

CONDUCTIVE ADDITIVES AND INTER-PARTICLE VOIDS IN CARBON EDLC ELECTRODES

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INTRODUCTION

Porous carbons are the most widely used electrode material in electric double layer capacitors (EDLC's) due to their unique combination of: high surface area, porosity, conductivity and chemical compatibility with a range of protic and aprotic electrolytes [Burke, 2001; Pandolfo & Hollenkamp, 2006].

EDLC electrodes are commonly prepared from a mixture of: powdered activated carbon, a conductive additive (e.g. graphite/carbon black) and a binder; which is subsequently coated onto a metallic substrate. Whilst the conductive additive improves the electrical connectivity of the carbon mixture, its presence (and form) can also alter the porosity and voidage of the carbon electrode. Carbon EDLC electrodes can be regarded as having a hierarchy of porosity ranging from fine nanopores, contained within individual activated carbon particles, through to the micron-sized pores (or voids) created by the packing of carbon particles into the electrode bed/coating. While the majority of the electrode surface area (and hence the bulk of the capacity) is associated with the carbon nanopores (especially pores < 5 nm), the accessibility and percolation of the electrolyte to fine pores will ultimately be influenced by the network of larger pores and voids which serve as electrolyte pathways. In addition, large pores and voids also act as electrolyte reservoirs thereby improving electrolyte accessibility and ensuring sufficient ions are available to avoid electrolyte depletion.

In this study we investigate the effect of conductive carbon additives on the conductivity and inter-particle porosity/void volume of carbon electrodes, and discuss their contribution to EDLC performance.

EXPERIMENTAL

The electrode coatings were prepared by stirring and ball-mixing an aqueous slurry of three solid ingredients: (i) polymeric binder – sodium carboxy-methyl cellulose; (ii) conductive carbon – (*carbon black or graphite*) and (iii) microporous activated carbon. Mixing is continued until a stable suspension of the required viscosity is obtained. The latter is adjusted by addition of water to the slurry. The mix is then coated onto clean 30µm aluminum foil, with thickness determined by the choice of calibrated grooved rod. Wet coated foils were then dried in an oven (without compaction) and stored over a desiccant until required. The properties of carbons employed in this study are listed in Table 1.

Once dried, each coated foil was assessed for carbon loading ($\text{mg}\cdot\text{cm}^{-2}$), coating thickness (typically ~90 µm) and film resistance. Electrode resistance was determined by sandwiching the coated foil between two 1 cm^2 metal discs under light pressure ($10 \text{ kg}\cdot\text{cm}^{-2}$) and resistance was measured directly using a milli-ohm meter.

Mercury intrusion/porosimetry, on the unsupported carbon coatings/films, was performed using a Micromeritics Autopore II 9220 high-pressure mercury porosimeter with a maximum operating pressure of 414 Mpa (60,000 psi) which is capable of accessing open pores down to ~4 nm in size. Prior to analysis, carbon films were peeled from their aluminium backing, dried and evacuated to <50 µmHg.

Electrochemical testing was performed using a Solartron 1470 analyser. Measurements were conducted on 1 cm × 1 cm sections (in a two electrode configuration), immersed in dry acetonitrile solutions containing 1 M Et_4NBF_4 (Honeywell) as a supporting electrolyte and maintained under an atmosphere of dry nitrogen.

Table 1. Properties of carbons used in this study.

Sample	Powder Resistivity* (under 40kg.cm ⁻² Load)	BET Surface Area	Particle Size (D ₅₀)
	[mΩ.cm]	[m ² .g ⁻¹]	[μm]
Conductive carbons			
SFG-6 (graphite)	11.5	16	6
L6 (carbon black)	36.0	273	-
Activated carbon			
Maxsorb -20	41.0	1856	8.9

* measured according to Espinola *et al.*, 1986.

RESULTS AND DISCUSSION

A range of electrode coatings, of varying thicknesses were prepared, using the same carbon mixture composition, and the physical properties of selected carbon electrodes are shown in Table 2. As expected, the carbon loading and dry electrode thickness increase with an increase in metering thickness. The electrode resistance also shows a small increase with coating thickness although the increase is not generally observed to be linear. The lack of linearity is most likely due to a significant resistive contribution from the carbon - aluminium collector interface [Taberna *et al.*, 2003] which becomes less significant with the increase in coating thickness.

Table 2. Properties of aluminium supported carbon electrodes (carbon mixture: activated carbon + 10% binder + 20% L6 carbon black).

Run no.	Metering thickness	Carbon loading	Average dry electrode* thickness	Electrode Resistance*	Coating Porosity**
	[μm]	[mg.cm ⁻²]	[μm]	[Ω]	[%]
5/60	60	2.7	94	0.083	45.4
5/100	100	3.6	102	0.090	45.9
5/150	150	5.7	162	0.103	44.8

* includes 30μm Al collector; **determined by mercury porosimetry

The porosity of the carbon coatings were not observed to vary significantly with coating thickness (Table 2). This observation is supported by the similarity of their respective mercury intrusion profiles shown in Figure 1. The intrusion profiles also show three distinct regions of porosity within the coatings (depicted in the Figure). The region centred from ~1-2 μm is attributed to the presence of inter-particle voids between carbon particles within the coating. Voids of this size are consistent with the 8.9μm (D₅₀) particle size of the activated carbon (Table 1). These voids are largely formed by the close packing of activated carbon particles although there will be some contribution from the presence of the carbon black. The intermediate region shows a broad cluster of porosity in the 0.02-0.1 μm region which is attributable to the 'intra-aggregate' porosity of the carbon black which is composed of rigid aggregates of nanometre sized primary particles [Hess & Herd 1993]. The rising peak at <0.01 μm can be attributed to the larger mesopores, within the activated carbon particles, that are penetrated at high intrusion pressures. It should be noted, however, that as the lower limit of the mercury penetrometer is ~4 nm, and the activated carbon is predominantly microporous (> 90% less than 2 nm), relatively little of the activated carbon 'internal' porosity is measured. Hence, the technique of porosity/voidage determination by mercury porosimetry is highly suited to this study and capable of identifying important contributions to electrode performance, capacitance and kinetics.

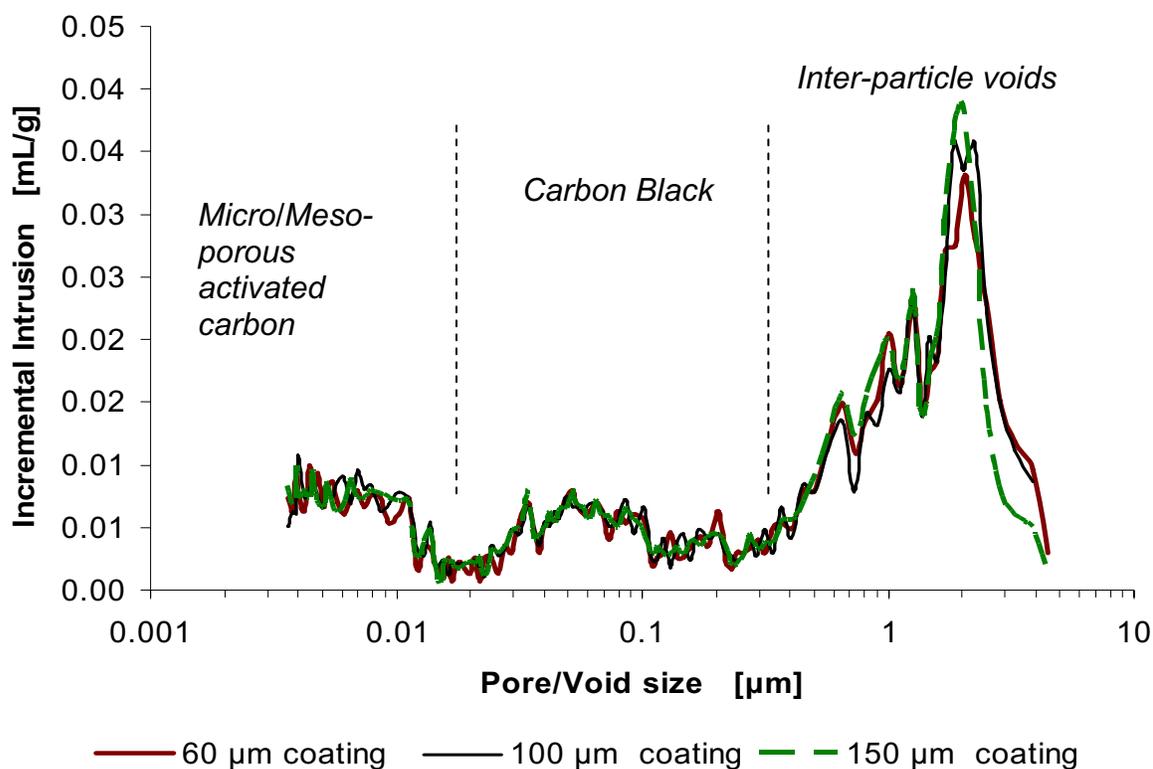


Figure 1. Mercury intrusion profiles of carbon films of differing thickness (refer to Table 2).

Effect of increasing carbon black concentration

To investigate the effect of conductive filler on electrode performance and porosity, a series of electrodes were prepared with increasing amounts of carbon black and a summary of their physical properties is presented in Table 3.

Table 3. Properties of aluminium supported carbon electrodes with varying amounts of conductive carbon black.

Run No.	Amount of L6 [wt.%]	Active material loading [mg.cm ⁻²]	Average coating thickness [μm]	Electrode Resistance* [Ω]	Median Pore/Void Size** (by volume) [μm]	Bulk Density** [g.mL ⁻¹]
15	0	3.6	77	38.5	1.02	0.51
22	1.25	4.3	91	0.16	1.00	0.53
20	2.5	4.2	90	0.18	1.05	0.53
12	5	3.6	78	0.15	n/a	n/a
17	10	4.2	90	0.14	1.06	0.54
14	20	3.9	86	0.11	0.60	0.53
16	40	4	89	0.08	0.07	0.56
18(av)	80	3.3	84	0.08	0.05	0.63
19(av)	20% SFG6	4.5	87	10.3	0.815	0.54

* includes 30μm Al collector; **determined by mercury porosimetry

Table 3 indicates that the addition of even a small quantity of carbon black (1.25 w/w%) to the coating mixture results in a very large improvement in reducing electrode resistance. A 100 μm coating of the activated carbon mixture with no carbon black (L6) has an electrode resistance of 38.5 Ω and decreases to 0.16 Ω with the addition of 1.25% (w/w) carbon black to the coating mixture. As there is relatively little difference in the intrinsic resistivity of the carbon black and activated carbon (Table 1), this improvement can be attributed to the improved particle connectivity achieved by the incorporation of the carbon black. The carbon black, which has a highly 3-dimensional structure of fused conductive nanoparticles, is very effective in attaching to, and filling the inter-particle voids between the irregularly packed carbon particles. Increasing the proportion of carbon black continues to reduce the film resistance of the coating although the rate of improvement is greatly reduced, and in some cases, the higher levels of carbon black are not warranted. Interestingly, the use of SFG-6 (graphite flakes) as a conductive additive is not as effective as carbon black; despite the intrinsic lower resistivity of the graphite (Table 1). This can be attributed the more expanded 3-D structure of the carbon black which is more effective in filling voids whilst maintaining good contact (and hence electrical connectivity) with surrounding particles.

An increased proportion of carbon black also affects the porosity and density of the coating. With increasing carbon black content, coatings generally show a decrease in median pore size and an increase in bulk density (Table 3). These changes are consistent with the hypothesis that carbon black is occupying the inter-particle void space of the coating and is supported by their corresponding mercury intrusion profiles of carbon films (Figure 2) which clearly shows a decrease in the intrusion volume associated with inter-particle voids, with increasing carbon black content, and also a decrease in the median size of the voids. A corresponding increase in the 0.02 -0.1 μm region, which is attributable to the ‘intra-aggregate’ porosity of the carbon black, is also observed.

The results confirm that not only are carbon blacks very effective in improving the electrical connectivity of the carbon coating, but, particularly at higher concentrations, they also modify the macro-porosity of the coating by decreasing the size of the inter-particle porosity and introduce additional porosity that may be characteristic of the type of carbon black employed.

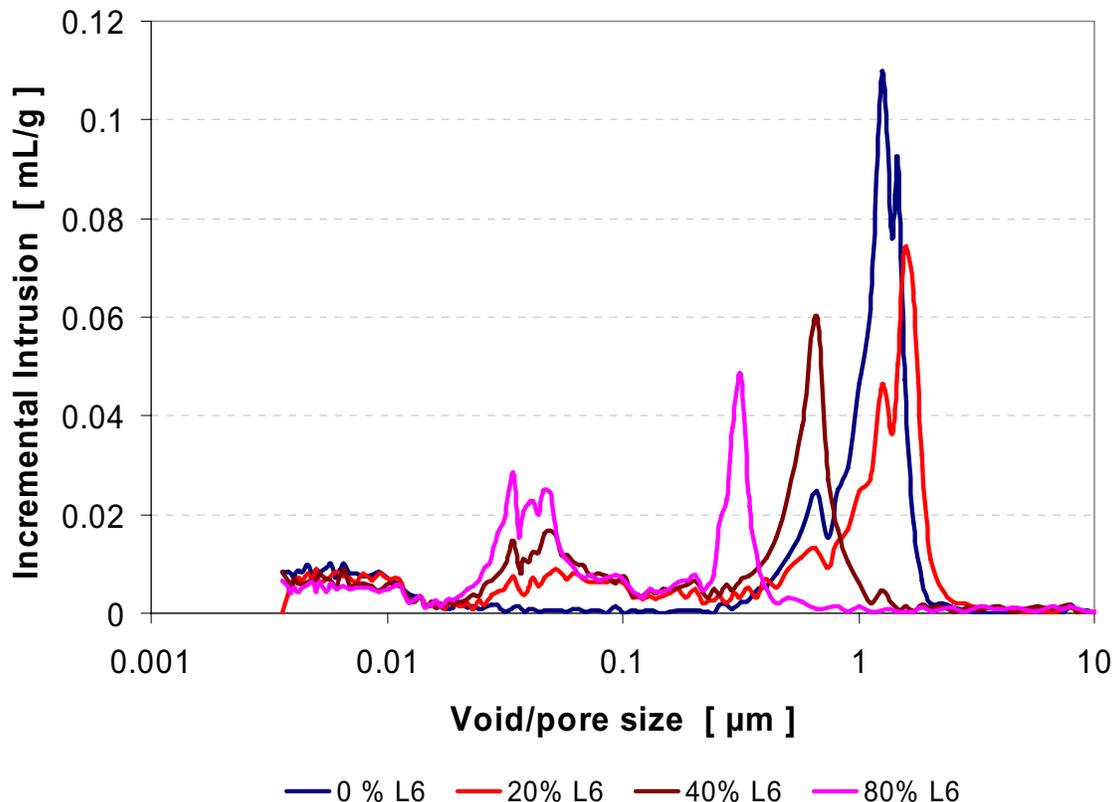


Figure 2. Mercury intrusion profiles of carbon films of with increasing amounts

of conductive carbon black (L6).

Electrochemical analysis

Cyclic voltammograms (CV) were recorded for sample electrodes from each of the coatings identified in Table 3, at scan rates ranging from 1 to 2000 $\text{mV}\cdot\text{s}^{-1}$. The results, expressed as specific capacitance (in $\text{F}\cdot\text{g}^{-1}$) normalized to the highest recorded value, are plotted in Fig 3.

In Figure 3, the data are plotted with a logarithmic scale for the scan rate so as to highlight the intermediate range of scan rates where the measured capacitance begins to decrease rapidly (compared with the plateau values at lower scan rates). With this treatment, it is clear that electrode capacitance is maintained at scan rates up to $\sim 50 \text{ mV s}^{-1}$. At higher sweep rates, capacitance falls away relative to the highest values. This is a universally observed phenomenon (for porous carbon supercapacitor electrodes) which is associated with the combination of electrode resistance and restricted solution diffusion within the porous network of the electrode [Conway, 1999; Wu and Wang, 2002]. The influence of the first of these factors is apparent from a consideration of the data for electrode resistance in Table 3. Most of the electrodes register resistance of $<0.2 \Omega$, which indicates that the concentration of conductive carbon is sufficient to extend the conductive network throughout the electrode.

In the absence of a conductive carbon in the dispersions (0 wt. % L6), electrode resistance is more than two orders of magnitude higher (38.5Ω) and the electrochemical response only yields the expected capacitance at the lowest scan rate. In this case there is insufficient conductivity in the electrode to access its surface area on a reasonable timescale despite the high porosity of the coating.

The finding of a strong relationship between bulk resistance and the accessibility of capacitance at different rates was confirmed with the electrodes containing SFG6 (e.g. 20% SFG 6) in which the electrode resistance was also high ($\sim 10 \Omega$).

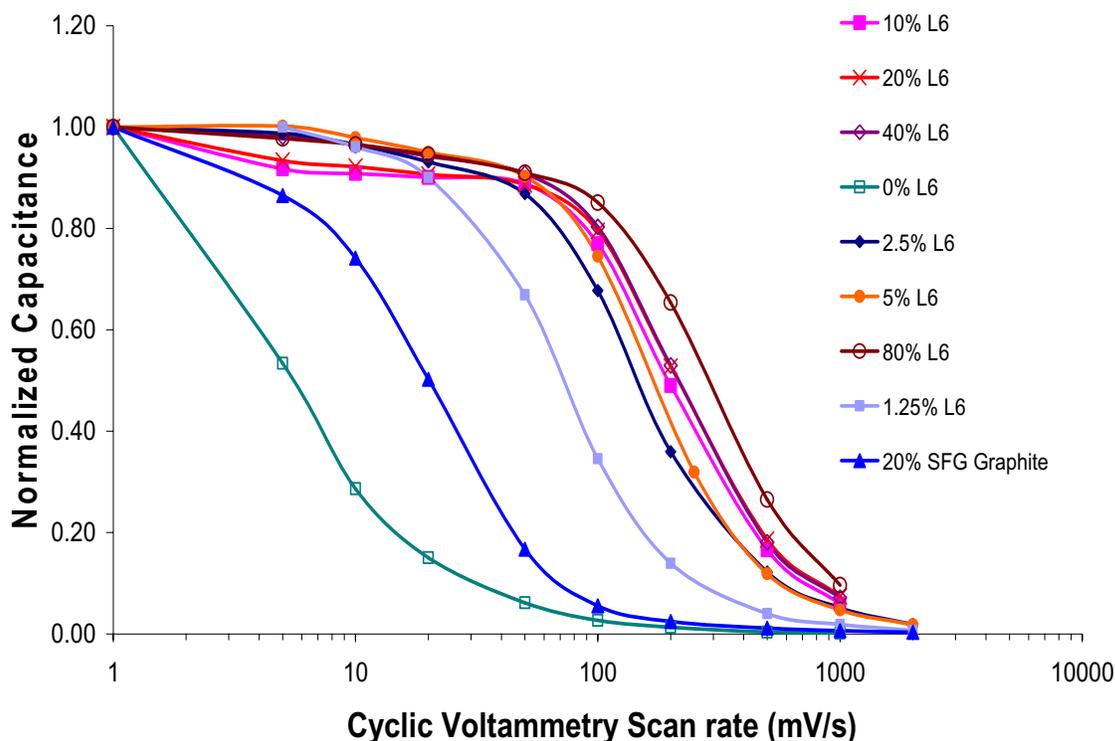


Figure 3. Plot of normalized capacitance versus scan rate for electrodes outlined in Table 3.

CONCLUSIONS

Through the interpretation of porosity and intrusion data, and correlation to the electrochemical response, this study has confirmed that, not only are carbon blacks very effective in improving the electrical connectivity of the carbon coating, but they also modify the macroporosity of the electrode coating. At high concentrations carbon blacks decrease inter-particle porosity and introduce additional porosity that may be characteristic of the type of carbon black employed. Significantly, though, increases beyond a few weight percent of carbon black do not alter the characteristics of the electrochemical response, and at very high concentrations, the capacitance per unit electrode weight decreases as the difference in specific surface area between the activated and conductive carbons is emphasised.

It is observed that electrode coatings prepared from a carbon slurry have a highly macroporous structure and that electrolyte accessibility to individual activated carbon particles is unlikely to be the limiting factor to accessing capacitance. Electrochemical testing has confirmed the strong relationship between bulk electrode resistance and the accessibility of capacitance at different rates.

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