

ELECTROCHEMICAL ENERGY CONVERSION AND STORAGE - BATTERIES, FUEL CELLS AND ELECTROCHEMICAL CAPACITORS

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Summary

This chapter seeks to take the reader from basic chemical concepts to a full appreciation of the underlying principles and applications of energy storage in supercapacitors, batteries and fuel cells, and to an understanding of their relative strengths and weaknesses both technically and in a commercial context. The historical development of each type of storage device and the key advances are summarized.

1. Introduction

The photograph in Figure 1 shows Winshields Crag on Hadrian's Wall in beautiful Northumberland, England, a World Heritage Site. For nearly 2000 years, Hadrian's Wall has brooded over the borderlands between Scotland and England. In that time, kings and queens have come and gone, empires have risen and fallen, but not a single gram of coal or milliliter of oil has been made.

There is no doubt that the world is heading towards a major energy crisis (among other major crises) and this is giving impetus to an increasingly urgent search for more sustainable and environmentally friendly means of converting and storing energy.



Figure 1. Winshields Crag on Hadrian's Wall, County of Northumberland, United Kingdom.

This chapter deals with three electrochemical methods of converting and/or storing energy: electrochemical capacitors (also known as supercapacitors or ultracapacitors), batteries and fuel cells. These share common characteristics: they all require two solid electrodes in contact with a solid, liquid or gel electrolyte, the energy storage or conversion processes take place at the phase boundary between an electrode and the electrolyte, and the movement of ions and electrons attendant on the conversion or storage processes are physically separated in space.

The primary difference between electrochemical capacitors on the one hand and fuel cells and batteries on the other is that energy is stored in the former type of device by charging the capacitor from an external electrical power source, whilst in the latter, energy is released from chemicals and converted to electricity. Thus, in electrochemical capacitors no electron transfer (Faradaic) processes take place across the electrode/electrolyte interface; in contrast, in fuel cells and batteries during discharge, electron transfer takes place at the electrodes, and chemical species are reduced at, *i.e.* accept electrons from, the cathode and are oxidized at, *i.e.*, lose electrons to, the anode, with the electrons traveling around the external circuit from anode to cathode.

2. Electrochemical Capacitors

A capacitor is a device that stores energy *via* the charging of two electronically conducting 'plates' separated by an insulating medium, the dielectric; in the simplest capacitor, the dielectric is air. If two metal plates separated by such a dielectric are connected to a Direct Current (D.C.) power supply, electrons will flow from the positive

(+) pole of the power supply to one plate, rendering the latter negatively charged, and from the other plate to the negative (-) pole of the supply, leaving the plates equally and oppositely charged, see Figure 2. It may be useful when considering hybrid supercapacitors to bear in mind that so long as at least one of the plates of the device has a potential that increases linearly with charge (see Figure 2), the device may be considered a capacitor. Charging will continue until the voltage across the capacitor is equal to that imposed by the external supply, or until the dielectric starts to breakdown.

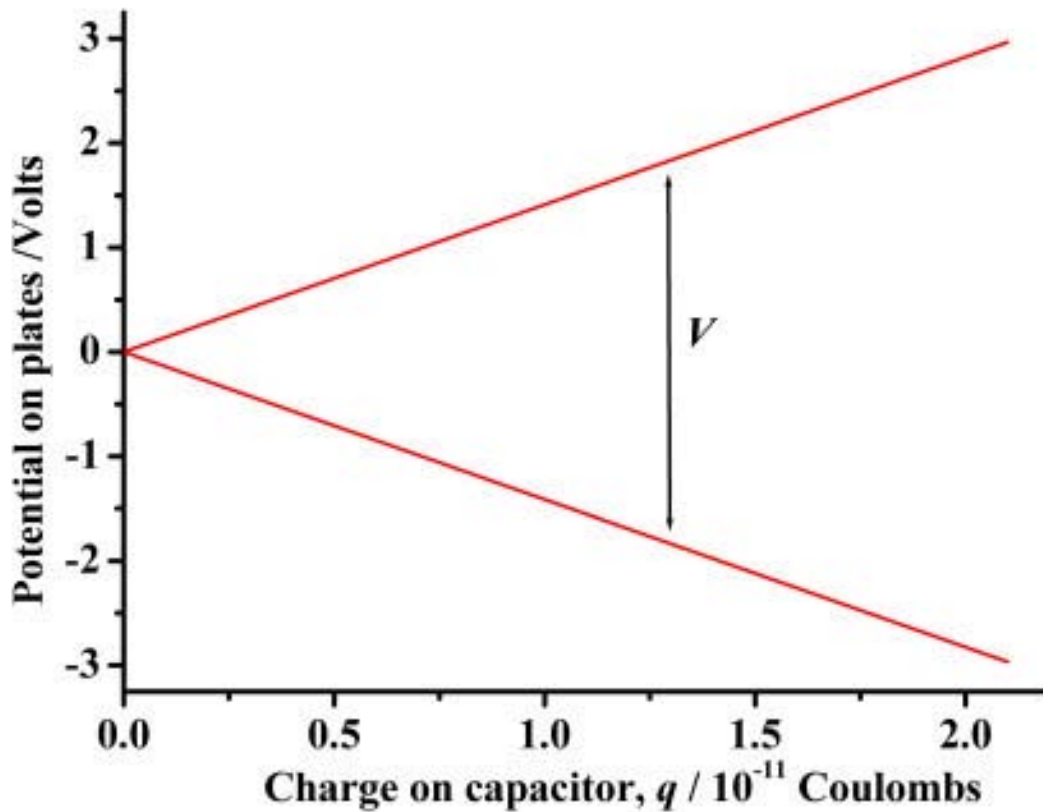


Figure 2. The variation in the potentials of the individual plates of a 3.54×10^{-12} Farad (F) air capacitor during charging. V is the voltage across the plates.

2.1. Capacitance and Capacitors

The relationship between the capacitance or charge storing capacity C in Farads (F), the separation of the plates d and the dielectric constant of the insulator, ϵ , is:

$$C = A\epsilon\epsilon_0/d \quad (1)$$

A is the area of each of the two plates, ϵ_0 is a constant called the permittivity of free space, $8.854 \times 10^{-12} \text{ F m}^{-1}$ and ϵ is the dielectric constant. Thus, a typical air capacitor in an electronics kit has an area of 4 cm^2 ; $\epsilon = 1$ for air, and so for a plate separation of 1 mm the capacitance is $3.54 \times 10^{-12} \text{ F}$. One Farad is an extremely large capacitance, and

values of μF , nF or even pF (10^{-6} F , 10^{-9} F or 10^{-12} F , respectively) are more usually quoted.

As the capacitor charges, the voltage across its plates, V , is given by Eq. (2):

$$C = q/V \quad (2)$$

where q is the charge placed on the positive plate (that generates an equal and opposite charge on the negative plate) in Coulombs, C. The variation in V with q is shown in Figure 3; the energy stored in the capacitor charged to a voltage V is the area under the plot in Figure 3; from simple geometry (the area of a triangle) the area is:

$$\text{Area} = \text{energy } E \text{ stored in Joules (J)} = 0.5qV \quad (3)$$

From Eq. (2):

$$E = 0.5CV^2 \quad (4)$$

From Eqs. (2) and (4) it can be seen that a 1F capacitor can store 1 C of charge at 1 V, or 0.5 Joule of energy. More generally, 1 Joule is defined:

$$1 \text{ Joule} = 1 \text{ Amp} \times 1 \text{ V} \times 1 \text{ s} \quad (5)$$

A typical 1.5 V AA battery holds 2.8 “Ampere hours” (Ahr); *i.e.* 2.8 A for 1 hour at 1.5V, or $2.8 \times 3600 \times 1.5 = 15120$ Joules. The plates of an air capacitor capable of holding such energy at the same voltage would each have an area of $1.5 \times 10^{12}\text{ m}^2$!

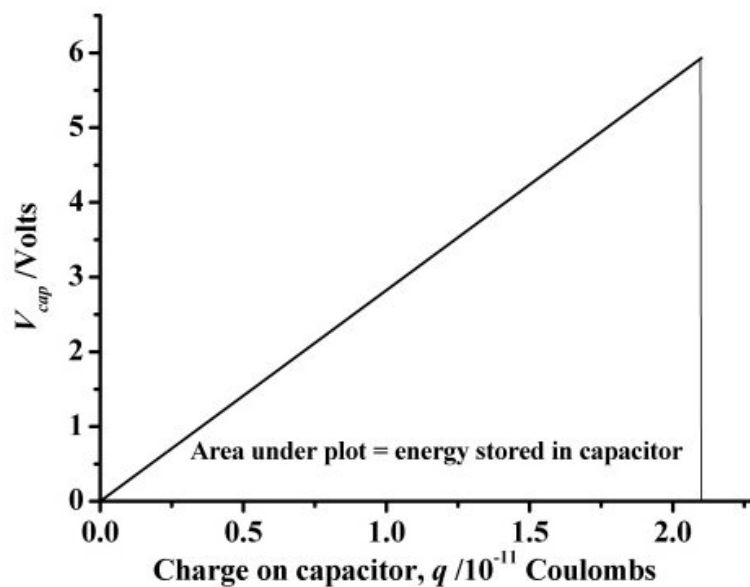


Figure 3. The variation in the voltage across the plates, V , of the air capacitor in Figure 2.

To store more energy or charge, a dielectric having a high(er) ϵ could be employed, the area of the plates increased, V could be increased and d reduced; the development of electrochemical capacitors has exploited all of these options.

Electrochemical capacitors are often referred to as supercapacitors or ultracapacitors, and there is also a modification known as hybrid capacitors. Supercapacitors are charge storage devices which rely simply upon the charging of the electrical double layer of high surface area carbon electrodes in liquid (usually aqueous) electrolytes. Hybrid supercapacitors are a cross between a capacitor and a battery, and are dealt with in more detail after the section on batteries (Section 3) below.

To understand how an electrochemical capacitor works it may be helpful to go back to basics and describe first how the simple treatment of capacitance given above relates to the double layer at the electrode/electrolyte interface.

2.2. The Electric Double Layer

Figure 4 shows a schematic of the Helmholtz model of the double layer at a positive electrode immersed in aqueous electrolyte; ‘electrode’ is employed rather than ‘plate’ in electrochemical capacitors. The term ‘electrolyte’ is usually taken to refer to the salt which dissolves in the solvent to produce solvated oppositely charged ions; *e.g.* table salt, sodium chloride, dissolves in water to produce solvated (aq = aqueous, s = solid) sodium and chloride cations and anions, respectively:

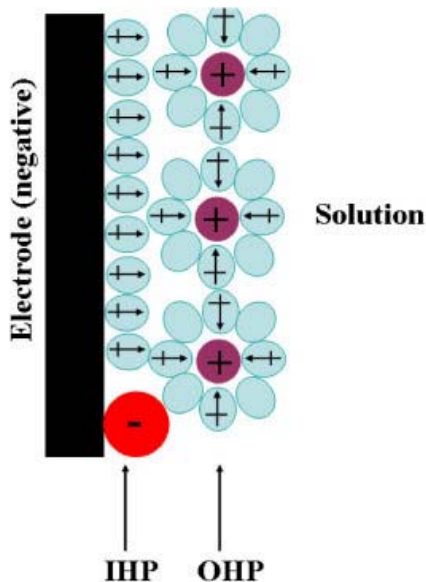


Figure 4. Schematic representation of the Helmholtz model of the electrode/electrolyte interface. IHP = Inner Helmholtz Plane, OHP = Outer Helmholtz Plane. Dipoles are represented by crossed arrows, some are omitted for clarity.

The ions render the solvent conducting. Note, however, that the term ‘electrolyte’ is often used for the dissolved salt and solvent together. To avoid confusion, the states (s, aq *etc.*) of the various chemical species taking part in cell reactions will be omitted.

As water molecules have a dipole (represented by a crossed arrow – the cross is the electropositive end, *i.e.*, the hydrogen atoms, and the arrowhead the electronegative oxygen atom) they are attracted to the electrode with their dipoles aligned in the direction of the electric field, electronegative oxygen atoms attracted by the positive charge on the electrode. The centers of the adsorbed water molecules form the Inner Helmholtz Plane (IHP). Cations, with their attendant solvation envelope of electrostatically attracted water molecules, are also attracted to the electrode, and their centers form a sheet of charge at the Outer Helmholtz Plane, (OHP).

In effect, the (electrode/IHP) and (IHP/OHP) interfaces form two capacitors in series, the total capacitance C_H of which is given by:

$$1/C_H = 1/C_{IHP} + 1/C_{OHP} \quad (7)$$

If the radius of the water molecule is r_{water} and a is the distance from the electrode surface to the OHP, then combining Eqs. (7) and (1) gives:

$$1/C_H = Ar_{\text{water}}/\epsilon\epsilon_0 + A(a - r_{\text{water}})/\epsilon\epsilon_0 \quad (8)$$

where ϵ is the dielectric constant of water. The radius of a typical cation is 2×10^{-10} m, the radius of water is 1×10^{-10} m and the dielectric constant of water = 80. In considerations of the electrode/electrolyte interface, Double Layer capacitances are often quoted in $F m^{-2}$, *i.e.*, as C_H/A , and feeding the above values ($a = 6 \times 10^{-10}$ m) into (8) gives $C_H/A = 1.2 F m^{-2}$. In practice, double layer capacitances have been found to vary between *ca.* $0.05 - 0.5 F m^{-2}$, and so the theoretical value is somewhat high. This is due to the value of ϵ chosen; $\epsilon = 80$ assumes that the water molecules are free to rotate and tumble, and so re-orientate if the direction of the electric field changes. This is not the case for the water adsorbed at the electrode, which is unable to move, and the water between the IHP and OHP which has only very restricted mobility. Calculations suggest $\epsilon = 6$ for the former and 30 for the latter, which gives $C_H = 0.27 F m^{-2}$, in fairly good agreement with experiment- and still a very large value!

This is the first key reason for the large capacitance of electrochemical capacitors: the very small value of d .

2.3. The Evolution of Supercapacitors

Taking the nomenclature employed in the review by Brodd *et al* supercapacitors have evolved through four generations since the NEC Corporation under license from SOHIO first introduced their Supercapacitor™ in August 1978. The first generation supercapacitors were employed to provide backup power for computer and appliance memories and were symmetric in design, *i.e.*, both electrodes comprised high surface

area porous carbon separated by an aqueous electrolyte. Activated porous carbon can have surface areas typically in the range $700 - 2000 \text{ m}^2 \text{ g}^{-1}$, significantly increasing A in Eq. (1) above the geometric area of the electrodes, and hence the capacitance; the specific capacitance can be up to *ca.* 4 F g^{-1} . This is the second key effect contributing to the high storage capacity of supercapacitors: the very large surface area of the electrodes.

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Biographical Sketch

Professor P. A. Christensen was born in South Shields, UK on May 28 1960. He was educated at South Shields Grammar Technical School for Boys; Exeter College, Oxford University (B.A. Hons Natural

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He worked with Dr. Andrew Hamnett as a PDRA in the Inorganic Chemistry Laboratory, Oxford University from 1985 to 1989, after which he took up a Lectureship in Physical Chemistry in the Chemistry Department of Newcastle University. He was promoted to Senior Lecturer in 1996, Reader in 2001 and was awarded a Personal Chair in Pure and Applied Electrochemistry in 2004. He held the position of sub-Dean in the Faculty of Science from 1999 to 2002 and Dean of Graduate Studies in the Faculty of Science, Agriculture and Engineering from 2002 to 2006. In 2002, he moved to the School of Chemical Engineering and Advanced Materials in the University.

PAC was one of the founding Directors of NewChem Technologies Ltd in 2002 and of Clarizon Ltd in 2005, both of which are spin-out companies from Newcastle University, and the latter also from Hong Kong University. In 2006 he joined Gen-X Energy Ltd, a fuel cell company, as Chief Scientist and non-Executive Director. PAC has published over 120 papers on electrocatalysis, photochemistry and *in-situ* Fourier Transform Infrared Spectroscopy, with particular emphasis on water and wastewater treatment and fuel cell development. He has been researching fuel cell electrocatalysis for over 20 years. He co-authored a postgraduate textbook on electrochemistry, "Techniques and Mechanisms in Electrochemistry", London., Chapman and Hall 1994. He has been a member of the Business Development Team of the Fuel Cell Applications Centre (FCAF) since its inception in 2004. The FCAF is part of the Centre for Process Industries, a regional government Centre of Excellence, based in Wilton on Teeside.