



The properties and performance of carbon produced through the electrochemical reduction of molten carbonate: A study based on step potential electrochemical spectroscopy

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ABSTRACT

Carbons with BET specific surface areas of $500 \text{ m}^2 \text{ g}^{-1}$ have been produced through the electrolytic reduction of molten $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3\text{-Na}_2\text{CO}_3$ at the eutectic composition (43.5:25:31.5 mol%) onto graphite at 600°C and 0.30 A cm^{-2} under a 60 mL min^{-1} CO_2 gas flow. These carbons have been shown to consist largely of amorphous carbon with some spherical and flake-like conglomerates. Functionalised oxygen has been observed in synthesised carbons using FTIR and XPS. Synthesised carbons have been investigated in 3-electrode cells and analysed using cyclic voltammetry and step potential electrochemical spectroscopy (SPECS) at room temperature. Capacitances as high as 450 F g^{-1} have been observed at 0.0833 mV s^{-1} scan rates. The EDLC and pseudo-capacitive behaviour of produced carbons have been analysed and it has been found that the produced carbons behave hybrid capacitors with considerable pseudo-capacitive contributions. The performance of synthesised carbons has been compared to that of activated carbon derived through the chemical activation of carbon from the pyrolysis of coconut husks and to the reported capacitances of commercial activated carbons.

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1. Introduction

Since the mid-eighteenth century humanity has shown an ever-increasing reliance on access to efficient, affordable energy to facilitate transport, lighting, warmth, and the comforts of modern life [1]. Of particular importance to the functioning of many of these comforts of modern life is the reliable storage and release of electrical energy. In past and recent times much of this energy demand has been supplied by petroleum based fuels [2]; however, the environmentally damaging and inherently limited nature of petroleum based fuels make it necessary for alternative methods of energy storage to be pursued [1,2]. As such, in recent decades, a considerable amount of effort has been put into the development of efficient energy storage devices, particularly batteries, fuel cells, and supercapacitors.

Supercapacitive materials tend to have high surface areas and are able to form thin dielectric layers which enhance electric energy storage [2]. As a result of this, supercapacitors exhibit

capacitances much greater than those of normal electrolytic capacitors [2]. Due to the lack of permanent chemical and physical changes that supercapacitors experience upon charge and discharge, the devices show good cycle-life and high specific power, but relatively low specific energy [3,4]. The discharge times for supercapacitors are, however, considerably shorter than those of batteries and fuel cells [5]. As such supercapacitor applications are relatively limited in areas where long term, slow release, electrochemical energy storage is desirable, such as in the energy supplies for vehicles, portable computers, and mobile phones; however, they are invaluable in areas such as memory protection, back-up power supplies, and in other areas requiring rapid charge-discharge cycling [2]. In recent years, there has been significant research directed towards increasing the specific energy of supercapacitors while maintaining the high specific power of the materials [3].

Supercapacitors may be separated into three major categories, each giving us some information about the electrochemical behaviour of the material. Electrochemical double layer capacitors (EDLCs) are non-faradaic devices in which energy storage occurs electrostatically, via positive-negative charge separation at the electrode-electrolyte interface [2,6,7]. Due to the absence of

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chemical changes during their operation, EDLCs exhibit long cycle lives with good cycle stability [2]. The main electrode materials used in the construction of EDLCs are carbon-based materials, and the preferred methods of increasing the capacitance of these materials tends to be through increasing the surface area and electrical conductivity of the material [7]. Compared to this, pseudocapacitors store charge through fast, reversible redox reactions at or close to the electrode-electrolyte interface [7]. Supercapacitors of this form often consist of metal oxides (such as RuO_2) or conductive polymers [2,7]. This form of supercapacitor tends to show increased energy densities compared to EDLCs, at the expense of reduced cycle life [2]. The third class of supercapacitors are those of a hybrid structure which shows characteristics of both EDLCs and pseudocapacitors [2].

A range of materials may be used in supercapacitor devices depending upon the desired properties of the final device. Common materials used in the construction of these devices include transitional metal oxides, metal nitrides, metal sulfides, metal carbides, and carbon-based materials [2,8]. Carbonaceous materials in particular have been investigated as a cheap and flexible material for use in supercapacitors. Activated carbons and carbon gels with capacitances between 50 and 130 F g^{-1} in aqueous media have been previously investigated [9–11], as have carbon nanotubes [10–14], nano and mesoporous carbons [15–17], templated carbon nanostructures [18], and carbide-derived carbons [10,19,20]. Recent research into chemically modified graphene has produced composites of polyaniline electropolymerised onto the surface of graphene, which show capacitances as high as 230 F g^{-1} in aqueous sulfuric acid [8]; however, these materials are relatively complex to synthesise. As such it is desirable that a simpler, less expensive method of producing carbons for use as supercapacitor electrode materials be found. Of the potential methods for producing these carbonaceous materials investigated in recent years, a promising method is the electro-reduction of molten carbonate salts [21]. This path of carbon synthesis is of particular interest as a medium temperature method of producing carbonaceous products with physical properties that depend heavily on the conditions of deposition [21–29]; however, at this time, relatively little is known about the electrochemical performance and charge-storage potential of these materials. This work investigates charge storage mechanisms in carbons produced in a molten

$\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3\text{-Na}_2\text{CO}_3$ (43.5:25:31.5 mol%, [22]) eutectic under a set of standard conditions, with a particular focus being placed upon identification of the relative contributions of EDLC and pseudocapacitive charge storage on the total capacitance of these carbons. This is achieved through electrochemical characterisation by step potential electrochemical spectroscopy (SPECS) in three electrode cells. SPECS is a versatile technique which has previously been used to characterise the influence of applied potential and state of charge on the kinetics of diffusion through manganese dioxide electrodes [30–33], and in differentiating faradaic and non-faradaic charge storage contributions in manganese dioxide electrodes [34]. More recently the technique has also been adapted and expanded for use in the characterisation of charge storage processes in carbons and other electrode materials, with focus being placed on rate performance and the development of a suitable model for use in the analysis of SPECS results [35,36]. Due to the versatility of the SPECS technique it was judged to be a good analysis technique for use in the separation of charge storage contributions.

2. Experimental

2.1. Carbon synthesis

Carbons were synthesised in three electrode cells (Fig. 1) containing a molten ternary $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3\text{-Na}_2\text{CO}_3$ electrolyte at the eutectic composition (43.5:25:31.5 mol%). The ternary carbonate eutectic was prepared in house from Li_2CO_3 , K_2CO_3 and Na_2CO_3 (Sigma-Aldrich, >99%). Carbonate powders were initially dehydrated under atmospheric conditions at 100°C for at least 24 h following which the powders were mixed together at the eutectic composition and ball-milled at 170 rpm in 10 forward and 10 reverse, 2 min cycles using a Fritsh Pulverisette 6 zirconia ball mill. Ternary eutectics were fused at 500°C for 1 h under a 60 mL min^{-1} CO_2 flow and allowed to cool to room temperature prior to being reheated for carbon synthesis.

The mechanism of carbon reduction was examined by cyclic voltammetry prior to bulk carbon electrodeposition so as to confirm that carbon deposition was proceeding without unexpected impurities. Electrochemical experiments were controlled using a Pine Wavenow potentiostat.

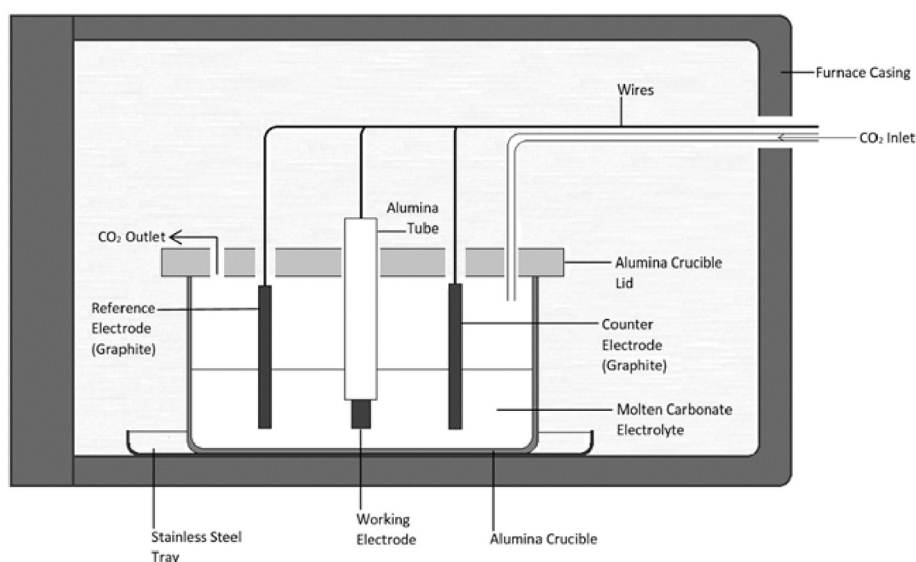


Fig. 1. Schematic for the electrochemical cell setup used throughout this research.

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