



A Step Potential Electrochemical Spectroscopy Analysis of Electrochemical Capacitor Electrode Performance



Madeleine F. Dupont, Scott W. Donne*

Discipline of Chemistry, University of Newcastle, Callaghan, NSW 2308, Australia

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ABSTRACT

Step potential electrochemical spectroscopy (SPECS) has been developed as an electrochemical method for application to electrochemical capacitors, in this case for an activated carbon electrode in 0.5 M H₂SO₄. The method involves the application of a sequence of small potential steps over the potential window used by the electrode under study, followed by a relatively long rest time after each potential step. Modelling of the SPECS data has been used to extract the contributions made by electrical double layer charge storage and diffusional (redox) processes to the total electrode performance. Outcomes from the application of this approach highlight the dominant charge storage mechanisms at both high and low cycle rates, as well as allow differentiation of ‘capacitor-like’ or ‘battery-like’ electrode behaviour. The SPECS data has also been analysed so as to enable calculation of voltammograms at different scan rates for the electrode system. Finally, electrode performance data has also been presented and discussed.

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1. Introduction

1.1. Electrochemical energy storage

The reliable and sustainable production of energy is a critical issue for present and future society. Current fossil fuel based energy production is neither sustainable nor environmentally conscious, while the current crop of renewable energy sources are neither of sufficient scale or cost effective to be taken up broadly by society. As such, significant advances are required in these areas to ensure an energy secure future. In particular, two issues related to renewable energy production and utilization that are of key significance are efficiency and intermittency, both of which can be improved through the use of electrochemical energy storage technologies. Many examples exist in both the popular and scientific literature to demonstrate these advantages [1–5].

Electrochemical energy storage and conversion technologies cover a broad spectrum of devices, including those based on electrolytic and electrochemical capacitors, battery systems and fuel cells [6]. Within each of these categories there are also numerous chemistries, each of which have their own performance characteristics. Often a Ragone diagram (gravimetric or volumetric

energy density versus power density) is used to assess device performance; however, these are not the only system properties that are of importance [1,2]. Other characteristics such as cyclability, cost effectiveness, safety and environmental concerns can all play a part in dictating the applicability of a device [1]. In this work our focus is on electrochemical capacitors, which are typified by high power densities, low energy densities, and excellent cyclability [7].

1.2. Electrochemical capacitors

The majority of commercial electrochemical capacitors are symmetrical devices based on identical high surface area and porosity activated carbon electrodes immersed in either an aqueous or non-aqueous electrolyte [1]. Energy storage in these devices is via charge separation at the electrode-electrolyte interface; i.e., in the electrified double layer [1]. Research directions for these materials typically focus on novel and optimized carbon material structures and morphologies, and their interface with electrolytes, that ultimately maximize the amount of charge that can be stored at the interface. Activated carbon materials such as these provides 100–200 F/g, with an energy density of 1–2 Wh/kg, power densities up to 10⁴ W/kg, with minimal performance fade for over 10⁵ cycles [1,7–10].

The relatively low energy density of electrochemical capacitors is at the present time a significant impediment to their widespread

* Corresponding author. Tel.: +61 2 4921 5477.

E-mail address: scott.donne@newcastle.edu.au (S.W. Donne).

applicability. Ultimately the cost per Wh is too high for commercial uptake [1]. Strategies that have been proposed and used to improve this performance characteristic include using alternative electrolytes that enable a larger potential window, and/or using electrode materials that store charge via pseudo-capacitance, which is charge storage through the use of redox reactions at the electrode surface [2]. Materials that have been shown to exhibit pseudo-capacitance include various forms of carbon [11], conducting polymers (such as polypyrrole or polythiophene) [12,13], and metal oxides (such as ruthenium dioxide and manganese dioxide) [14,15]. In each of these cases charge is stored as a result of a facile, reversible redox (faradaic) process for the electrode material at the electrode-electrolyte interface. The energy that can be stored in the three-dimensional structure of the electrode material is higher than that stored at the two-dimensional electrode-electrolyte interface. One question that has arisen regarding the study of this class of materials is related to the relative fraction of charge stored as pseudo-capacitance versus charge stored in the double layer at the electrode-electrolyte interface.

1.3. Electrochemical characterization

The ultimate test of how a particular material performs as an electrochemical capacitor electrode is via electrochemical characterization, either in a half-cell (three-electrode) configuration, to focus specifically on the individual electrode material, or in a full cell, as would be used commercially. Certainly many electrochemical methods exist for characterizing materials; however, in the case of electrochemical capacitors cyclic voltammetry (CV) and constant current charge-discharge (CC) cycling are by far the most common. Electrochemical impedance spectroscopy (EIS) is also used, but certainly not as frequently as CV or CC cycling. Ultimately the CV and CC methods provide the user with performance data; i.e., specific capacitance (F/g) as a function of cycling rate, and perhaps some electrode characteristics; e.g., equivalent series resistance (ESR), but rarely is any quantitative mechanistic information provided.

EIS can be used to provide much more quantitative performance and fundamental information about the electrode or system, such as ESR, charge transfer resistance, double layer capacitance, diffusional characteristics, time constant, and reactive power, etc. [16]; however, this analysis is very dependent on the equivalent circuit chosen for modelling, and is also confined to just one potential within the window of the electrochemical capacitor. Furthermore, the application of EIS to two-electrode cells is potentially confounding since it is not clear which electrode is causing the cell response.

1.4. This work

In this work we have developed and applied step potential electrochemical spectroscopy (SPECS) to the study of electrochemical capacitor electrodes. This method has previously been used to examine the diffusion characteristics of battery cathode materials, particularly with a focus on examining the quasi-equilibrium discharge and charge characteristics, as well as the kinetics of diffusion through the active material structure as a function of applied potential and state of charge [17–20]. More recently, the SPECS method used in this work has been applied to manganese dioxide electrodes and successfully differentiated between the charge storage contribution from faradaic and non-faradaic processes [21]. Here we will use SPECS to differentiate the charge storage mechanisms used in electrochemical capacitor electrodes, as well as a means of examining the rate performance of an electrode material.

2. Experimental

2.1. Electrode materials and electrolytes

The activated carbon used in this work was prepared in a two stage process. The first stage involved the pyrolysis of coconut husks at 500 °C under a nitrogen atmosphere for 3 h. After cooling the resultant char was milled in a zirconia mill to produce a material with a mean particle size of ~20 μm. In the second stage, activation of the char was carried out with the addition of a small volume of concentrated H₃PO₄, with the resultant suspension again pyrolyzed at 700 °C for 1 h under a nitrogen atmosphere.

Electrodes made from the activated carbon were examined in a 0.5 M H₂SO₄ electrolyte prepared by dilution of 98% H₂SO₄ (98%; Merck) with Milli-Q ultra-pure water (resistivity > 18.2 MΩ.cm).

2.2. Surface area and porosity analysis

The surface area and porosity of the activated carbon sample was determined using a Micromeritics ASAP2020 Gas Adsorption and Porosity Analyzer. Samples were pre-treated by degassing under vacuum at 300 °C for 12 hours to remove surface water. A N₂ adsorption isotherm (at 77 K) was then measured on each sample covering the partial pressure (P/P₀) range 10⁻⁷–1. The specific surface area was then determined using the linearized BET isotherm, while sample porosity was determined using the DFT Plus V2.0 software package from Micromeritics.

2.3. Electrode casting

A mixture of the solid electrode components was made by lightly grinding together an 80:10:10 mixture of the activated carbon, carbon black (Cabot Vulcan XC72R; conductive agent), and poly(vinylidenedifluoride) (PVdF; binder) using a ceramic mortar and pestle (~5 min.). This mixture was then made into an ink by adding N-methylpyrrolidone (NMP, 99%) in a ratio of 20:1 solvent to solid (by weight). The ink was stirred for 30 minutes until evenly dispersed.

The working and counter electrodes were cast by dropping 50 μL (mass loading ~0.008 g/cm² active material) and 100 μL (0.023 g/cm²) of the ink, respectively, onto clean gold-coated stainless steel substrates. The gold-coated stainless steel substrates were prepared by first polishing with 1200 grit emery before being washed thoroughly with Milli-Q water, and wiped dry with a lint free tissue. Gold was then sputter coated onto the stainless steel substrate. The counter electrode had a greater mass than the working electrode to ensure that any limitations of the system were a result of the working electrode. The electrodes were then dried in air at 60 °C for at least 8 hours.

2.4. Electrochemical cell construction

The electrochemical cell used was based on a Swagelok 13 mm diameter perfluoroalkoxy alkane (PFA) T-junction. The coated working and counter electrodes were inserted loosely from opposite ends into the cell, initially leaving the third perpendicular port open. The two stainless steel electrodes were then pressed together at 1.7 MPa using a hydraulic press to ensure good cell conductivity, before the electrodes were secured (screwed) into place. The cell was then removed from the press, filled with electrolyte, sealed and left to equilibrate for ~12 h. After equilibration, the reference electrode (saturated calomel electrode; SCE; Radiometer Analytical) was inserted into the perpendicular port of the Swagelok cell and sealed in place with Parafilm. Unless otherwise stated, all potentials stated are with respect to the SCE.

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