Studies on activated carbon capacitor materials loaded with different amounts of ruthenium oxide

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Abstract

Ruthenium oxide–carbon composites with different loadings of RuO_2 on carbon have been synthesized by an electroless deposition process. Increase in RuO_2 loading results in increasing the specific capacitance of the composite electrode. The effect of temperature treatment on the performance of these materials has been studied in detail. Maximum capacitance was observed after heat treatment at $100°C$ for all the composites. Increasing the oxidation temperature further converts the Ru oxides to crystalline form, which leads to poor capacitance values. A maximum capacitance of 260 F/g was obtained for 20 wt.% RuO_2 loaded carbon treated at $100°C$. The volumetric surface area of the composite remains constant with increased RuO_2 loading. Since Ru oxides have a large pseudocapacitance, this increases the volumetric capacitance of the carbon significantly. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

In recent years various metal oxides have attracted attention for use as electrochemical capacitors in high-power applications [1]. The energy storage mechanism here is based on fast faradaic reactions, which occur at the interface between the oxide and the electrolyte [2]. Among the various metal oxides, ruthenium shows the best pseudocapacitive behavior. It has been shown that amorphous hydrous ruthenium oxide prepared by a sol–gel process exhibits much superior performance as compared with crystalline RuO_2 [3]. The amorphous structure leads to fast proton diffusion rates thus contributing to a high specific capacitance [4]. However, the cost of ruthenium and its compounds limits its wide spread usage in electric/hybrid vehicles and consumer electronics. Substitutes for Ru oxides do not show comparable energy and power densities [5,6].

Recent research efforts have attempted to minimize the Ru used by doping/alloying Ru with other oxides or dispersing RuO_2 over high surface area substrates. Following the first approach, Takasu et al. [7] synthesized RuO_2–MoO_3 films on a Ti substrate by a dip-coating process. A maximum pseudocapacitance of 208 F/g was achieved with 50 wt.% MoO_3 doped in the Ru oxide. Hu and Huang [8] electroplated ruthenium on a Ti substrate. However, the maximum capacitance obtained by them was only 100 F/g, much lower than 720 F/g reported for amorphous RuO_2. Wilde et al. [9] synthesized $SrRuO_3$ with perovskite type structure by coprecipitation of salts of Ru and Sr in 3 M KOH. Replacing Sr with La and Mn increased the capacitance significantly. A maximum capacitance of 160 F/g was achieved with 43 wt.% Ru in a La and Mn doped $SrRuO_3$ perovskite. Jeong and Manthiram [10] synthesized Cr doped Ru oxides by reduction of aqueous $K_2Cr_2O_7$ with Ru salt at pH > 6.5. They achieved a stable compound with capacitance of 740 F/g with 0.15 Cr incorporation in $Ru_{1-y}Cr_yO_2 \times H_2O$.

An alternate approach to reduce the amount of Ru is based on dispersing RuO_2 on a support with large surface area. Several carbonaceous materials with large surface areas serve as candidates for substrate materials [11]. Compared with Ru, carbon is very cheap. Further, carbon also gives rise to electrochemical capacitance. However, the specific capacitance obtained in this case is dependent on the pore size distribution and surface area [12]. Although activated carbon based double layer capacitors exhibit good power densities, the energy density is significantly lower as compared with amorphous RuO_2. By synthesizing RuO_2–C composites, the specific capacitance is increased as compared with bare

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carbon. Further, the amount of Ru is reduced thus making the final material less expensive and more attractive for commercial applications.

Using the above approach, Miller et al. [13] synthesized Ru/C aerogel composite electrodes by chemical vapor impregnation of ruthenium into carbon aerogels. A maximum specific capacitance of 206 F/g was achieved with 35 wt.% Ru loading. Zheng and Jow [14] reported a significant increase in power density by mixing their amorphous Ru oxides with 20 wt.% carbon black. Sato et al. [15] reported a 20% increase in specific capacitance by loading 7.1 wt.% Ru in activated carbon. In a previous publication, [16] we reported results from a RuO_2–C composite synthesized using an electroless deposition technique. It is seen that Ru is dispersed on the carbon matrix in the form of very small particles. Loading a small amount of RuO_2 (9 wt.%) on carbon increases the capacitance from 98 to 190 F/g. In this study we demonstrate that varying the amount of Ru in the deposit can enhance the specific capacitance of these composite electrodes further. The change in capacitance with Ru loading has been studied along with the effect of heat treatment on each loading.

2. Experimental

Ruthenium oxide–carbon composites were synthesized by electroless deposition of Ru on activated carbon in an alkaline bath. The carbon particles were immersed in an aqueous bath of ruthenium chloride, sodium hypophosphite, di-ammonium hydrogen citrate and ammonium oxalate. The pH and bath temperature were controlled to prevent precipitation of Ru. The bath composition and deposition conditions have been reported previously [16]. The amount of carbon used for deposition was kept constant (1 g). Varying the amount of $RuCl_3$ in the bath controlled the final amount of Ru in the composite. Different composites with 5, 9, 15 and 20 wt.% Ru oxide loaded on carbon were synthesized using this technique.

After plating the samples were filtered and dried. The exact loading of ruthenium was determined by a volumetric titration of the remaining bath. EDAX analysis indicated the presence of Ru on the surface of carbon. Hitachi S-2500 with iridium software was used for EDAX and SEM studies. Surface area of the composites was determined by BET analysis using Pulse Chemisorb 2000 (Micromeritrics Inc.). The effect of temperature on Ru performance was studied by heating the dried samples at 100, 200, 300 and 400°C in oxygen atmosphere for 3 h.

The metal-loaded carbon was mixed with 5% PTFE and ground to form a paste. Pellets of thickness 130–150 μm, weighing from 3 to 4.5 mg were prepared by cold-pressing the paste between two tantalum meshes. Electrochemical characterization of these materials was done using a three-electrode set-up with 1 M H_2SO_4 as the electrolyte, SCE as the reference electrode and Pt as the counter electrode. The

dimensions of the counter electrode were 2.1 cm by 2.0 cm. All measured potentials are referred to SCE reference electrode. Cyclic voltammetry, galvanostatic charge–discharge studies were used to characterize the materials. A potential window of 0.9 V was used in the case of both voltammograms and charge–discharge profiles.

3. Results and discussions

Fig. 1 presents the scanning electron micrographs of the RuO_2–C composites for two different weight percents of Ru. Fig. 1a and b show the morphology of the 15 wt.% loaded RuO_2–C composite at high and low magnifications, respectively, as revealed by SEM. Similar pictures for the 9 wt.% composite are seen in Fig. 1c and d. At high magnifications (Fig. 1a and c) the presence of Ru nanoparticles deposited on the surface of the activated carbon is revealed. The particles seem to be well adherent to the surface of carbon. Energy dispersive spectroscopy confirmed the identity of these particles as ruthenium. The 15 wt.% composite has larger clusters of Ru nanoparticles (Fig. 1c) as compared with the 9 wt.% composite (Fig. 1a). Electroless deposition proceeds by the formation of active sites on the surface of the substrate. The active sites are the nuclei for further deposition of the metal. Increasing the amount of $RuCl_3$ in the bath causes more amount of Ru to be deposited on carbon sites that already have some Ru nanoparticles on their surface. Hence bigger clusters are seen for the 15 wt.% composite as compared with the 9 wt.% deposit. Varying the deposition temperature and pH can control the cluster size. Increased temperatures and high pH values lead to faster deposition of Ru, which in turn causes the formation of large clusters. In this study all depositions were done at a temperature of 90°C and pH of 9.5.

Fig. 2 shows the cyclic voltammograms (CV) of 5 wt.% RuO_2–C composite treated at different temperatures at a scan rate of 1 mV/s. The CV is mostly featureless in the potential window of 0–0.9 V. The magnitude of the currents observed change with varying oxidation temperature. The anodic and cathodic currents decrease with increase in treatment temperature. The capacitance of the material was determined by integrating the anodic and cathodic charges. At 100°C, the total capacitance of this deposit was 153 F/g. This value decreased to 60 F/g at 400°C.

Further, complete reversibility is seen for pellets treated at 100 and 200°C, i.e. the ratio between anodic and cathodic charges is close to 1. The Q_a/Q_c ratio for the pellet treated at 100°C is 0.95, indicating that the faradaic reaction at the particle surface is fast and reversible. However, voltammograms of pellets treated at 300 and 400°C show increasing amounts of irreversibility. The charge efficiency drops to 0.79 at an oxidation temperature of 400°C. In our previous study on 9 wt.% composite, we found that heating the sample beyond 100°C decreases its capacitance and charge efficiency. The trend observed here is similar to that. CVs
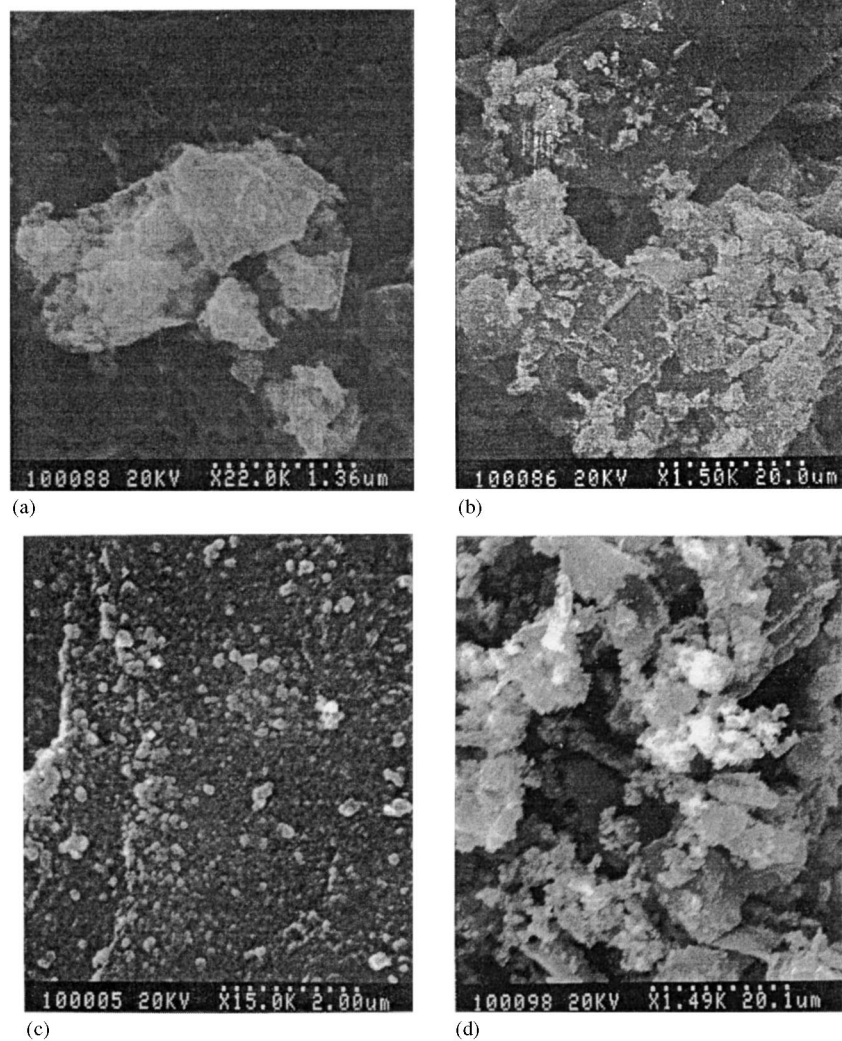
Fig. 1. SEM pictures of the composite materials: (a) 15 wt.% composite at high magnification; (b) 15 wt.% composite at low magnification; (c) 9 wt.% composite at high magnification; (d) 9 wt.% composite at low magnification.
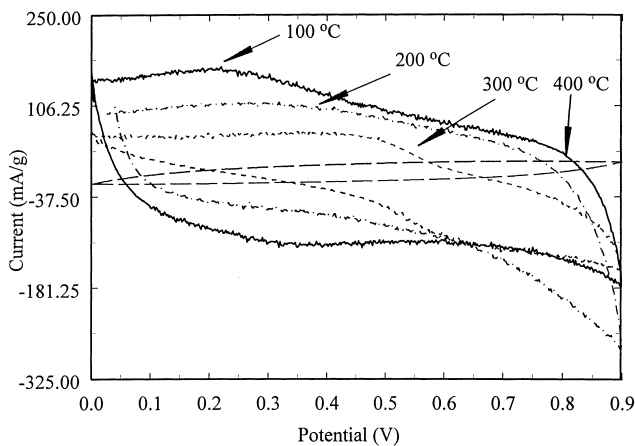

Fig. 2. Comparison of voltammograms of 5 wt.% RuO_2–C composite treated at different temperatures at a scan rate of 1 mV/s.

of 15 and 20 wt.% RuO_2 loaded carbon also follow the same pattern. From the above studies we could conclude that heating at 100°C yields the best performance for the RuO_2–C composite.

Fig. 3 shows CVs of pellets treated at 100°C with different Ru oxide loading. The capacitance increases from 145 F/g for the 5 wt.% composite to 260 F/g for 20 wt.% RuO_2 loading. The bare carbon has a specific capacitance of 98 F/g. The increase in specific capacitance with Ru loading arises due to the pseudocapacitance associated with RuO_2. The coulombic ratio (Q_a/Q_c) does not change with the amount of Ru present in the composite (0.95 at 5 wt.% to 0.93 at 20 wt.%). This indicates that the charge–discharge process at the particle–electrolyte interface is influenced more by the oxidation temperature than by the Ru oxide loading on the carbon surface. Similar results have been seen
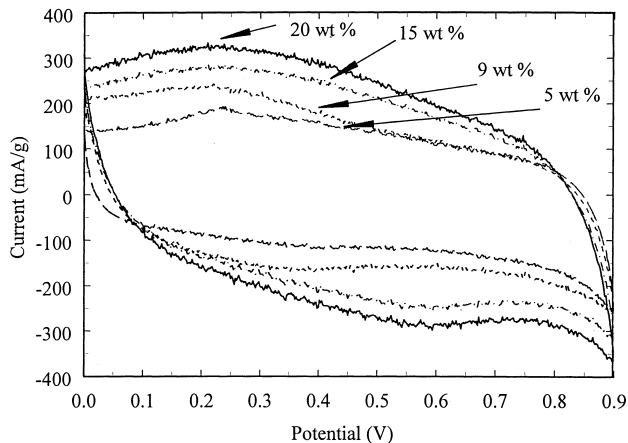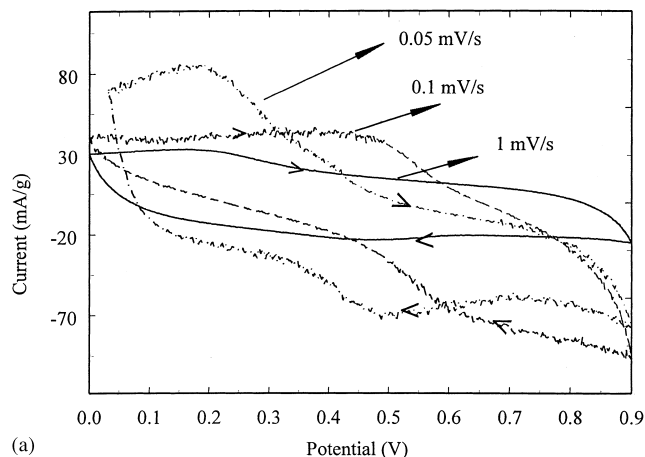
Fig. 3. Comparison of voltammograms of pellets with different loadings of Ru oxide oxidized at 100°C at a scan rate of 1 mV/s.

by Miller et al. [13] and Sato et al. [15] for their RuO_2–C composite synthesized by different techniques.

In order to investigate the effect of temperature further, CVs were done at different sweep rates on all the composites. At 100°C increasing the scan rate results in increasing anodic and cathodic currents. However, the opposite behavior is observed for composites heated at 400°C. Fig. 4a presents the CVs of the 5 wt.% RuO_2–C composite. In this case, decreasing the sweep rate results in increasing the total capacitance of the composite. Further, the coulombic ratio increased from 0.79 at 1 mV/s to a 0.86 at 0.05 mV/s. X-ray diffraction patterns of RuO_2–C composites treated at different temperatures reveal that the degree of crystallinity increases as the oxidation temperature increases. Mckeown et al. [17] have shown that the faradaic reaction in Ru oxides is controlled by the rate of proton and electron transport through the oxide. Maximum capacitance is obtained when both electron and proton transport rates are optimized. Removal of structural water from the oxide at 400°C results in lowering the proton transport through the oxide. Hence, an optimum amount of water content in the composite is critical to maximize the capacitance values. According to Zheng et al. [4], amorphous Ru oxides allow the whole bulk of RuO_2 to be utilized for energy storage due to the fast proton transport rates. Increasing the oxidation temperature results in utilizing only the surface of the oxide. In Fig. 4a, lowering the sweep rates allows more amount of time for the proton to access the bulk of the oxide. Hence, the specific capacitance increases with decrease in scan rate. Similar behavior is seen with different loadings of Ru onto carbon. Fig. 4b presents CVs of RuO_2–C treated at 400°C at a sweep rate of 0.1 mV/s. The profiles are similar to each other and in all cases an increase in capacitance with decrease in scan rate.

Fig. 5 summarizes the specific capacitance obtained for different RuO_2 loadings at various oxidation temperatures. The capacitance obtained at 50°C is lower than that seen for 100°C. According to Mckeown et al. [17] charge storage in

(a)
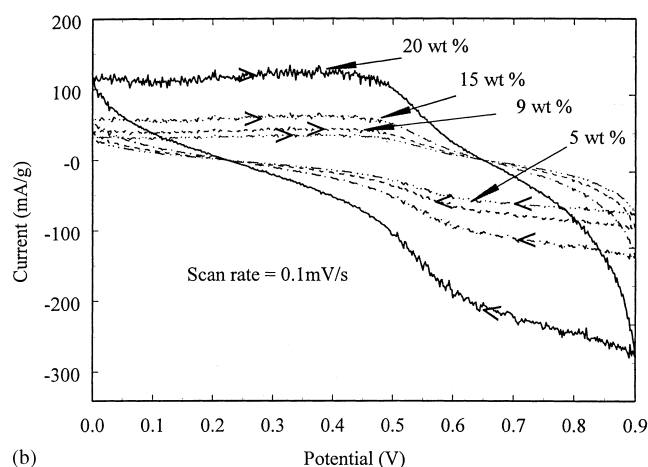
(b)

Fig. 4. (a) Comparison of voltammograms of pellet of 5 wt.% composite heat treated at 400°C at different scan rates. (b) Comparison of voltammograms of pellet with different loadings of ruthenium oxide oxidized at 400°C.
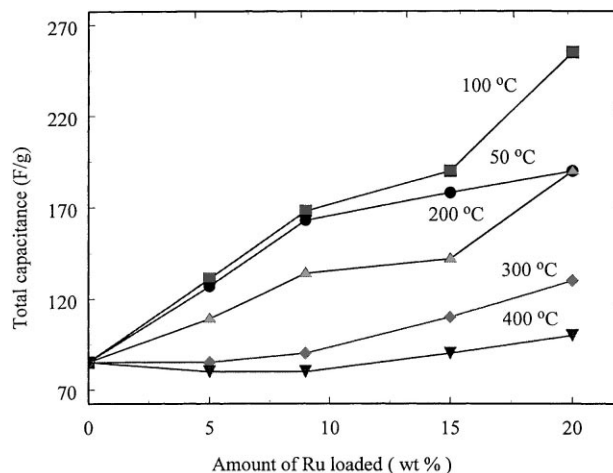

Fig. 5. Change in specific capacitance of the composite electrode for different amounts of RuO_2 loading. For each loading the material was oxidized at different temperatures.

Table 1
Comparison of surface area and capacitance for RuO_2–C electrodes with different loadings of Ru oxide

Amount of RuO_2 loaded	Surface area (m^2/g)	Volumetric surface area (m^2/cm^3)	Specific capacitance (F/g)	Volumetric capacitance (F/cm^3)
0	1200	213.84	98	17.5
5	1100	206.05	145	27.2
9	1060	207.05	185	36.13
15	960	200.36	235	49.04
20	845	187.02	265	57.55

RuO_2 is maximized when facile transport pathways exist for both electrons and protons. In our case, this is achieved only at $100°C$ and hence the capacitance values are at a maximum for all the composites at this temperature. Further, a linear increase in capacitance is seen with increased loading of RuO_x on the carbon substrate at this temperature. Since, the composite is amorphous in nature, the entire bulk of RuO_x takes part in the faradaic reaction and the capacitance increases with increase in RuO_x loading. However, at higher oxidation temperatures due to the removal of structural water the proton transport rate is lower and not all of the bulk oxide is utilized in the faradaic reaction. This results in a smaller increase in capacitance with increase in RuO_x loading as seen by the capacitance values for temperature treatments at 300 and $400°C$.

Apart from CVs, charge–discharge studies were done on all the composites. Fig. 6 shows the variation of capacitance for the composite electrode with increasing discharge current densities. It is seen that the rate of decrease of capacitance with increase in current densities is higher for the 20 wt.% than the 5 wt.% composite. At 5 wt.% RuO_2 loading, the capacitance remains constant with increase in discharge currents. However, for 20 wt.% RuO_2 loading the specific capacitance starts decreasing for discharge currents greater than 250 mA/g. Similar results are also seen for the 15 wt.% composite. Fig. 1 shows that increased RuO_2 loading leads to formation of large clusters of Ru nanopar-
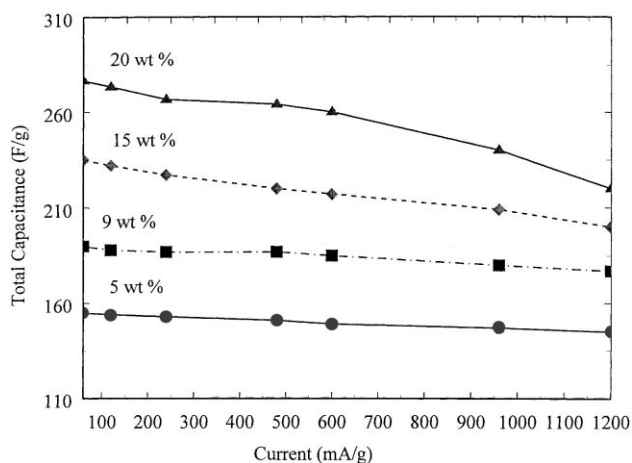
ticles on the carbon surface. This increases the distance the proton has to travel to access the entire bulk oxide. Hence, at higher current densities mass transfer becomes limiting and the capacitance starts decreasing.

Table 1 shows the change in surface area of the composite material for different loadings of carbon. It is seen that the BET surface area of the RuO_2–C composite decreases with increase in RuO_2 content. The BET surface area of the bare carbon is 1200 m^2/g. After loading this with 20 wt.% RuO_2, the BET surface area decreases to 845 m^2/g. RuO_2 has a much higher bulk density (6.97 g/cm^3) as compared with activated carbon (0.2 g/cm^3). On loading RuO_2 on carbon, the total weight of the composite increases for a given volume of material, due to the higher density of RuO_2. This results in reducing the BET surface area, as this is normalized to the weight of the material. According to Miller et al. [13] a more useful measure for comparison is to normalize the surface area based on the volume of the composite. Table 1 shows that the volumetric surface area of the RuO_2–C composite does not change significantly with increased ruthenium loading. This is to be expected since a small amount of RuO_2 is dispersed over the large surface of the carbon substrate. SEM results shown in Fig. 1 reveal that ruthenium nanoparticles are incorporated to the carbon surface after electroless deposition. While this increases the weight of the composite no significant change in volume is seen. Hence, the volumetric capacitance of the composite electrode increases much more than the specific capacitance with increased RuO_2 loading as shown in Table 1.

4. Conclusions

Electroless deposition has been used to synthesize RuO_2–C composite materials. By varying the amount of ruthenium salt in the bath it is possible to load large quantities of ruthenium onto the surface of carbon. SEM analysis reveals the presence of nanoparticles of Ru on the surface of carbon. Heating the composite leads to removal of structural water from the ruthenium oxide. This optimizes the rate of proton and electron transport through the oxide. Maximum capacitance is obtained after heating the samples to $100°C$ for all the composites. Increasing the oxidation temperature further changes the amorphous ruthenium oxide to crystalline form thereby leading to a drastic decay in performance. On

Fig. 6. Variation of total capacitance with increase in current density for the RuO_2–C composites.

loading RuO_2 on carbon, the total weight of the composite increases for a given volume of material, due to the higher density of RuO_2. While this reduces the BET surface area, the volumetric surface area remains constant for different loadings of RuO_2. A maximum capacitance of 260 F/g (57.55 F/cm^3) was obtained for 20 wt.% RuO_2 loaded carbon treated at 100°C.

Acknowledgements

References

[1] B.E. Conway, Electrochemical Supercapacitors, Scientific Fundamentals and Technological Applications, Kluwer Academic Publishers, Dordrecht, 1999.

[2] K.-C. Liu, M.A. Anderson, J. Electrochem. Soc. 143 (1996) 124.

[3] J.P. Zheng, P.J. Cygan, T.R. Jow, J. Electrochem. Soc. 142 (1995) 2699.

[4] J.P. Zheng, T.R. Jow, J. Electrochem. Soc. 142 (1995) L6.

[5] V. Srinivasan, J.W. Weidner, J. Electrochem. Soc. 144 (1997) L210.

[6] T.-C. Liu, W.G. Pell, S.L. Ronerson, B.E. Conway, J. Electrochem. Soc. 145 (1998) 1882.

[7] Y. Takasu, T. Nakamura, Y. Murakami, Chem. Lett. 12 (1998) 1215.

[8] C.C. Hu, Y.H. Huang, J. Electrochem. Soc. 146 (1999) 2465.

[9] P.M. Wilde, T.J. Guther, R. Oesten, J. Garche, J. Electroanal. Chem. 461 (1999) 154.

[10] Y.U. Jeong, A. Manthiram, Electrochem. Solid State Lett. 3 (5) (2000) 205.

[11] H. Shi, Electrochem. Acta 41 (1996) 1633.

[12] D.W. Firish, Binderless carbon capacitor electrodes produced by polymer pyrolysis, in: Electrochemical Capacitors II, PV 96-25, The Electrochemical Society, 1996, p. 235.

[13] J.M. Miller, B. Dunn, T.D. Tran, R.W. Pekala, J. Electrochem. Soc. 144 (1997) L309.

[14] J.P. Zheng, T.R. Jow, J. Power Sources 62 (1996) 155.

[15] Y. Sato, K. Yomogida, T. Nanaumi, K. Kobayakawa, Y. Ohsawa, M. Kawai, Electrochem. Solid State Lett. 3 (2000) 113.

[16] M. Ramani, B.S. Haran, R.E. White, B.N. Popov, Synthesis and characterization of hydrous ruthenium oxide–carbon supercapacitors, 2000, submitted for publication.

[17] D.A. Mckeown, P.L. Hagans, L.P.L. Ccarette, A.E. Russel, K.E. Swider, D.R. Rolison, J. Phys. Chem. B 103 (1999) 4825.