

Sol–Gel Synthesis and Characterization of Carbon/Ceramic Composite Electrodes

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We have fabricated carbon/ceramic composite electrodes with an interconnected network of carbon particles in a silica-based gel. The resulting electrodes were porous and electrically conductive and exhibited excellent stability. BET adsorption measurements combined with electrochemical techniques such as cyclic voltammetry and electrochemical impedance spectroscopy showed that 50% of the carbon surface area was accessible electrochemically.

Introduction

Carbon electrodes are widely used in electrochemical charge storage, energy generation, and catalysis.^{1–4} Various techniques have been developed for the synthesis of these electrodes. For example, carbon particles can be combined with an organic polymer binder such as poly(vinylidene difluoride) (PVDF), poly(tetrafluoroethylene) (PTFE), or ethylene/propylene/diene polymer (EPDM) forming a conductive, porous composite electrode.^{5–7} Carbon particles can also be embedded into a metallic support such as stainless steel,⁸ and carbon aerogels have been used to fabricate high surface area electrodes.⁹ The carbon particles used for these applications are typically about 1–10 μm in diameter and have a wide range of crystal structures and morphologies.^{3,4,10–12} Both low surface area graphite particles and high surface area carbons are used for the anode in lithium ion batteries.¹¹ High surface area carbon blacks are commonly used for electrochemical capacitors.^{3,12}

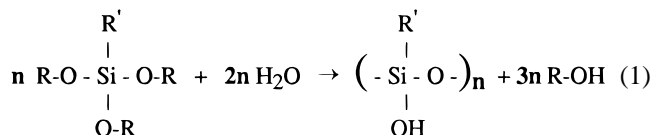
For electrochemical applications, the carbon particles should be electrically connected and provide a high surface area. The size of the channels between the particles as well as the diameter of the pores within the particles should be large enough to provide access for the electrolyte with minimal iR drop and relatively short path lengths for ion transport. In addition, the films should be durable and stable under repeated electrochemical cycling. Although organic binders are widely used in the fabrication of carbon electrodes for electrochemical applications such as intercalation hosts and supercapacitors, improvements in the mechanical integrity and thermal stability of these films could result in significant improvements in device performance.

In this paper, we report on the fabrication and characterization of carbon/ceramic composite electrodes. We demonstrate the feasibility of this approach using silica-based gel as a binder for graphite particles, and we show that porous films with good electrical conductivity can be obtained. The ceramic binder has the advantage that the hydrophobicity, polarity, and rigidity can be controlled by chemical modification of the gel precursors. A similar approach has been reported for the fabrication of carbon/ceramic composite electrodes for bioanalytical sensors.¹³ Here we report on the stability, porosity, and conductivity of carbon/ceramic composite electrodes using differential thermogravimetric analysis (TGA/DTA), BET gas adsorption, and scanning electron microscopy. The electrochemical properties

are characterized using voltammetry and electrochemical impedance spectroscopy (EIS) in inert electrolytes.

Experimental Section

The general procedure for the preparation of the silica sol was as follows. An alkoxysilane precursor was combined with an organic solvent and a catalyst, such as HCl or KOH. The sol was then mixed with carbon particles which, after gelation, are incorporated in the resulting ceramic network. The gelation occurs through hydroxylation of the precursor by water under ambient conditions, and subsequent polymerization is achieved through condensation reactions in which alkanols are formed. The overall reaction can be represented as follows:



where the side groups R and R' can be methyl, ethyl, phenyl, etc. By changing the side groups or by adding a second precursor, the properties of the final ceramic matrix can be tailored for a specific application.^{13,14}

The influence of the gel precursor on the properties of the resulting carbon/ceramic composite film was investigated using four different precursors: methyltrimethoxysilane (MTMS), propyltrimethoxysilane (PTMS), tetramethoxysilane (TMOS), and phenyltriethoxysilane (PTES). The films were deposited on thin titanium foil. The flexibility and hardness of the films depended on the precursor used. The flexibility increased in the order TMOS, PTES, MTMS, and PTMS. The films prepared with TMOS and PTES were relatively brittle, while MTMS and PTMS resulted in hard and mechanically stable films. Hence, the film properties can be tailored to specific needs. For instance, in applications where high geometric surface area electrodes are required, PTMS could be used so that a device consisting of two electrodes and a separator can be assembled and encased in a cylinder. Electrochemical experiments were performed on carbon/ceramic films with MTMS and PTMS as precursors, respectively. In the following, the results obtained on MTMS samples are described in detail; the experiments on samples using PTMS as precursor gave essentially the same results.

A typical example of the fabrication of the sol was as follows: 2 mL of MTMS (Aldrich, 98%), 0.1 mL of HCl (J.T. Baker, 36.5–38%, reagent grade), and 7 mL of methanol (Sigma-Aldrich, HPLC grade) were mixed, and subsequently 4 g of graphite particles (Ultra Carbon Corp., microcrystal grade graphite powder, 2–15 μm , 99.9999%) was added. This formulation was chosen to give about 20 wt % of the inorganic binder material. Carbon/ceramic composite electrodes were prepared by applying the resulting black paste to fluorine-doped tin oxide (Libby-Owens-Ford, 8 Ω/\square) or copper or steel mesh substrates. After about 14 h of gelation at room temperature, dark matte films were obtained. The conductivity of the films was measured using a four-point probe method and was generally found to be about 1 S cm^{-1} . As a result of the stresses generated during the gelation process,¹⁴ the maximum film thickness for single layers was limited to about 0.1 cm. Thicker films were prepared by sequentially depositing several layers and allowing the films to dry for about 12 h between successive applications of the gel.

BET surface area measurements were performed on a Coulter SA 3100 using nitrogen as the adsorbing gas. Samples of the carbon/ceramic films as well as the silica-based gel films were obtained by removing fragments from the supports. The surface area of the carbon particles was obtained using the material as received. A 10-point BET analysis was used, and the correlation coefficients were larger than 0.999 for all the graphite and carbon/ceramic composite samples. Prior to the measurements the samples were outgassed under vacuum at 150 $^{\circ}\text{C}$ for 45 min. Differential thermogravimetric analysis (TGA/DTA) was carried out on a TA Instruments SDT 2960. The experiments were performed in air at a scan rate of 30 $^{\circ}\text{C}/\text{min}$ from 20 to 1000 $^{\circ}\text{C}$, and $\beta\text{-Al}_2\text{O}_3$ was used as the reference. Scanning electron microscopy was performed on an AMRAY 1860 FE at beam acceleration voltages of 5–10 kV. Samples were prepared by depositing films of the silica-based gel or the carbon/ceramic composite onto steel microscope stubs.

Electrochemical experiments were performed in both water and propylene carbonate. Aqueous solution were prepared from distilled and deionized (Millipore, Milli-Q system) water with a resistivity of 18 $\text{M}\Omega\text{ cm}$. Nonaqueous solutions were prepared using propylene carbonate that was vacuum-distilled and dried over 4 \AA molecular sieves. The inert electrolytes LiClO_4 (Alfa-Aesar, P.A. grade) or tetrabutylammonium tetrafluoroborate (TBABF_4) (Sachem, electrometric grade) were vacuum dried prior to use. The propylene carbonate solutions had a water content of less than 20 ppm. Electrochemical impedance spectroscopy was performed with a Solartron 1260 FRA and a Solartron 1286 ECI. A three-electrode cell arrangement was used in all experiments with a platinum mesh counter electrode, a saturated calomel electrode (SCE) as reference in aqueous solutions, and Ag^+/Ag as reference in propylene carbonate. The Ag^+/Ag reference electrode was prepared by inserting a clean silver wire in a glass tube fitted with a Vycor tip; the electrolyte solution was 0.1 M AgClO_4 + 1 M LiClO_4 in propylene carbonate. The experiments in propylene carbonate were performed in an argon-filled glovebox.

Results and Discussion

Scanning electron microscopy (SEM) was used to evaluate the structure of the composite films and the silica-based gel. Films of the silica-based gel were very dense with pore sizes smaller than 1 μm . Since the pore sizes were smaller than the size of the graphite particles, this result implies that in the

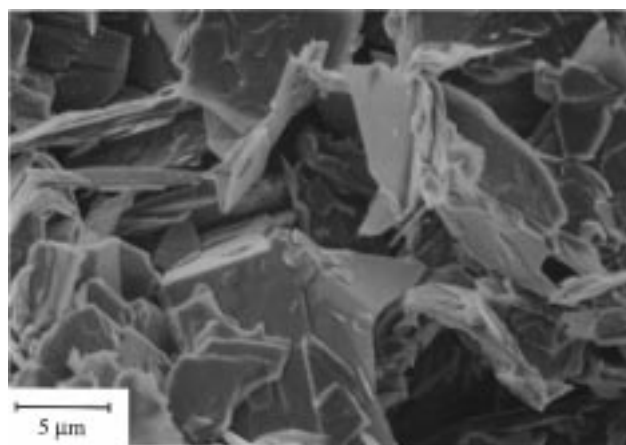


Figure 1. Top view SEM image of a carbon/ceramic composite film using graphite powder and MTMS as gel precursor.

formation of the carbon/ceramic composite films the graphite particles do not occupy existing pores in the silica-based gel network but that the gel is formed around the graphite particles.

Figure 1 shows a top view SEM image of a composite film. The specimen represents a film prepared on a microscope stub where the top layer was slightly polished. This figure shows that the randomly stacked particles consist of platelets, defined by the layer structure of crystalline graphite, which are relatively uniform in size. The films are porous and are characterized by an interconnected network of carbon particles held together by the silica gel.

From BET measurements the surface area of the graphite powder was determined to be 6 $\text{m}^2\text{ g}^{-1}$. The average particle size is about 10 $\mu\text{m} \times 10 \mu\text{m}$, and using a density of 2.25 g cm^{-3} ,¹⁵ the thickness of solid platelets can be calculated to be about 0.15 μm . Figure 1 shows that most platelets are about 1 μm thick, implying that the particles exhibit microscopic roughness or some porosity. We note that for applications such as electrochemical capacitors carbon particles with specific surface areas of $\geq 500 \text{ m}^2\text{ g}^{-1}$ are typically used.^{3,12} Silica-based gel films prepared on Teflon substrates were relatively dense with a surface area of less than 1 $\text{m}^2\text{ g}^{-1}$; the BET measurements did not yield a reliable value for such low surface areas. The surface area of the carbon/ceramic composite films was determined to be 3.5 $\text{m}^2\text{ g}^{-1}$. Since the silica-based gel constitutes about 20% of the total weight of the carbon/ceramic composite film, it is concluded that 73% of the total graphite surface area is accessible for gas adsorption.

Figure 2 shows the results of TGA/DTA experiments. The weight loss versus temperature curves are shown in Figure 2a. From this figure it can be seen that the silica-based gel (curve a) loses about 16% of its initial weight at around 500 $^{\circ}\text{C}$. This is close to the value of 21% expected for the complete conversion of the gel to SiO_2 . (The formula weights of the gel repeat unit and SiO_2 are 76.1 and 60.1 g, respectively.) The curve for the graphite powder (curve b) shows that the carbon is completely pyrolyzed at about 950 $^{\circ}\text{C}$. The carbon/ceramic composite material (curve c) is stable up to about 750 $^{\circ}\text{C}$, and at 1000 $^{\circ}\text{C}$ the weight loss is about 82%. The 18% remaining material corresponds to SiO_2 , which confirms that the initial weight percentage of the gel was about 21%.

Figure 2b shows the temperature difference (with respect to an inert reference ($\beta\text{-Al}_2\text{O}_3$)) for a silica-based gel (curve a) and a carbon/ceramic composite sample (curve b) as a function of the furnace temperature. This figure shows that the oxidation of both the silica-based gel and the graphite powder is exothermic. The carbon/ceramic composite material is pyrolyzed

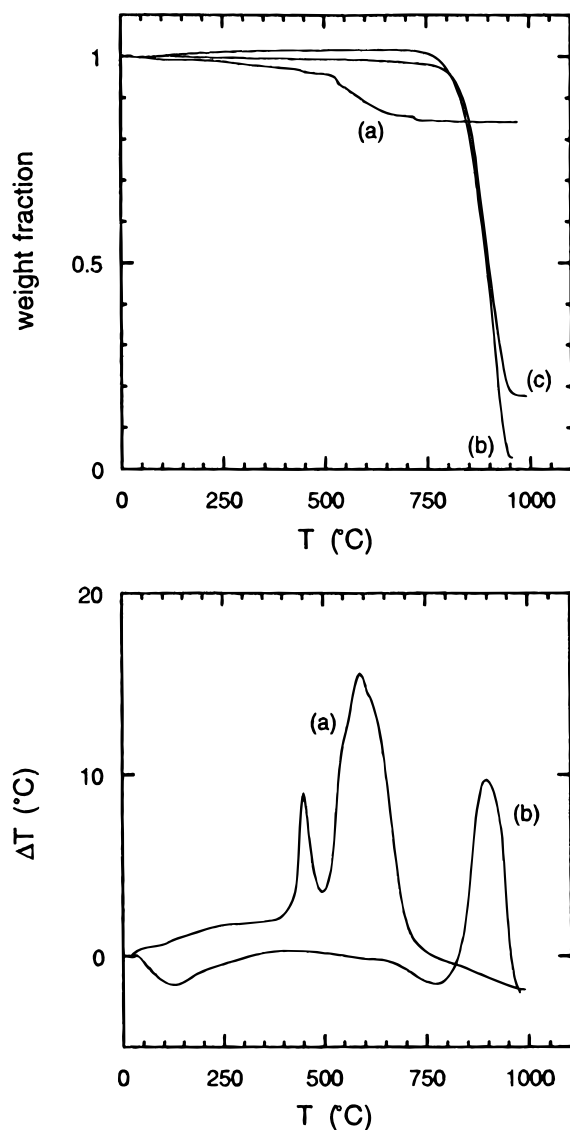


Figure 2. Thermogravimetric and differential thermogravimetric analyses of graphite powder, silica-based gel, and carbon/ceramic composite samples. The experiments were performed in air at a scan rate of 30 °C/min. The inert reference material was β - Al_2O_3 . (a, top) The sample weight normalized to the initial weight versus the furnace temperature for (a) silica-based gel, (b) carbon/ceramic composite, and (c) graphite powder. (b, bottom) The sample temperature with respect to the reference material versus the furnace temperature for (a) silica-based gel and (b) carbon/ceramic composite.

at significantly higher temperature than the silica-based gel, indicating that the gel network is stabilized by the presence of the graphite particles.

The electrochemical surface area is not necessarily the same as the value found in gas adsorption measurements since it depends on the morphology of the porous electrode and the wetting of the material by the solvent. The accessible surface area was characterized using voltammetry and electrochemical impedance spectroscopy in both aqueous and organic solvents and various electrolyte salts.¹⁶ The electrodes were prepared on a conductive tin oxide substrate which allowed the wetting of the films to be observed through the transparent glass support. Freshly prepared films were not wetted by aqueous solutions but were easily wetted by propylene carbonate solutions. After immersion in propylene carbonate with LiClO_4 or TBABF₄ as electrolyte, the films were also wetted in aqueous solutions.

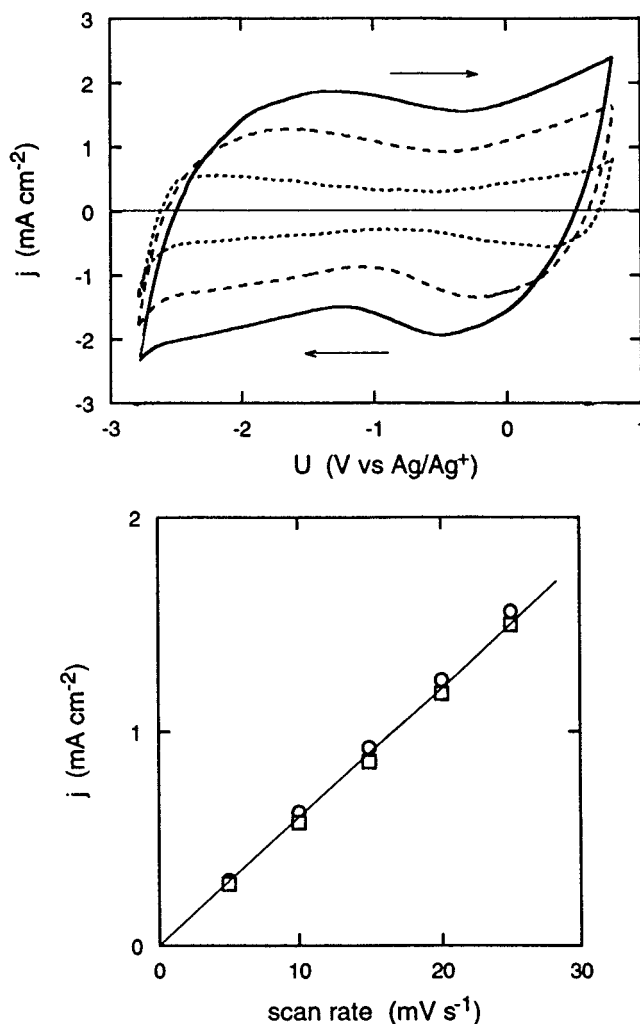


Figure 3. (a, top) Cyclic voltammograms for a carbon/ceramic composite electrode in propylene carbonate + 0.25 M TBABF₄ at a scan rate of 5 mV s⁻¹ (---), 15 mV s⁻¹ (---), and 25 mV s⁻¹ (—). The current density is the current normalized to the geometrical area. (b, bottom) The plateau current density versus scan rate for the same electrode as in (a). Both the anodic (○) and cathodic (□) current densities are shown.

Figure 3a shows current–potential curves for a carbon/ceramic composite electrode consisting of four successively applied layers in 0.25 M TBABF₄ in propylene carbonate as a function of scan rate. The curves are almost rectangular indicative of purely capacitive behavior. The potential window for an electrochemical capacitor in this solution is about 4 V. Impedance spectroscopy showed that the weak anodic and cathodic waves at around -1.6 and -0.4 V, respectively, do not correspond to Faradaic processes but are related to a slight change of the double-layer capacitance upon reversing the scan rate and are probably due to an adsorption process.^{2,17} The reversible double-layer capacitance can be obtained from the relation $C = j/\nu$, where j is the current density in the plateau region and ν is the scan rate. Figure 3b shows the limiting current density versus scan rate for this sample, and from the slope a capacitance of 61 mF cm⁻² is obtained. Similar results were obtained in aqueous solution using 0.3 M LiClO_4 as electrolyte: the electrochemical stability window is much smaller, between -0.5 and 0.3 V (SCE), but the capacitance of the electrode was close to the value found in propylene carbonate solution.

Impedance spectroscopy was used to determine both the capacitance and the time constant for the charging/discharging

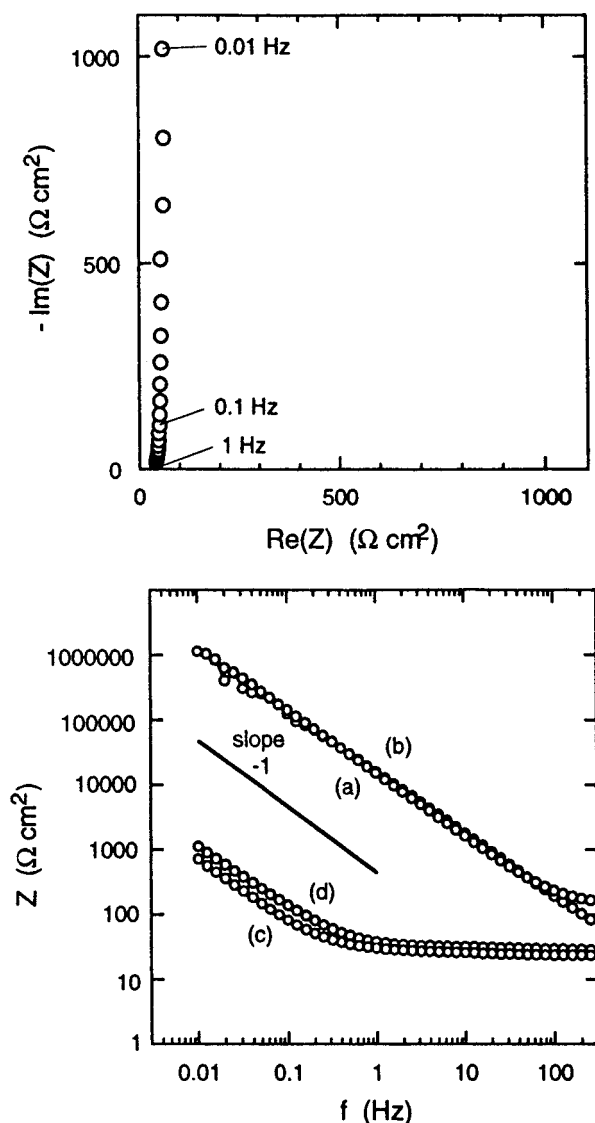


Figure 4. (a, top) The imaginary part of the impedance versus the real part for a carbon/ceramic composite electrode at -0.2 V (Ag^+/Ag) in propylene carbonate + 1 M LiClO_4 ; the 90° phase angle shows that a series RC circuit can be used to analyze the impedance results. (b, bottom) The modulus of the electrochemical impedance versus the frequency for a bare conductive tin oxide sample at -0.2 V (Ag^+/Ag) in propylene carbonate + 1 M LiClO_4 (a) and a carbon/ceramic composite electrode with tin oxide as a substrate (b–d): (b) freshly prepared carbon/ceramic composite electrode at 0.1 V (SCE) in water + 1 M LiClO_4 ; (c) the same electrode at -0.2 V (Ag^+/Ag) in propylene carbonate + 1 M LiClO_4 ; (d) the same electrode at 0.1 V (SCE) in water + 1 M LiClO_4 after recording curve c. The experiments were performed within the domain of stability of the solutions where the dc current was negligibly small; in this range, the results were independent of the applied potential. The amplitude of the modulation was 10 mV.

process of the carbon/ceramic composite electrodes. The experiments were performed both in aqueous solution and in propylene carbonate at various potentials. Within the stability ranges of the solutions, the electrodes are ideally polarizable, and the total impedance can be represented by a resistor, R , in series with the double-layer capacitance, C . Hence, in the frequency range where the slope of the Bode plot is -1 , the magnitude of the total impedance is equal to $(2\pi fC)^{-1}$, in which C is proportional to the accessible surface area. The time constant can be obtained from the frequency where a transition from capacitive to resistive behavior is observed. The width

of the transition region depends on the morphology of the film. If a distribution of pore sizes down to very small pores (< 1 nm) is present, the electrochemical accessibility of the surface area becomes frequency dependent. At very low frequencies, all the microscopic surface area may be accessible while at higher frequencies only parts of the surface that are connected to the electrolyte through large pores are accessible. As a consequence, constant phase angle (CPA) behavior is often observed for porous, high surface area carbon electrodes.^{2,4,17–19} The value of the transition frequency also depends strongly on the uncompensated resistance of the electrochemical cell, which should be low for most applications.

Figure 4a shows an impedance plot for a carbon/ceramic composite electrode in 1 M LiClO_4 in propylene carbonate at -0.2 V. At this potential, the electrode can be represented by the uncompensated cell resistance in series with the double-layer capacitance. The uncompensated series resistance is relatively large since the reference electrode was placed directly in the solution without a Luggin capillary. The phase angle is almost 90° , which is consistent with a macroporous film of nonporous graphite particles. It can be concluded that the carbon/ceramic composite films are sufficiently porous to avoid CPA behavior, and as a consequence, the surface area can be characterized by determining the frequency-independent double-layer capacitance.

Figure 4b shows the magnitude of the impedance, Z , versus the frequency, f , in a double-logarithmic plot for the tin oxide substrates with and without a carbon/ceramic composite film in both aqueous and propylene carbonate solutions in their respective stability windows. Curve a shows the Bode plot for a tin oxide electrode in 1 M LiClO_4 in propylene carbonate. Curve b shows the Bode plot for a carbon/ceramic composite film on a tin oxide substrate in 1 M LiClO_4 in water, which is found to be identical to that of the bare tin oxide substrate shown in curve a. In this case, only the geometrical surface area of the carbon/ceramic composite electrode is active. The double-layer capacitance was found to be about $10 \mu\text{F cm}^{-2}$, which is in agreement with previously reported double-layer capacitances for graphite electrodes in aqueous solutions.^{2,4} Curve c in Figure 4b shows the Bode plot for the same electrode in 1 M LiClO_4 in propylene carbonate where an increase in double-layer capacitance by about a factor 1000 is obtained, which corresponds to a similar increase of the active surface area. Curve d shows the Bode plot for the same electrode in aqueous 1 M LiClO_4 after immersion in 1 M LiClO_4 in propylene carbonate, and it is found that the curve now almost overlays curve c: these results confirm that the electrodes are only wetted in aqueous solution after immersion in the propylene carbonate solution.

Figure 5 shows a plot of the capacitance of carbon/ceramic composite electrodes in 0.25 M TBABF_4 in propylene carbonate, determined using both cyclic voltammetry and impedance spectroscopy, versus the weight of the films. It is seen that the capacitance increases linearly with weight in the range from 10 to 200 mF; there are no indications that increasing the geometrical area or the thickness of the film poses limitations to the attainable capacitance. The values obtained from the two experimental methods are in good agreement, and the slope of the plot represents the specific capacitance, C_s , which is determined to be 0.24 F g^{-1} .

The fraction of graphite surface area in the carbon/ceramic composite films that is electrochemically accessible can now be determined. Using a double-layer capacitance of $10 \mu\text{F cm}^{-2}$ and the BET surface area of $3.5 \text{ m}^2 \text{ g}^{-1}$, the maximum attainable specific capacitance for these films, C_m , is 0.35 F

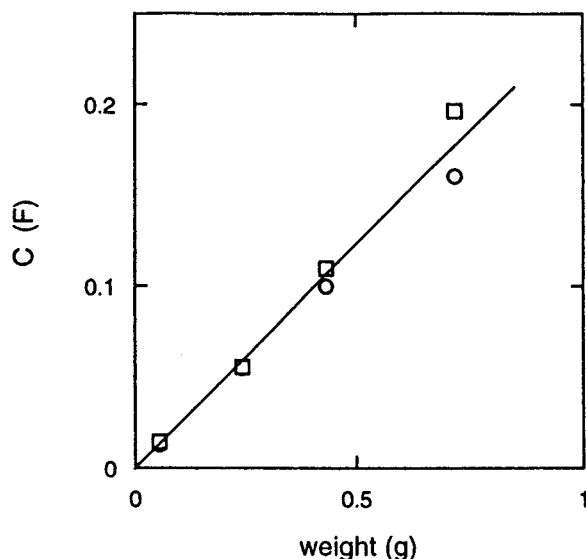


Figure 5. The capacitance of carbon/ceramic composite electrodes versus the weight of the films obtained in propylene carbonate + 0.25 M TBABF₄. The geometrical surface area was 3.1 cm² for all samples. The capacitance was determined using cyclic voltammetry (○) and impedance spectroscopy (□). The slope represents a specific capacitance of 0.24 F g⁻¹.

g⁻¹, and the fraction of surface area accessible for electrochemical applications is found to be 0.69. The total fraction of electrochemically accessible graphite surface area, f , is given by

$$f = \frac{A_c}{A_g} \frac{C_c}{C_m} \quad (2)$$

where A_c is the BET area of the graphite in the carbon/ceramic composite films, and A_g is the BET area of the graphite powder. Using $A_c/A_g = 0.73$, f is found to be 0.5; hence, the total percentage of electrochemically accessible graphite surface area is 50%. The rest of the surface represents the contact area between graphite particles and the silica-based gel network, particle-particle contacts, and regions in the film that are not accessed by the electrolyte solution.

Summary

Sol-gel synthesis is a novel approach for the preparation of high surface area carbon electrodes. The films are electrically

conductive, indicating that the carbon particles form an interconnected network in the silica-based gel. The films have a high porosity, and we have demonstrated that at least 50% of the total graphite surface is accessible electrochemically. The properties of the composite electrodes can be tailored for specific applications by modification of the gel precursors and the structure and morphology of the carbon particles.

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