Ragone Plot such as pseudocapacitors and hybrid capacitors. These comparisons demonstrate the tradeoff between power and energy density, and reinforce why EDLC's are a promising replacement for current battery technologies.

Introduction

Electrolytic capacitors are a type of capacitor named for the substance between its plates. The electrolyte polarizes the capacitor when a voltage is applied, which increases the maximum capacitance. They were invented by Eugene Ducreter in 1875 when he found that the thin oxidation layer that formed on one plate in an electrolytic cell acted as a one-way current valve. This discovery later found its first use during the switch from DC power to AC power as a low-pass signal rectifier, taking advantage of the polarity of the devices [1].

In 1957, H. Becker extended the concept to create the electrochemical double layer capacitor (EDLC), or supercapacitor. Supercapacitors use only liquid electrolytes and, due to their high surface area and non-reactive electrolytes, can store over 100x the amount of energy per unit mass than a regular electrolytic capacitor. Since then, other versions of supercapacitors have been invented, each with slightly different properties, but all with top prospects for becoming new energy storage technology [2].

Terminology

Energy density: energy stored per unit volume $[\frac{J}{m^3}]$

Faradaic: involving reduction and oxidation reactions

Power density: rate of energy transfer (power) per unit volume $[\frac{W}{m^3}]$

Specific capacitance: capacitance per unit mass $[\frac{F}{g}]$

Specific surface area: surface area per unit mass $[\frac{m^2}{g}]$

Working Principles

Electrolytic capacitors rely on a very thin metal oxide layer that functions as a dielectric between a metal electrode and an electrolyte solution. When the capacitor is charging, negatively charged ions from the electrolyte migrate to the dielectric in attraction to the electron “holes” on the other side, just as electrons migrate towards or away from the dielectric in a parallel plate capacitor [1].

$$\text{Capacitance: } C = \frac{\varepsilon * A}{d} \qquad \text{[Eq. 1]}$$

The capacitance of electrolytic capacitors is tunable by adjusting either surface area (S) of plates or thickness of the thin metal oxide (d) in between the plates. However, as the oxidation layer is already just nanometers thick, reducing it any further can drastically lower the maximum operating voltage of the capacitor, as it will be more susceptible to dielectric breakdown.

ELDC’s achieve very high capacitance values in a similar manner. They are formed from two electrodes divided by a permeable membrane called a separator and an electrolyte (Figure 1). When the capacitor charges, solvated ions (ions surrounded by solvent molecules) experience a force from the charge accumulating on the electrodes. The ions travel across the separator and onto the surface of the electrode. The ions remain solvated, so that the solvent itself forms a thin insulating layer between the charge layer in the electrode and the ion layer in the electrolyte [3]. Thus, two double layers (or Helmholtz double layers) of charge accumulate, one at each electrode (Figure 1).

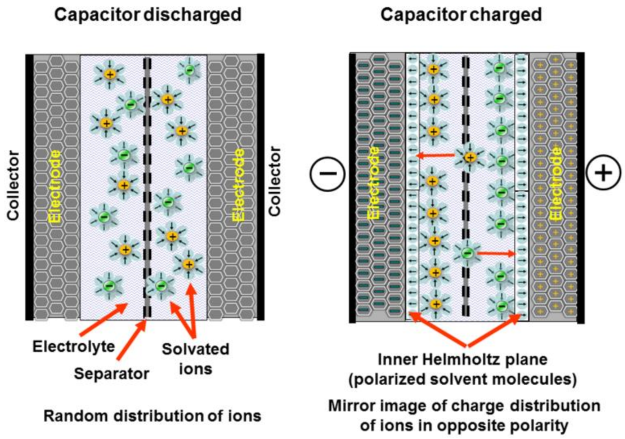

Figure 1: [3] Structure and operation of EDLC

Each double layer is topologically similar to the ideal double plate capacitor, so Equation 1 may also be used to approximate the capacitance of each layer in the EDLC. Note that the thickness of the dielectric (d) is roughly the thickness of the solvent molecules, which is on the order of angstroms (10^{-10}m), allowing high capacitances to be reached [4]. The total capacitance of the EDLC is the equivalent series capacitance of both double layers:

$$C_{tot} = \frac{(C_a * C_b)}{(C_a + C_b)} \qquad \text{[Eq. 2]}$$

As an example, if the solvent has a relative permittivity of 8 and a characteristic diameter of 7Å, one of the double layers in the capacitor will have a capacitance of $0.1\frac{F}{m^2}$, and the total capacitance will be $0.05\frac{F}{m^2}$.

When combined with an electrode material like activated carbon, which has a specific surface area of 1000-2000 m^2/g, the capacitance can be hundreds to thousands of Farads [5].

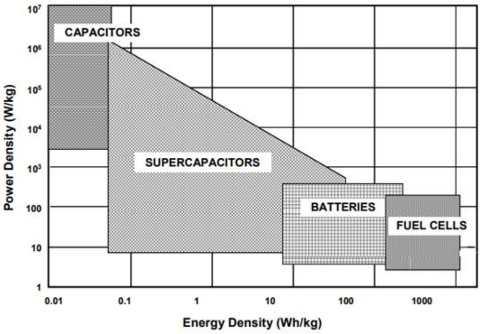

Figure 2: [12] Ragone plot of supercapacitors relative to other energy storage devices

A clear advantage of EDLC's over other capacitor constructions is the high specific capacitance values they can achieve. These devices also have higher power densities than electrochemical cells (batteries) because their internal resistances are much lower than that of batteries. They also have higher energy densities than other capacitors, though still lower than batteries (Figure 2) [6].

However, the maximum operating voltage of a single EDLC is limited by the high electric fields present in the double layer. The example capacitor mentioned above would have an electric field of $1.4\frac{GV}{m}$ in each double layer if charged to 2 V. This means that the electric fields within EDLCs are high enough to cause dielectric breakdown in many insulators, even at relatively low voltages. For this reason, the maximum operating voltages of most EDLC's are limited to 2.5-2.7 V. This voltage is reduced to around 1 V if the solvent used is water. Higher voltage capacitors can be constructed by placing multiple capacitors in series, though this increases the equivalent series resistance of the device. Another disadvantage is that the high capacitance and equivalent series resistances (~1 mΩ), means that the RC time constant for these devices is on the order of seconds, limiting their applications to DC currents, even though the devices are not polarized [5].

Research Challenges

Currently, the two approaches to research are industrial and academic. The first is in pursuit of cheaper, simpler, safer manufacturing processes. The latter is directed towards two major goals: the development of electrodes and the improvement of the electrolyte, the two major components of a supercapacitor cell.

The development of electrodes is important for optimizing the electrical characteristics of EDLC supercapacitors. As discussed in Working Principles, capacitor performance is directly proportional to two factors, electrode surface area and the thinness of the dielectric layer. Studies into the respective fields of morphology and materials are being conducted to increase maximum capacitance values; however, there is more opportunity for improvement in electrodes. This work approaches nanoscience, as materials at that size have much higher surface to volume ratios, allowing for higher reactivity. Carbon in particular is drawing attention for its availability and excellent conductive properties on the nanoscale.

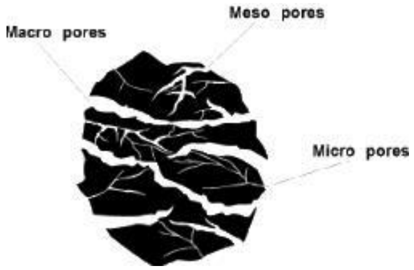

Figure 3: [7] Porous nature of activated carbon

There are three main nano-carbons of interest: activated carbon powder, graphene and carbon nanotubes, and aerogel. The porous structure of activated carbons can drastically increase surface area (Figure 3), however some micropores may be too small to allow interaction with electrolyte ions. Additionally, they must be sintered directly onto the electrode during production. Carbon nanotubes and graphene have significantly lower specific surface areas, but they have much higher charge:surface-area efficiency due to their uniformity and can be grown onto the electrode. Recently, it was found that curving the graphene walls concavely increases energy density [8]. Carbon aerogel also shows remarkable uniformity and, like graphene, it can be grown directly onto target substrates. The pore size of aerogels is tunable during production process, which means it can be optimized to match different electrolyte solutions [6, 9].

The other component of supercapacitor cells is the electrolyte-solvent complex. The basic properties of the electrolyte solution strongly influence many properties of the cell, such as operating temperature range, power and energy densities, toxicity, and internal resistance. As liquids, these come in aqueous or organic form (Figure 4) Aqueous solutions' (e.g. KOH) lifespans are temperature dependent, as modelled by the Arrhenius equation. Organic solutions (e.g. Acetonitrile) have high dielectric constants, and so have higher cell voltages, but are more toxic and require larger pores for interaction. A large portion of research goes into finding the optimal pairing of electrolyte solution and electrode current collectors [10].

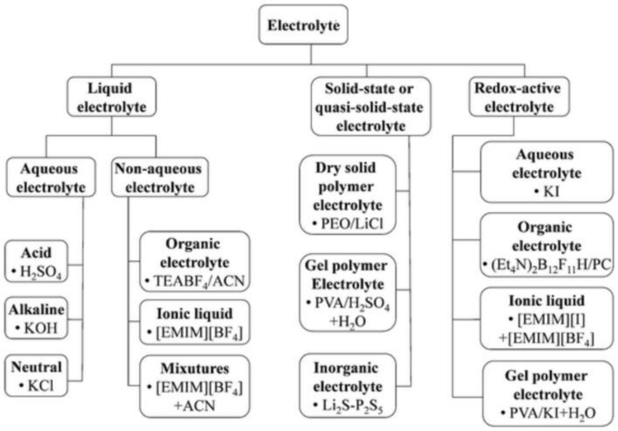

Figure 4: [10] Taxonomy of supercapacitor electrolytes

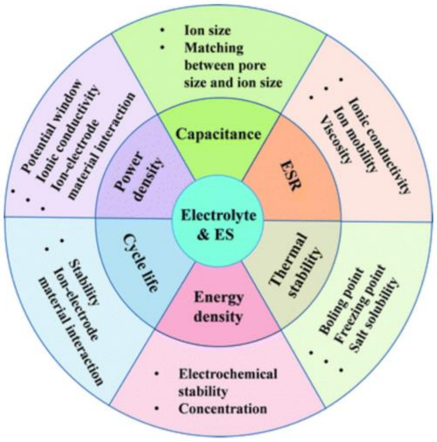

Figure 5: [10] Electrolyte Influence on supercapacitor characterizes

Classifications

Electrolytic double layer capacitors make up one subgroup of supercapacitors. While EDLC's rely solely on electrostatic potentials to store energy, other supercapacitor types also utilize electrochemical energy storage, making them more like batteries. As such, they often achieve higher energy densities at the cost of power density and lifetime. This relation can be observed in a Ragone plot (Figure 2).

Pseudocapacitors store energy by transferring electrons between the electrolyte and the electrode. These reactions are faradaic processes, but they occur at much faster rates than the reactions in batteries since the ions do not form chemical bonds to the electrode atoms. [6]

Hybrid capacitors utilize both electrochemical and electrostatic methods of storage, one at each electrode. This systemic asymmetry creates a net polarization and loses much of the reversibility that the other systems have.

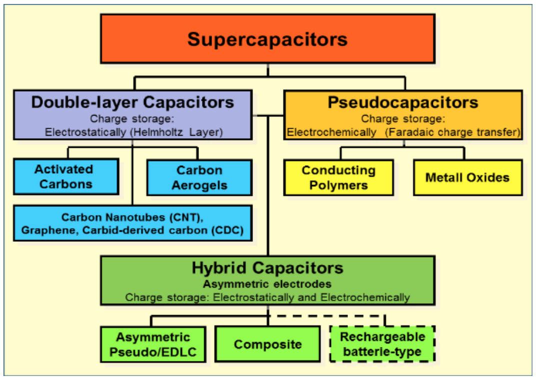

Figure 6: [11] Taxonomy of different supercapacitor constructions

Conclusion

Supercapacitors, especially EDLC's, are able to achieve high capacitance values and energy densities while maintaining the power density that is characteristic of capacitors. Additionally, because the charge storage is non-faradaic, the cycle stability is on the magnitude of 10^6 full cycles before significant degradation. This balance is ideal for a power source, the last push necessary towards the economic feasibility and popularization of electric cars. Beyond the automotive industry, supercapacitors could play key roles in the development of space travel, communications systems, and emergency medical equipment.

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