Carbon black supercapacitors employing thin electrodes

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ABSTRACT

Carbon black supercapacitors that employ thin (∼1 μm) electrodes were produced by coating and inkjet printing on a conventional current collector or directly on a separator membrane. The simplicity and diversity of ultrathin electrode fabrication were facilitated by the physical form of carbon black, which can be described as a fine particle of around 100 nm in size. It was established that the performance of carbon black in thin supercapacitor electrodes may be compared with carbon nanotube and graphene materials in those instances where fast frequency response is desired from the supercapacitor. At the same time, the fast response supercapacitors that employ nanotubes and graphenes have presently involved more elaborate fabrication routes. RC time constant of 354 μs and phase angle of −75° at 120 Hz is demonstrated for carbon black supercapacitors that employ SC3 carbon black of 1800 m^2 g^{-1} surface area.

1. Introduction

Supercapacitors, ultracapacitors, or electrochemical double layer capacitors are the synonyms of energy storage devices, whose domain of energy density versus power density cannot be accessed neither by electrolytic or electrostatic capacitors, batteries, or fuel cells [1]. Although still evolving into the area of ever more energy containing and powerful devices, supercapacitors have already been able to address the increasing needs of electronic (cell phones, digital cameras, etc.), industrial (uninterruptible power supplies, grid conditioning, windmills, cranes, etc.) and transportation/automotive (trains, busses, cars) sectors [2]. Being unique, in terms of combination of characteristics including power density, temperature range, life cycle and safety, supercapacitors may also be used complementary to batteries, and, in a few certain cases, supercapacitors can even replace batteries [2]. Recently, supercapacitors were also shown to expand their potential application into the realm of electrolytic capacitors for ac line-filtering [3], showcasing that novel carbons (e.g. graphenes), which together with improved conventional carbons (e.g. activated carbons) [4] as well as high-voltage and high-stability electrolytes [5] may provide a pathway for further adoption and expansion of supercapacitors in various applications.

The most common construction of supercapacitors consists of two carbon electrodes, deposited on current collectors (e.g. aluminum foil), and sandwiched together with a non-electronically conducting separator membrane in the middle [1]. Usually, supercapacitor electrodes are fabricated by coating or extrusion with a thickness of around 100 μm for energy density reasons. Thinner electrodes (∼10 μm) are not uncommon for electronic applications of supercapacitors, as the thickness of electrodes is one of the factors determining the Equivalent Series Resistance (ESR) and the power density of supercapacitors [6,7]. Furthermore, ultrathin electrodes (∼1 μm) can provide superb power density characteristics and rapid response, and, as demonstrated in this study, supercapacitors containing thin electrodes can be fabricated by employing conventional carbon black materials.

Recent work on supercapacitors that use thin electrodes with good ion transport characteristics has exemplified the potential of graphenes [3] and carbon nanotubes [8] for supercapacitors of high frequency response operation. The supercapacitors based on these materials were shown to outperform the conventional activated carbon supercapacitors at high frequencies, whose sluggishness is governed by the complexity of torturous porous network of activated carbon electrodes, resulting in decay of operation above around 0.1 Hz [3] and, in rare instances, in around 10–20 Hz range [9].

In this work, we have continued the exploration of carbon solutions for high frequency response applications of supercapacitors. We demonstrate that carbon blacks can be employed for thin (∼1 μm) electrodes in supercapacitors, allowing fast frequency response operation facilitated by the short length of pores within the carbon black material. In this respect, we have shown that carbon black can be advantageous alternative to presently more

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expensive carbon nanotubes [8] and graphenes [3] in fast frequency response supercapacitors, potentially finding application in ac line-filtering in electronic devices and in pulse applications of supercapacitors. We also demonstrate that, in addition to conventional manufacturing routes, such as coating, carbon black electrodes can be produced by printing, such as inkjet printing, and deposited directly on separator membranes for ultrathin and flexible supercapacitor architectures.

2. Experimental

Two approaches for fabrication of carbon black electrodes were used. In the first approach, the electrodes were produced by the traditional coating procedure of casting of carbon black ink containing 2 wt.% of solids on top of a 25 μm thick conductive vinyl current collector (Intelicoat Tech.). The solids in ink constituted of 10 wt.% of polytetrafluoroethylene (PTFE) binder (Aldrich, 60 wt.% PTFE dispersion in water) and 90 wt.% of SC3 carbon black (Cabot Corp.), which were ultrasonically dispersed in isopropyl alcohol solvent. The utilized carbon black, SC3, displays a gravimetric capacitance of 115 F g^{-1} with an organic electrolyte and a surface area of around 1800 m^2 g^{-1} [10]. For coatings, we used a Mayer rod, which produced a 25 μm thick wet coating and around 1 μm thick electrodes after drying at 60 °C overnight. To manufacture a prototype supercapacitor in the HS test cell (Hohsen Corp.) [11], we sandwiched a 30 μm thick cellulose separator (TF4030, Nippon Kodoshi Corp.) between two 1.35 cm in diameter carbon black electrodes and used an aqueous, 25% potassium hydroxide (KOH), electrolyte solution. The utilized HS test cell was an alternative solution to assembling a supercapacitor in a coin cell. Similar cells are widely used in industrial and academic research and development. The construction of the HS test cell is depicted and described elsewhere [11].

In our second fabrication approach, thin carbon black electrodes were produced directly on separator membranes by inkjet printing (Fujifilm Dimatix printer). One or both sides of membrane were deposited with carbon black electrodes of around 1 μm in thickness. Cellulose separator (TF4030, Nippon Kodoshi Corp., 30 μm thick) or polypropylene (PP) separator (Celgard 2500, 25 μm thick, 55% porous, typical pore size of 0.21 μm by 0.05 μm) were used. In the case of cellulose separator, we printed the electrodes on one side of separator and then folded the membrane so that the electrodes face each other. Prior to folding, expanded graphite, ABG1010 (Superior Graphite), displaying around 20 m^2 g^{-1} surface area, was manually rubbed on top of carbon black electrodes to serve as current collector. The graphite flakes were well-entrapped within fibrous cellulose separator. 25% KOH electrolyte solution was used with supercapacitors printed on cellulose separator. In the case of polypropylene (PP) separator, we printed supercapacitor electrodes on opposite sides of one membrane. The electrodes were spatially registered with respect to each other. No current collector was used in this case, so that the carbon black electrodes were directly contacting the HS test cell positive and negative terminals. 1.8 M triethylmethylammonium tetrafluoroborate in acetonitrile (TEMABF$_4$/AN) from Honeywell was used as electrolyte solution with supercapacitors printed on PP separators.

For inkjet printing, inks containing from 2 to 4 wt.% of SC3 carbon black were used. Carbon black was ultrasonically dispersed in n-methylpyrrolidone (NMP) solvent. 4 wt.% (with respect to carbon black weight) of polymeric binder, polyvinylidene fluoride (PVDF) was used. The produced inks were stable over a few days inside the inkjet cartridges. SC3 carbon black employed no surface treatment agents for ink formulations, as it is known that NMP is a good dispersing solvent for carbon black [12].

The ^{19}F NMR data were collected at 27 °C. Samples for NMR were prepared by dispersing 0.176 g of SC3 carbon black or RP20 activated carbon (Kuraray Chemicals) in 4 mL of 1.8 M TEMABF$_4$/AN by ultrasonic sonication.

3. Results and discussion

Carbon black is not a new material for supercapacitor electrodes [13,14]. It has primarily been used as conductive additive at 2–10 wt.% loadings to activated carbons for reduction of ESR and the fraction of electrolyte weight in supercapacitors (e.g. organic electrolyte solution is currently the most expensive part of supercapacitor) [15], but carbon black has also been used as a primary carbon material in supercapacitor electrodes [13,16]. Although, a wide variety of other carbon forms may be used for electrodes, such as activated carbon particulates, activated carbon fibers and cloths, carbon aerogels, carbon nanotubes and graphenes [14], carbon black can provide an economical large-scale [17] alternative to the other commercially existing electrode materials and the ability to produce ultrathin (<1 μm) electrodes. Nevertheless, the two drawbacks of conventional carbon black in supercapacitor electrodes have been identified in the case when carbon black was used as primary electrode material in conventional thick layer electrodes. Firstly, the poor packing density of existing commercial grades of carbon black of high surface area results in the low volumetric capacitance of devices, and, secondly, the poor mechanical stability of produced carbon black electrodes (probably due to the larger number of smaller carbon black particles compared with activated carbon particles) may require an increased amount of polymeric binder for electrode fabrication [14]. To resolve the packing density drawback of commercial carbon black, we designed new carbon black materials of high surface area and improved packing [10,16]. As for the mechanical stability of electrodes described in this report, we have not observed any issues for thin (~1 μm) electrodes produced by coating or inkjet printing. An example of inkjet-printed electrodes on cellulose or PP separator membranes is shown in Fig. 1(a). We think that a few factors contributed to a good mechanical stability of electrodes. Firstly, the small thickness of electrodes ensures fast and homogeneous electrode drying after deposition without formation of cracks or flakes in carbon mass. The small thickness also ensures that only around 10 carbon black aggregates are stacked on top of each other, which may be small enough for the utilized binder to work efficiently throughout the electrode thickness. Secondly, we think that the utilized substrates, that are conductive vinyl, cellulose and PP, may have been more effective in terms of providing adhesion to carbon black, compared with metallic substrates, such as nickel or aluminum. A control experiment with a draw-down deposition of carbon black on a nickel foil resulted in electrodes that could be easily wiped off by finger sliding, which was not the case when electrodes were deposited on conductive vinyl foils.

The production of thin electrodes (~1 μm) was enabled by the physical form of carbon black. A simplified description of carbon black is an aggregate of a number of near spherical particulates, which are referred to as the primary particles. The size of primary particles can vary, but production of carbon black with primary particles of diameter down to 8 nm is currently feasible. The number of primary particles in carbon black aggregates can vary as well, for example from one to few tens or possibly hundreds, which results in the carbon black aggregate sizes of up to 500 nm, but, usually, the aggregate size is around 100 nm. It is important to note that we were able to disperse carbon black down to aggregate level in inks used for inkjet printing, as illustrated in Fig. 1(b), which we also confirmed by TEM particle statistical analysis. The number of primary particles and the arrangement of them in the aggregates dictate the structure and packing ability of carbon black [17]. The high surface area (>1000 m^2 g^{-1}) of carbon black is achieved via
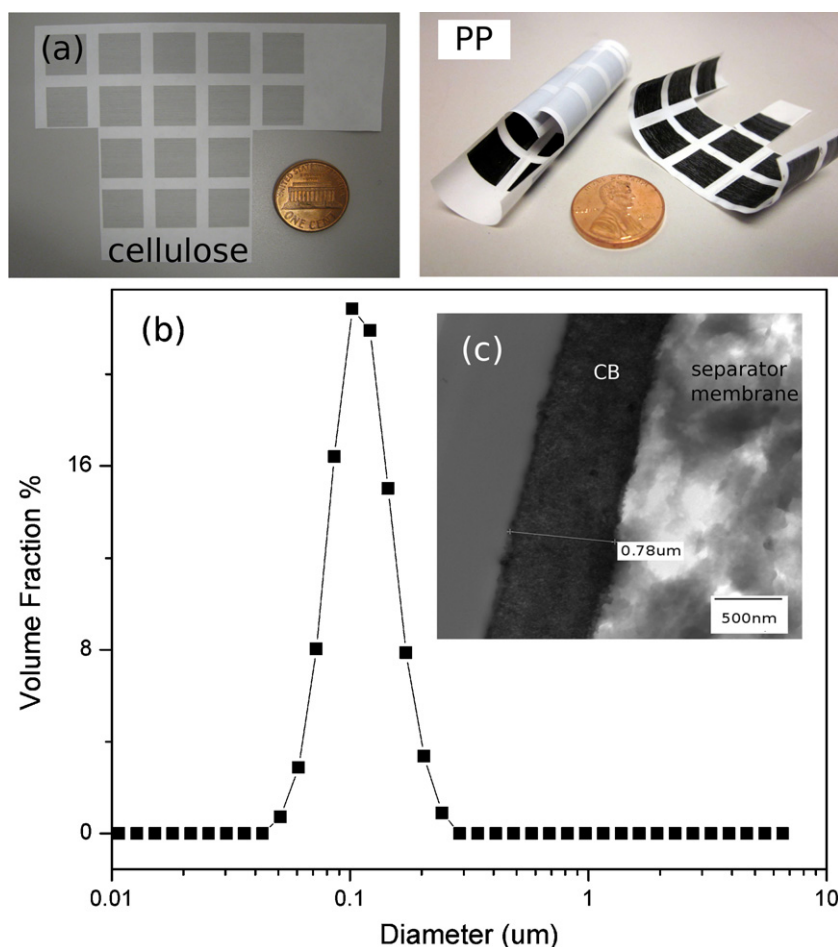
Fig. 1. (a) Examples of supercapacitor electrodes (1 cm × 1 cm), which were inkjet-printed on one side of cellulose separator membrane, and one or both sides of polypropylene (PP) separator membrane. (b) Particle size distribution of inks containing 4 wt.% SC3 carbon black in NMP solvent. (c) TEM image of cross-section of SC3 carbon black electrode on PP separator membrane.

creating porosity within the primary particles. Indeed, if no porosity is present, the surface area for carbon black having 8 nm diameter primary particles is around 400 $m^2 g^{-1}$, which was calculated assuming an intrinsic density of carbon black of 1.8 g cm^{-3}. The porosity in carbon black varies from mild surface pitting to the actual hollowing out of primary particles. Often times additional carbon black porosity in the 10 nm range is observed, which is due to the voids between primary carbon black particles within aggregates [10,16]. Due to the small primary particle size, the surface area of carbon black can be considered to be more accessible than that of high surface area activated carbons, whose particles are usually few microns in diameter and consists predominantly of micropores (<2 nm). The surface accessibility of carbon black is believed to be due to the short path-lengths of pores within carbon black primary particles.

Recently, a novel manufacturing method for supercapacitors has been introduced, where electrodes are directly deposited onto the surface of separator membrane by coating or printing [18]. The electrodes, in that study, constituted of carbon nanotubes (specific capacitance of 33 F g^{-1} with an organic electrolyte), which simultaneously served as active material and current collector, due to the nanotube's high electronic conductivity. It is known, on the other hand, that carbon blacks have traditionally served as pigment for inkjet printing. Although, low surface and chemical surface modifications of carbon blacks in traditional inks render them unsuitable for supercapacitor applications, the newly developed SC3 carbon black (specific capacitance of 115 F g^{-1} with an organic electrolyte

[10]), formulated in ink without surface modification, is suitable for inkjet-printed supercapacitors.

In our study, the electrodes printed on single side of cellulose separator were tested with aqueous KOH electrolyte solution and those printed on both sides of PP were tested with 1.8 M TEMABF$_4$/AN organic electrolyte solution. To prevent a possible penetration of carbon black inside the separator, which would create an electrical short, we used a 25 μm thick PP separator membrane (Celgard 2500), which displays a typical pore size of 0.21 μm by 0.05 μm according to its manufacturer (Celgard) and is used with organic electrolytes only due to the hydrophobicity of PP. The minimum pore size of 0.05 μm is, therefore, smaller than the size of carbon black aggregates in the ink (see Fig. 1(b)), allowing electrodes to stay on top of PP separator (see Fig. 1(c)) and us to inkjet-print electrodes on opposite sides of single separator (see Fig. 1(a)). Previously, to be able to print electrodes on opposite sides of single cellulose separator using carbon nanotubes, the separator was treated with layers of PVDF polymer prior to deposition of electrodes [18].

Accessible micro-porous structure of novel high surface area carbon black, SC3, as well as the ability to utilize it in thin electrodes, prepared via conventional coating or inkjet printing, makes SC3 an attractive candidate for high frequency response supercapacitors. More elaborate manufacturing conditions were previously reported in the literature for graphene and carbon nanotube high frequency supercapacitors, where vertically oriented graphenes directly on nickel current collector were synthesized
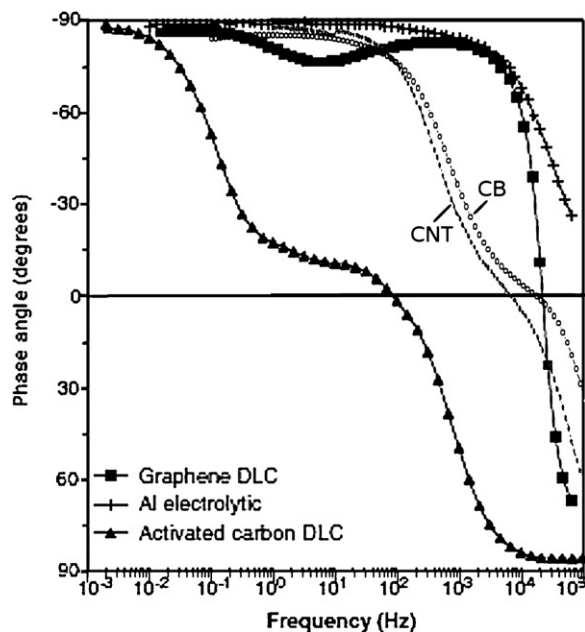
Fig. 2. Frequency response of carbon black (CB) supercapacitor, which utilizes SC3 carbon black electrode on conductive vinyl current collector and KOH electrolyte solution, in comparison with the literature data for graphene, carbon nanotube (CNT) and activated carbon supercapacitors. The results for SC3 carbon black supercapacitor are superimposed with the graphs published in literature.

Fig. 3. ^{19}F NMR scans of dispersions containing the same mass loadings of SC3 carbon black and RP20 activated carbon in 1.8 M TEMABF$_4$/AN.

by using radio-frequency plasma-enhanced chemical vapor deposition (CVD) [3], and the multiwall carbon nanotubes produced by CVD were electrophoretically deposited onto nickel foil substrates and subjected to a hydrogen furnace treatment [8]. In both of these cases the resulting electrodes presented an open structure which could be easily accessed by electrolyte ions. Nevertheless, the graphene electrodes displayed lower degree of tortuosity for electrolyte ion motion and, therefore, allowed higher operating frequency of graphene supercapacitor. Fig. 2 shows the superposition of literature data for carbon nanotube [8], graphene [3], and activated carbon [3] supercapacitors with our results for SC3 carbon black supercapacitor. The results for all these various materials were obtained with analogous KOH electrolytes and, thus, we can compare the carbon performance in these supercapacitors. The graphene supercapacitor shows its operation, exemplified by the phase angle being close to −90°, even at frequency of around 10 kHz, which is well above 120 Hz that may be needed for ac line-filtering [3]. At 120 Hz, however, the graphene supercapacitor displays a phase angle of −82°. In comparison to graphene supercapacitor, SC3 carbon black supercapacitor, produced by conventional coating of carbon black electrodes on conductive vinyl current collector, shows a phase angle of −75° at 120 Hz with the same 25% KOH electrolyte solution, which was used in graphene supercapacitor [3]. The carbon black supercapacitor also displays −45° phase angle at 641 Hz and 0° phase angle at 16.7 kHz, where the latter is in close proximity to the 0° phase angle of graphene supercapacitor.

Based on the results of Fig. 2, it is evident that SC3 carbon black supercapacitor is able to operate at frequency that is comparable to or better than that of multiwall carbon nanotube supercapacitor [8]. We can only speculate why this may be possible. It is possible that the carbon nanotubes may have been uncapped, allowing the ions of electrolyte to access the insides of the nanotubes and, thus, making the ions to experience increased tortuosity in their motion. This resulted in reducing the cut-off frequency of operation of carbon nanotube supercapacitor. Although, vertically aligned and capped carbon nanotubes may ideally provide faster frequency of supercapacitor operation, the present results on this system indicate
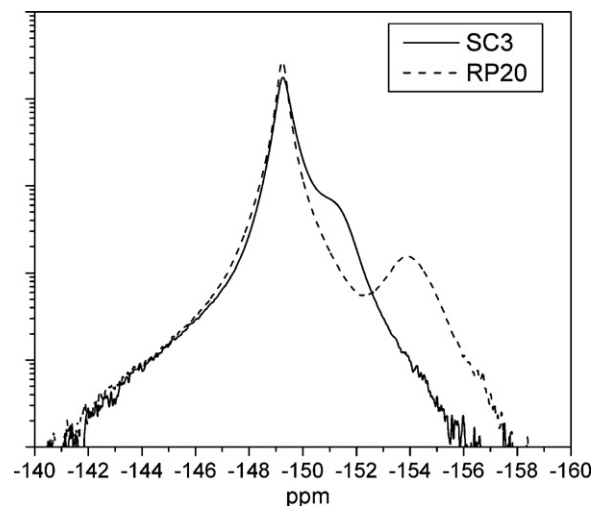
that achieving high operating frequencies is a challenging endeavor [19].

Fig. 2 also shows the data for a typical activated carbon supercapacitor [3]. We believe that much faster response of carbon black supercapacitor in comparison with activated carbon supercapacitor can be attributed to fast accessibility of carbon black surface by electrolyte ions, which may be a result of short lengths of pores within carbon black. To verify this concept, we performed a nuclear magnetic resonance, ^{19}F NMR, comparison of surface accessibility of carbon black, SC3, and commercial supercapacitor-grade activated carbon, RP20, by BF$_4^-$ ions of 1.8 M TEMABF$_4$ electrolyte (see Fig. 3). Two peaks can be clearly resolved in ^{19}F NMR, corresponding to BF$_4^-$ free in solution ($\sim$−149.2 ppm) and BF$_4^-$ absorbed on the surface. The upfield shift seen for absorbed BF$_4^-$ is due to the large magnetic susceptibility of carbon. The separation of NMR peaks between the adsorbed and free BF$_4^-$ ions is about 1750 Hz ($\sim$4.6 ppm) for RP20, while it is only about 550 Hz for SC3. The line width of the free BF$_4^-$ peak is around 190 Hz for SC3 and around $\sim$140 Hz for RP20. These results indicate faster exchange rate between the adsorbed and free BF$_4^-$ ions in SC3, which, taking into account the similarity in the pore widths for SC3 and RP20 [10], is due to much shorter pore lengths in carbon black in comparison to activated carbon.
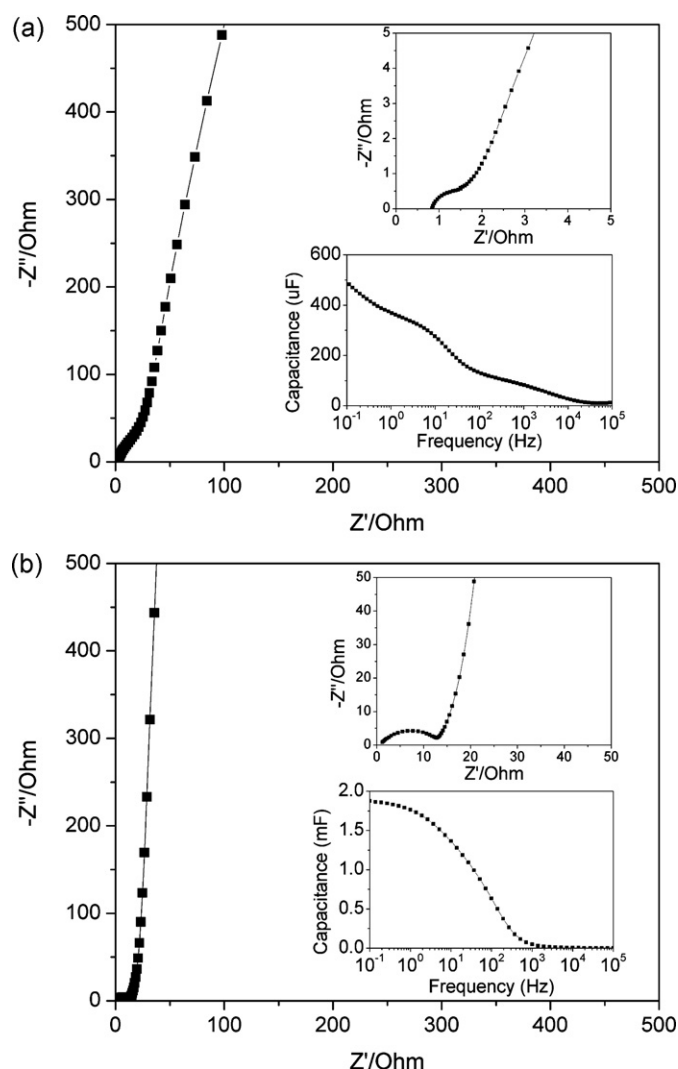
The spectroscopy scans of complex impedance of SC3 carbon black supercapacitor is shown in Fig. 4(a), from which we also derive the resistance, $R = Z'$, and capacitance, $C = (2\pi f Z'')^{-1}$, as a function of frequency, f, where Z' and Z'' are the real and imaginary parts of impedance. The capacitance, C, as a function of frequency is shown in Fig. 4(b). As indicated Miller et al. [3], the divergent behavior of capacitance at around 20 kHz is an artifact of the series-RC circuit model, following which the capacitance and resistance are derived. This artifact needs to be ignored. At 120 Hz, SC3 carbon black supercapacitor shows 800 μF capacitance (compared with 60 μF for bare vinyl current collector which we used), 0.44 ohms resistance, and, thus, the RC time constant of 354 μs. These values may be compared with the results for the graphene supercapacitor obtained at 120 Hz [3]: 175 μF capacitance (compared with 25 μF for bare nickel current collector used in that work), 1.1 ohms resistance, and the RC time constant of 200 μs. In both cases (SC3 carbon black and graphene supercapacitors), same KOH electrolyte solution was used and the electrodes were of similar sizes (diameter of 1.35 and 1.6 cm for carbon black and graphene electrodes, respectively). As in the case of graphene supercapacitor, capacitance saturation (horizontal behavior) at lower frequencies
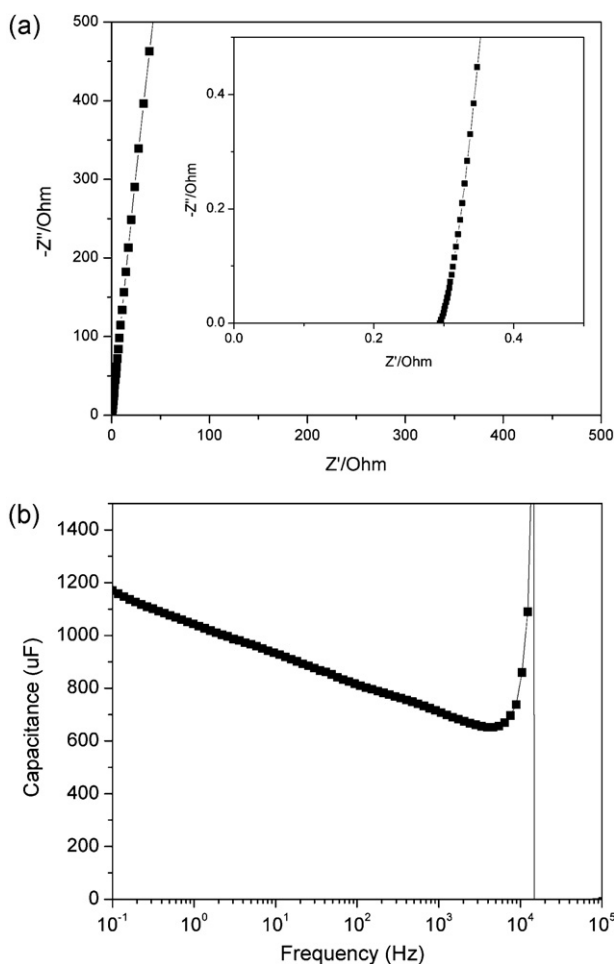
Fig. 4. (a) Impedance spectroscopy scans and (b) derived capacitance for carbon black supercapacitor, which utilizes SC3 carbon black electrode on conductive vinyl current collector and 25% KOH electrolyte solution.

Fig. 5. Impedance spectroscopy scans and derived capacitance of SC3 carbon black supercapacitors, which were inkjet-printed on (a) cellulose separator utilizing 2 wt.% carbon black inks and (b) PP separator using 4 wt.% carbon black inks. KOH electrolyte and 1.8 M TEMABF$_4$/AN electrolyte were used for supercapacitors utilizing cellulose and PP separators, respectively.

is not observed for SC3 carbon black supercapacitor, suggesting an involvement of a second, lower-rate charge storage process [3].

The impedance spectroscopy scans for inkjet-printed supercapacitors are shown in Fig. 5. SC3 carbon black supercapacitors printed on cellulose separator display a phase angles of $-63°$ at 120 Hz and $-45°$ at 764 Hz with KOH electrolyte. Nevertheless, a remarkable drop in capacitance, from around 500 μF at low frequencies down to 120 μF (see Fig. 5(a)), and high resistance of around 4.9 ohms are observed at 120 Hz. We attribute these results to unoptimized current collector layer, which, in this case, was expanded graphite flakes, manually deposited by rubbing on top of electrode surface. At the same time, some performance deterioration may have come due to using two separators (each 30 μm thick) in the supercapacitor (electrodes were printed on one side of separator), because we were concerned with having an electrical short if electrodes were printed on opposite sides of a single cellulose separator. To be able to produce a functional inkjet-printed supercapacitor containing electrodes on opposite sides of a single separator, we used a PP separator, which has pores that are smaller than the particle size of carbon black in the ink. 1.8 M TEMABF$_4$/AN organic electrolyte solution and no additional current collector were used in this case. The impedance scans are shown in Fig. 5(b), which indicates that the capacitive behavior is present up to around 200 Hz, after which a series-passive contribution (high frequency semicircle) dominates the impedance behavior. The maximum capacitance (horizontal behavior in the inset of Fig. 5(b)) is achieved as low frequencies of below 1 Hz, but

diminishes slowly in the 10 Hz range, so that the results may be comparable to the fastest activated carbon supercapacitors which use organic electrolytes [9]. We believe that our results for SC3 on PP separator are presently limited by the current collecting ability of supercapacitor.

Although needing further optimization and development, we believe that printable carbon black supercapacitors remain an interesting fabrication approach. Eliminating or diminishing the volume occupied by current collectors (usually 25 μm thick foils) can lead to improved volumetric capacitance of supercapacitors, as more space in the supercapacitor's body will be available for active material instead of current collectors. The improvement in space availability will depend on the thickness of electrodes, increasing for thinner electrodes. For SC3 carbon black electrodes of 115 F g^{-1} in organic electrolyte, an additional thin layer, serving as a current collector, may need to be used to alleviate the problem of higher ESR due to insufficient electronic conductivity of electrodes. Sufficiently conductive and printable carbon nanotubes of 33 F g^{-1} with organic electrolytes [19] may be employed for producing an optimized carbon black supercapacitor that employs thin electrodes deposited directly on separator.

4. Summary

Supercapacitors containing thin ($\sim$1 μm) carbon black electrodes, produced by conventional coating or inkjet printing were studied. It was shown that SC3 carbon black can be used as active material in supercapacitor electrodes operating at high frequency. Although carbon black supercapacitors demonstrate operation at frequencies lower than those achieved by graphene supercapacitors, they can satisfactory operate at 120 Hz and display 800 μF capacitance versus 175 μF, which was achieved by graphene supercapacitor of similar dimensions. Simple electrode fabrication for carbon black supercapacitor positively differentiates it from more complex production approaches adopted for graphene or carbon nanotube supercapacitors. One of fabrication approaches, which we explored, included inkjet printing of carbon black supercapacitor directly on a commercial separator membrane, thus, expanding the range of materials for single substrate-integrated supercapacitors.

Acknowledgements

References

[1] B.E. Conway, Electrochemical Supercapacitors, Kluwer Academic/Plenum Publishers, New York, 1999.
[2] J.R. Miller, A.F. Burke, Electrochem. Soc. Interface (Spring) (2008) 53–57.
[3] J.R. Miller, R.A. Outlaw, B.C. Holloway, Science 329 (2010) 1637–1639.
[4] P. Smith, et al., 16th Int. Supercapacitor Seminar on DLC 2006, Deerfield Beach, FL, 2006.
[5] J.-H. Choi, Y.-M. Chang, PCT Int. Appl. WO 2008026873 (A1), 2008.
[6] R. Kotz, M. Carlen, Electrochim. Acta 45 (2000) 2483–2498.
[7] T.L. Wade, High Power Carbon-based Supercapacitors, PhD Thesis, School of Chemistry, The University of Melbourne, 2006.
[8] C. Du, N. Pan, J. Power Sources 160 (2006) 1487–1494.
[9] V. Ruiz, A.G. Pandolfo, J. Power Sources 196 (2011) 7816–7822.
[10] A. Krause, P. Kossyrev, M. Oljaca, S. Passerini, M. Winter, A. Balducci, J. Power Sources 196 (2011) 8836–8842.
[11] http://www.hohsen.co.jp/en/products/detail.php?id=2.
[12] A. Basch, R. Horn, J.O. Besenhard, Colloids Surf. A: Physicochem. Eng. Aspects 253 (2005) 155–161.
[13] F. Beck, M. Dolata, E. Grivei, N. Probst, J. Appl. Electrochem. 31 (2001) 845–853.
[14] A.G. Pandolfo, A.F. Hollenkamp, J. Power Sources 157 (2006) 11–27.
[15] A.G. Pandolfo, G.J. Wilson, T.D. Huynh, A.F. Hollenkamp, Proceedings of Int. Conference on Carbon 2007, Seattle, WA, July 15–20, 2007.
[16] P. Kossyrev, Proceedings of the 6th International Symposium ECCAP Advanced Automotive Battery & EC Capacitor Conference, Orlando, FL, May 19–21, 2010.
[17] J.-B. Donnet, R.C. Bansal, M.-J. Wang, Carbon Black: Science and Technology, second ed., Marcel Dekker, Inc., 1993.
[18] L. Hu, H. Wu, Y. Cui, APL 96 (2010) 183502.
[19] Y. Honda, et al., Electrochem. Solid-State Lett. 10 (2007) A106.