Journal of Power Sources 196 (2011) 1–12

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Review

Conducting-polymer-based supercapacitor devices and electrodes

Graeme A. Snook[a,*], Pon Kao[b], Adam S. Best[b]

[a] CSIRO Process Science and Engineering, Box 312, Clayton South, Victoria 3169, Australia
[b] CSIRO Energy Technology, Box 312, Clayton South, Victoria 3169, Australia

ARTICLE INFO

Article history:
Received 22 February 2010
Received in revised form 11 June 2010
Accepted 18 June 2010
Available online 15 July 2010

Keywords:
Supercapacitor
Ultracapacitor
Conducting polymer
Cycle-life
Specific energy
Specific power

ABSTRACT

Supercapacitor electrodes and devices that utilise conducting polymers are envisaged to bridge the gap between existing carbon-based supercapacitors and batteries to form units of intermediate specific energy. This review looks at the major conducting polymer materials, namely, polyaniline, polypyrrole, polythiophene and derivatives of polythiophene, as well as composites of these materials with carbon nanotubes and inorganic battery materials. Various treatments of the conducting polymer materials to improve their properties are considered and comparisons are made with other supercapacitor materials such as carbon and with inorganic battery materials. Conducting polymers are pseudo-capacitive materials, which means that the bulk of the material undergoes a fast redox reaction to provide the capacitive response and they exhibit superior specific energies to the carbon-based supercapacitors (double-layer capacitors). In general conducting polymers are more conductive than the inorganic battery materials and consequently have greater power capability. On the downside, conducting polymers swell and contract substantially on charge and discharge, respectively. Consequently, cycle-life is poor compared with carbon-based supercapacitors which generally only charge via adsorption and desorption of ions (giving typically a few thousand cycles for conducting polymers compared with >500 000 cycles for carbon-based devices).

Contents

1. Introduction

Supercapacitors are designed to bridge the gap between batteries and capacitors to form fast charging energy-storage devices of intermediate specific energy. They are seen to have a potential

---

* Corresponding author. Tel.: +61 3 95458863; fax: +61 3 95628919.
E-mail address: Graeme.Snook@csiro.au (G.A. Snook).

0378-7753/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jpowsour.2010.06.084

market both in hybrid electric vehicles and pure electric vehicles to improve regenerative braking (through fast charge capability) and deliver larger acceleration (through fast discharge capability). Traditionally, capacitors have been constructed using a set of parallel conducting plates separated by an insulator. Capacitive charge of opposite sign builds up on the respective plates in response to a voltage difference between them. The capacitances are delivered in mF and μF quantities [1]. In more recent times, capacitors have been developed that give hundreds to thousands of Farads and these are usually known as supercapacitors, or ultracapacitors, and were initially constructed from carbons of high surface area [2]. These are in fact two capacitors connected in series with a conducting liquid media linking them. Such a supercapacitor device derives its performance from a so-called double-layer capacitance and is therefore often referred to as an (electric or) electrochemical double-layer capacitor (EDLC). The capacitance in these devices is stored as a build up of charge in the electrical double-layer in the solution interface close to the surface of the carbon to balance the charge in the carbon material.

Another type of supercapacitor, referred to as a pseudo-capacitor, derives its capacitance from the storage of charge in the bulk of a redox material in response to a redox reaction. This fast redox reaction [3–5] acts like capacitance (hence the name pseudo-capacitance). A pseudo-capacitor typically stores a greater amount of capacitance per gram than an EDLC, as the bulk of the material (not just the surface layer) reacts. On the other hand, an EDLC has faster kinetics as only the surface of the carbon is being accessed. An example of a pseudo-capacitive material is a conducting polymer (CP) (the conductivity of which was first reported in 1963 by Weiss and co-workers in Australia [6–8] and first utilised in supercapacitors in the mid 1990s [4]) and it is this material that will be the subject of this review. The review will focus on work done post-2000 but for a comprehensive description of work pre-2000 readers should consult Ref. [9]. The concept of 'bridging the gap' with batteries to form conducting-polymer-based supercapacitors with superior specific energy compared with carbon-based alternatives is illustrated in Fig. 1.

Conducting polymers are rendered conductive through a conjugated bond system along the polymer backbone. They are typically formed either through chemical oxidation of the monomer (for example with iron chloride) [5] or electrochemical oxidation of the monomer. Two oxidation reactions occur simultaneously – the oxidation of the monomer and the oxidation of the polymer [10] with the coincident insertion of a dopant/counter ion (e.g. Cl^-). The dopant or doping level (in this p-type conducting polymer) is typically below 1 dopant per polymer unit: approximately 0.3–0.5, i.e., 2–3 monomer units per dopant. This is limited by how closely the positive charges (so-called polarons) can be spaced along the polymer chain. The polymers that are most commonly studied for use in supercapacitor devices are polypyrrole, polyaniline, and derivatives of polythiophene [11]. The typical dopant level for these polymers, as well as their typical specific capacitances and voltage ranges, are given in Table 1.

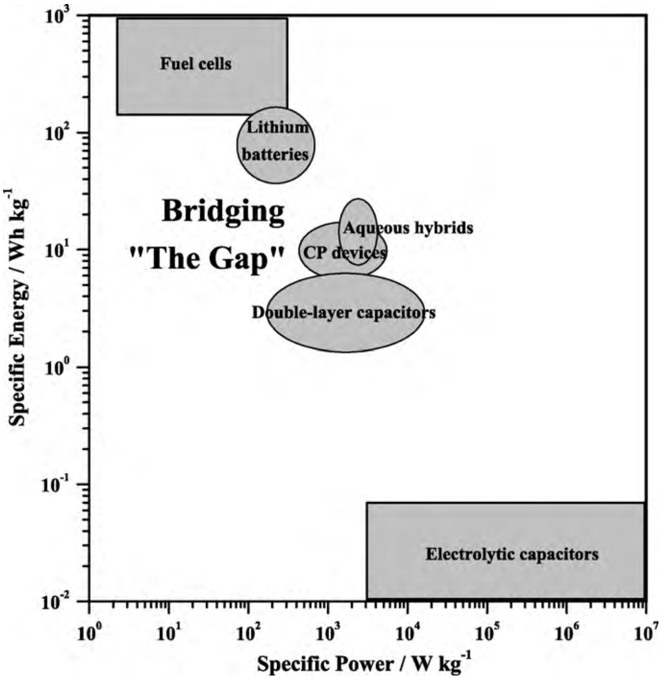

Fig. 1. Ragone plots for different types of energy-storage devices; where CP is conducting polymer.

The difference between EDLCs and conducting-polymer-based supercapacitors is shown schematically in Fig. 2. In general, carbon-based supercapacitors have high power capabilities, due to the fast sorption and desorption of ions, but a low specific energy [13]. Conducting polymers should improve the device as they undergo a redox reaction to store charge in the bulk of the material and thereby increase the energy stored and reduce self-discharge. One significant drawback of these materials is the relatively low power (or lower rate of charge–discharge) due to the slow diffusion of ions within the bulk of the electrode. Nevertheless, it is still proposed that conducting polymers can bridge the gap between batteries and double-layer supercapacitors as these electrodes have better kinetics than nearly all inorganic battery electrode materials (pseudo-capacitive materials) [13].

Conducting polymers are generally attractive as they have high charge density and low cost (compared with the relatively expensive metal oxides) [14,15]. It is possible to develop devices with low equivalent series resistance (ESR), high power, and high energy [16]. Polyaniline can exhibit a charge density of 140 mAh g^{-1}, which is slightly lower than that obtained with expensive metal oxides such as $LiCoO_2$ [17,18] but much higher than that given by carbon devices that often deliver less than 15 mAh g^{-1} (perhaps ~40 mAh g^{-1} for the individual electrode) [14]. Carbon–carbon symmetric supercapacitor devices can achieve a specific power of 3–4 kW kg^{-1} and a specific energy of 3–5 Wh kg^{-1} when fully packaged [13,19,20], while a conducting polymer supercapacitor, based on polyaniline, can achieve a slightly lower power at 2 kW kg^{-1} but double the specific energy (10 Wh kg^{-1}) [19]. As will be discussed in Section 3, the weight used for the calculation of specific energy

Table 1
Theoretical and experimental specific capacitances of conducting polymers.

Conducting polymer	Mw (g mol^{-1})	Dopant level	Potential range (V)	Theoretical specific capacitance (F g^{-1})	Measured specific capacitance (F g^{-1})[a]
PAni	93	0.5	0.7	750	240
PPy	67	0.33	0.8	620	530
PTh	84	0.33	0.8	485	–
PEDOT	142	0.33	1.2	210	92

Cited from Ref. [5]. Mw is molecular weight per unit monomer (g mol^{-1}), PAni is polyaniline, PPy is polypyrrole, PTh is polythiophene and PEDOT is poly(3,4-ethylenedioxythiophene).

[a] Cited from Ref. [12].