

Electrophoretic and Electrolytic Deposition of Ceramic Coatings on Carbon Fibers

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Abstract

Alumina, zirconia, titania, lead zirconate titanate, hydroxyapatite and chemically bonded ceramics in the system $\text{CaO-SiO}_2\text{-P}_2\text{O}_5$ were deposited via electrophoretic or/and electrolytic deposition methods on individual carbon fibers, bundles and felts, which served as cathodic substrates. Experimental conditions were determined for formation of uniform deposits of controlled thickness. After burning out of carbon fibers the corresponding ceramic replicas can be obtained. The possibility to form multilayer alumina/zirconia hollow fibers with sharp interfaces between alumina and zirconia layers has been demonstrated. Obtained coatings and fibers were studied by SEM. Experimental results obtained by electrophoretic and electrolytic deposition methods were compared. © 1998 Elsevier Science Limited. All rights reserved

1 Introduction

Methods of coating formation on fibers^{1–10} have attracted attention for development of advanced composites. Ceramic coatings are necessary for optimization of the fiber/matrix bonding,^{2,5} oxidation protection of non-oxidic fibers and prevention of fiber–matrix interfacial degradation at elevated temperatures.^{5–7} It is known that mechanical properties of fiber-reinforced composites could be improved by the use of coated fibers.^{2,5,9} Toughening mechanisms related to crack deflection, debonding and the role of interfacial fiber coatings were discussed in literature.^{1–5,9}

Coating techniques have attained strong interest for development of hollow fibers and microtubes. Individual carbon fibers, carbon fiber bundles and felts, polyester fibers were used as burnable templates for formation of hollow ceramic fibers.^{11–14} Hollow ceramic fibers are of interest for electronic,^{12–14} biomedical¹⁵ and other^{11,16} applications.

A number of techniques such as laser ablation,³ sol–gel,^{5,9} sputtering,^{2,14} electrolytic deposition,^{17,18} electrophoretic deposition^{19,20} and others^{4,10,11} have been used for coating formation on fibers. Electrolytic and electrophoretic deposition allows important advantages such as rigid control of coating thickness, uniformity and deposition rate. These methods offer the added attraction of simple and low cost equipment, low preparation temperature, and high purity of deposits.^{17–21}

Electrodeposition can be performed by cathodic^{17,18,22–24} or anodic methods.^{24–27} However, anodic deposition method has limited utility regarding possible materials to be deposited by this method and substrates used for deposition. Significant interest has focused on cathodic electrolytic deposition (CELD) due to the possibility of film formation on various conductive substrates. In this method metal ions or complexes are hydrolyzed by an electro-generated base to form oxide or hydroxide films on the cathodic substrate.^{17,18,22–24,28} Different chemical reactions available for the generation of base were discussed in the literature.^{24,28} A great deal of current research has been devoted to demonstration of the feasibility of CELD of various ceramic materials.^{17,18,22–24,28–33}

Electrophoretic deposition (EPD) is achieved via motion of charged particles towards an electrode under the applied electric field. Cathodic or anodic deposits can be achieved depending on particle charge. There are excellent reviews in the literature describing mechanism of EPD and application of this technique for processing of various materials.^{34,35} Recent studies have demonstrated that EPD can be used for consolidation of fiber reinforced composites making use of fibrous materials as working electrodes.^{36–39}

This paper presents results of EPD and CELD of various ceramic materials on carbon fibers and addresses different factors controlling coating thickness, morphology and deposition rate.

2 Experimental Procedures

2.1 Materials for electrophoretic deposition

Submicron alumina (Fluka Chemie AG), submicron zirconia partially stabilized with CeO₂ (TZ-12CE, TOSOH Zirconia Process Company) and PZT (PE-600, Fuji Titanium Industry Co.Ltd., average particle size of $\sim 1\mu\text{m}$) were used.

Submicron hydroxyapatite Ca₁₀(PO₄)₆(OH)₂ (HA) powders were prepared via a chemical precipitation method described in previous work.⁴⁰ As starting materials commercially guaranteed Ca(NO₃)₂·4H₂O (Aldrich Chemical Company, Inc.), (NH₄)₂HPO₄ (Merck) and NH₄OH (Palacid LTD) were used. The precipitation was performed at 70°C by slow addition of a 0.6M ammonium phosphate solution to a stirred reaction vessel containing 1.0 M calcium nitrate solution. The pH of the solutions was previously adjusted to 11 by addition of NH₄OH. Stirring was performed during 24 h at 70°C and 48 h at room temperature. The obtained precipitate was filtered, rinsed with water and finally with isopropyl alcohol, stored in a moisture free atmosphere for three weeks and milled in an agate mortar. The stoichiometry of the HA obtained was proven by chemical analysis.

Chemically bonded ceramic (CBC) in the system CaO–SiO₂–P₂O₅ with the composition 59.3% CaO, 17.2% SiO₂ and 23.5% P₂O₅ was prepared by a gel-precipitation technique similar to that, described in.⁴¹ Phosphoric acid H₃PO₄ (Frutarom Ltd), calcium nitrate Ca(NO₃)₂·4H₂O (Aldrich Chemical Company, Inc.), and silica sol (30 wt%, Merck) were mixed, stirred at 80°C (10 h), dried at 90°C (48 h) fired at 200, 400 and 600°C for 2 h and finally at 700°C for 24 h. Obtained powders were milled and stored in a desiccator.

Suspensions for electrophoretic experiments were prepared by ultrasonic agitation of ceramic powders in isopropyl alcohol. The powder concentration in the suspensions was in the region of 30–100 g litre⁻¹

2.2 Materials for electrolytic deposition

As starting materials, commercially guaranteed salts of TiCl₄ (Merck), ZrOCl₂·8H₂O (Fluka Chemie AG), Pb(NO₃)₂ (Riedel–de Haën AG) and hydrogen peroxide H₂O₂ (30 wt% in water, Carlo Erba Reagenti) were used. Stock solution 1 contained 0.005 M TiCl₄ and 0.01 M H₂O₂ in a mixed methyl alcohol-water (3:1 volume ratio) solvent. Stock solution 2 contained 0.005 M ZrOCl₂ and 0.01 M H₂O₂ in water. For preparation of stock solution 3 reagents were dissolved in water in a ratio Pb(NO₃)₂: ZrOCl₂: TiCl₄: H₂O₂ = 1: 0.52:0.48:10, the Pb(NO₃)₂ concentration was 0.005 M.

2.3 Substrates

Individual fibers, bundles (Tenax) and felts (Lydall, Inc.) were used as substrates. The diameter of the carbon fibers was 7 μm. Fiber length was up to several centimeters, and the bundles included up to 3000 individual fibers. The thickness of carbon felts was in the region of 0.1–0.3 mm, area of rectangular samples used as substrates was up to 5 cm².

2.4 Electrophoretic deposition

The electrophoretic cell included the cathodic substrate centered between two parallel counter-electrodes. The distance between the cathode and anode was 1.5 cm. Experiments were performed at a constant voltage regime, applied voltages were in region of 50–200 V, deposition times were from 10 s to 5 min. Laminated coatings were fabricated by multiple deposition accompanied by drying at room temperature.

2.5 Electrolytic deposition

The electrochemical cell for deposition in a galvanostatic regime included the cathodic substrate and two platinum anodes. Electrodeposition experiments were performed at 1°C (stock solutions 1 and 3) and at room temperature (stock solution 2). Cathodic deposits were obtained at current densities ranging from 3 to 30 mA cm². Deposition times were in the range of up to 5 min.

2.6 Characterization

Coating morphology was studied by a scanning electron microscope (Jeol, model JSM-840). Fiber diameter was evaluated by an optical microscope and SEM observations. X-ray, TG/DTA, Auger and other data for electrolytic titania, zirconia and PZT deposits, obtained from stock solutions 1, 2 and 3, respectively, were reported in previous papers.^{17,18,22,31,42,43}

3 Experimental Results

In electrophoretic experiments alumina, zirconia, PZT, HA and CBC particles were positively charged and moved towards the cathode under the applied field. Deposits of various thicknesses were obtained on individual carbon fibers, bundles and felts used as cathodic substrates. Figure 1(a) shows an SEM image of a green PZT deposit on an individual carbon fiber. EPD can also be performed on bundles of several carbon fibers. Figure 1(b) presents a green HA deposit obtained via EPD. The thickness of HA deposits obtained at a deposition voltage of 50 V and various deposition durations (up to 2 min.) was in the region of 2–30 μm. Figure 1(c) shows a CBC deposit on a carbon felt.

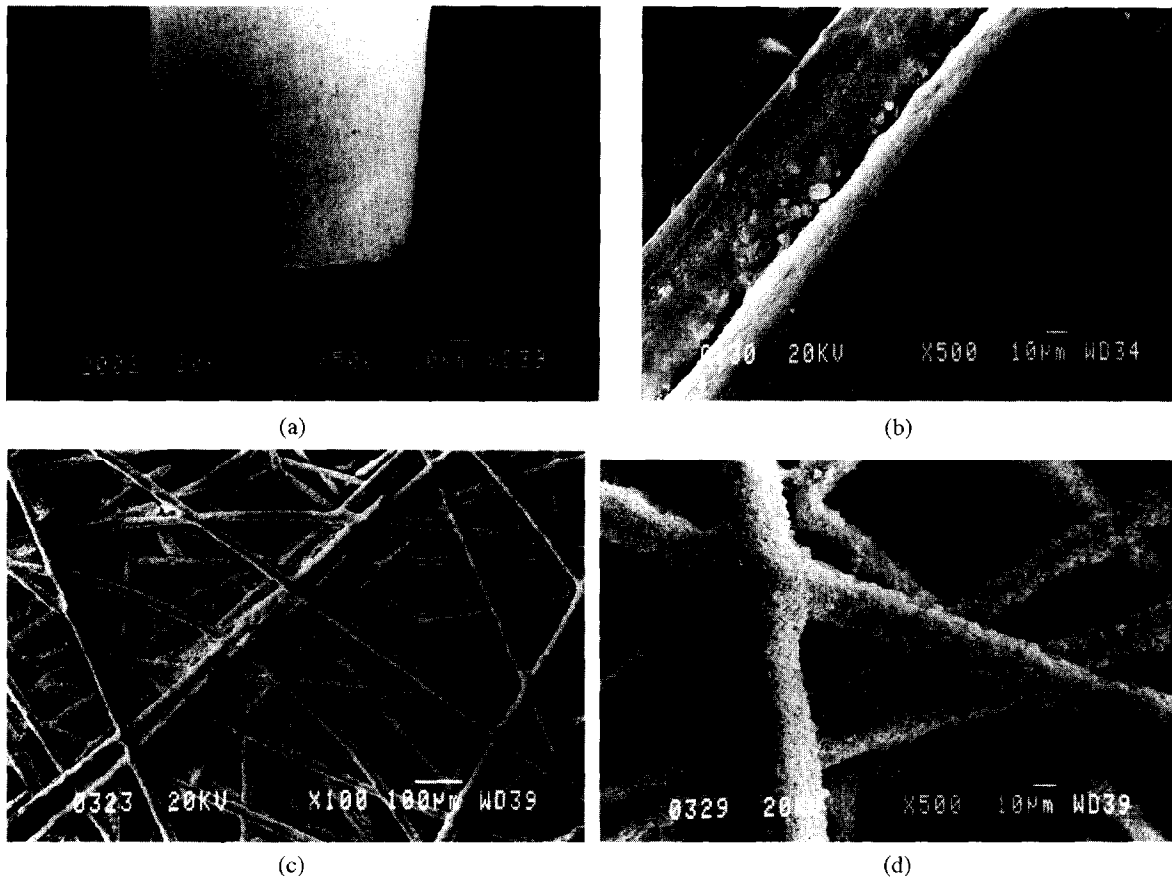


Fig. 1. SEM pictures of green electrophoretic deposits: (a) PZT on a carbon fiber; (b) HA on a bundle, consisting of several carbon fibers; (c, d) CBC on a carbon fiber felt [(c),(d)-different magnifications].

The CBC deposit appears non-uniform at higher magnifications [Fig. 1(d)] as relatively large CBC particles (up to several μm) were used for the deposition process.

Deposit thickness can be controlled by variation of deposition time and voltage. Figure 2 shows diameter of a green alumina deposit on an individual carbon fiber versus deposition time at deposition voltages of 25 V and 50 V. In Fig. 2 it can be

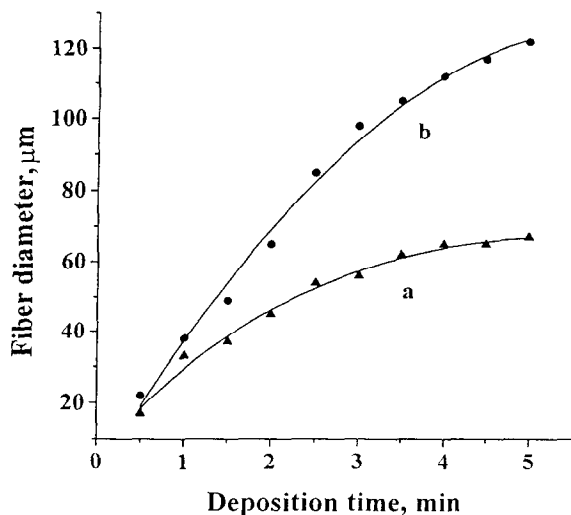


Fig. 2. Diameter of electrophoretic alumina deposits versus deposition time at deposition voltages of 25V(a) and 50 V(b).

seen that fiber diameter increases with deposition time at constant deposition voltage. The slope of the curve is steeper at the beginning of the deposition, however it decreases with time, indicating decrease of the deposition rate. Much higher values of fiber diameter were obtained at a deposition voltage of 50 V than those obtained at 25 V.

Sintering experiments performed in air led to burning out of carbon at temperatures exceeding 900°C and formation of hollow fibers. Figure 3 shows hollow alumina and HA fibers sintered at 1550 and 1150°C , respectively. Hollow fibers of various length (up to 5 cm) and diameters (up to $150\ \mu\text{m}$) were obtained.

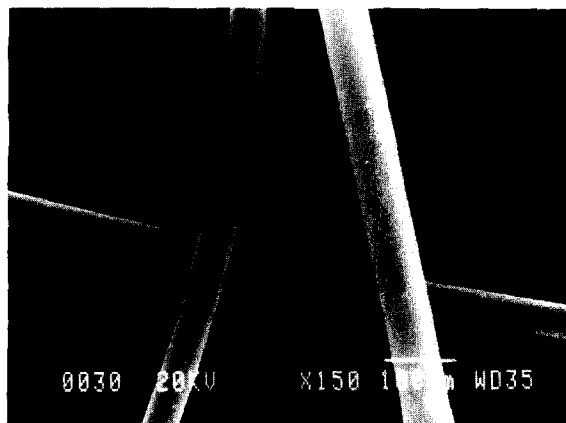
Laminated alumina/zirconia fibers were obtained by multiple electrophoretic deposition and firing of obtained deposits at 1000 , 1400 and 1600°C . This firing procedure facilitates reduction in microporosity, which is suggested to be a result of gas evolution during the burning out of the carbon. Multilayer hollow fibers (up to 30 layers) were obtained. The thickness of individual layers was in the range of $1\text{--}10\ \mu\text{m}$. Hollow multilayer fibers consisting of 2 and 16 layers after firing at 1400°C are shown in Fig. 4(a) and (b), respectively. SEM analysis indicates circular cross-sections of the fibers as well as individual layers and residual microporosity formed at this temperature. Figure 4(c)

shows SEM picture of cross-section of laminated fiber sintered at 1600°C. The dark layer is alumina while the brighter layers are zirconia. SEM observations revealed very sharp interfaces between alumina and zirconia layers. It is important to note that surface roughness of the interface is influenced by the particle size of the powders used in the deposition process. Fibers fired at 1600°C exhibited very little porosity.

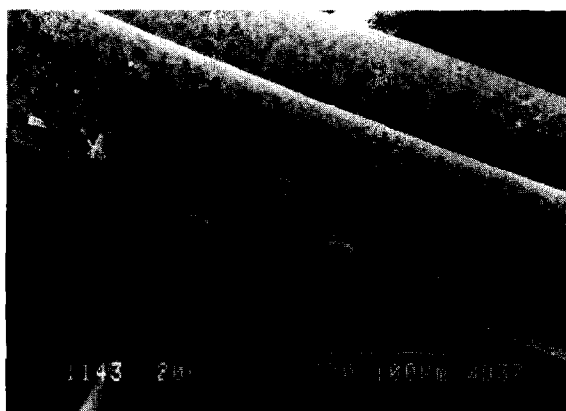
In previous CELD experiments the electro-deposition yield was studied under various experimental conditions.^{17,18,29,31,42} Deposit thickness can be controlled by variation of deposition time and current density. These results were utilized for formation of titania, zirconia and PZT deposits of controlled thickness on fibrous carbon substrates. Figure 5(a) shows a green titania deposit obtained via CELD. The deposit thickness is about 1 μm. The ultrafine size of the deposit particles is noteworthy, and far below the micrometer scale. Figure 5(b) shows a zirconia deposit on the carbon felt after thermal treatment at 150°C. An enlarged view [Fig. 5(c)] indicates very fine particle size. By variation of deposition time at constant current density of 20 mA cm⁻², deposits of different thickness up to 5 μm were obtained. However, at a deposit

thickness higher than 3 μm, crack formation was observed during the drying stage.

Figure 6 presents SEM pictures of PZT deposits formed via CELD and EPD on carbon fibers. These pictures obtained at the same magnification make it possible to compare the microstructures of CELD and EPD deposits. Scanning electron micrographs of the green deposits obtained via CELD [Fig. 6(a)] reveal a smooth, dense and continuous morphology. The size of deposit particles is



(a)

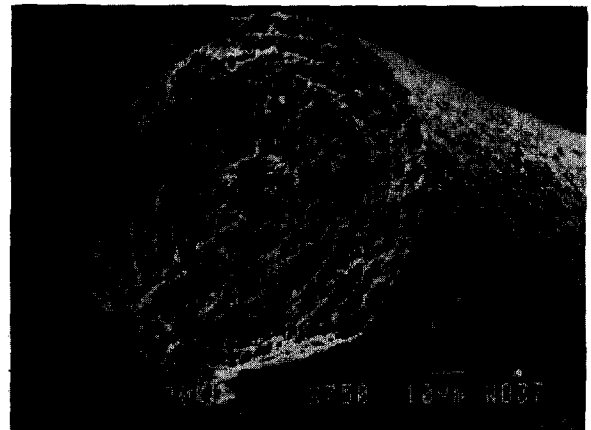


(b)

Fig. 3. SEM pictures of alumina (a) and HA (b) hollow fibers obtained via electrophoretic deposition and sintered at 1550 and 1150°C, respectively.



(a)



(b)



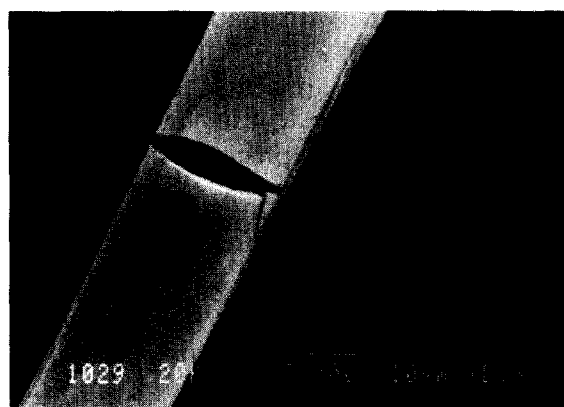
(c)

Fig. 4. SEM pictures of multilayer alumina/zirconia fibers obtained via electrophoretic deposition [(a)—2 layers, (b)—16 layers, thermal treatment at 1400°C] and a cross-section (c) of a multilayer fiber sintered at 1600°C.

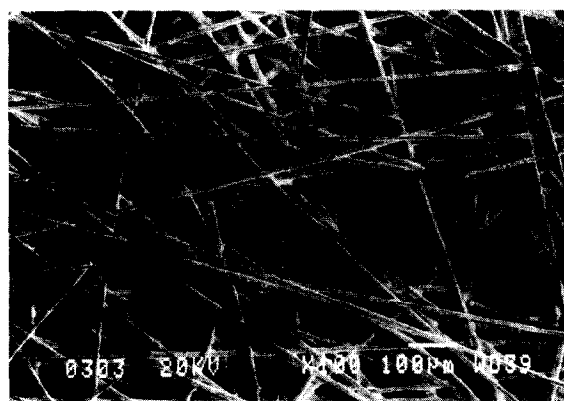
on nanometric scale. The green deposits obtained via CELD [Fig. 6(a)] are tightly attached to the substrate. As seen in Fig. 6(b) the maximum particle size in a deposit obtained via EPD is about $1\ \mu\text{m}$ and the deposit includes a significant amount of very fine particles. As seen in Fig. 6(b) pores up to $1\ \mu\text{m}$ were observed in the deposits.

4 Discussion

The reported results indicate that various ceramic materials can be deposited on fibrous substrates via



(a)



(b)

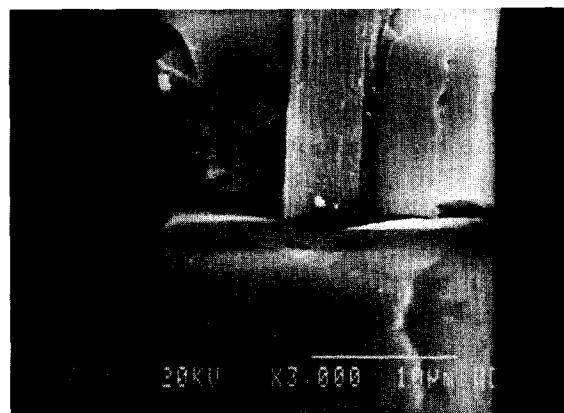


(c)

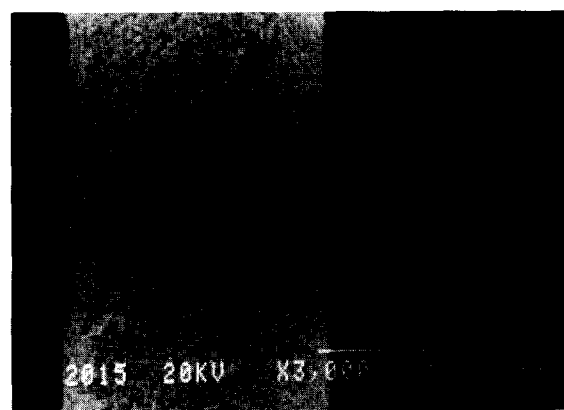
Fig. 5. SEM pictures of deposits obtained via CELD: (a) green titania deposit on a carbon fiber; (b),(c) zirconia deposit on a carbon fiber felt after drying at 150°C [(b),(c)-different magnifications].

EPD and CELD. It is important to note that due to the use of an electric field EPD and CELD are particularly suited for the formation of uniform deposits on substrates of complicated shape. The uniformity of ceramic coatings obtained via these methods results from the insulating properties of the deposits and electric field dependence of the deposition rate.^{40,42,44,45} However, as pointed out in,⁴⁴ deposit uniformity is limited by the particle size of the powders used for the deposition process. In order to obtain deposits of adequate diameter on carbon fibers, the size of individual particles should be significantly lower than the carbon fiber diameter.

Electrophoretic deposition is based on the use of ceramic particles. Electron microscopic investigations have shown that the microstructures of deposits were influenced by powder characteristics. Indeed, non-uniformity of CBC deposits observed at high magnifications [Fig. 1(d)] is attributed to relatively large CBC particles. It should be noted that PZT deposits obtained in EPD experiments were porous. This porosity is speculated to be a consequence of packing of relatively large PZT particles. Electrophoretic deposition of submicrometre powders offers advantages in fabrication of monolayer and multilayer coatings on carbon



(a)



(b)

Fig. 6. SEM pictures of green PZT deposits on carbon fibers obtained via CELD (a) and EPD (b).

fibers. The particle size and pore size distributions are determining factors for the packing situation within a deposit. It is important to note that powder systems made up from close-packed, fine particles are highly sinterreactive. Indeed, according to^{46,47} the densification rate depends inversely on the fourth power of particle size. As pointed out,⁴⁷ reduction of particle size from micrometric to nanometric scale increased densification rate by several orders of magnitude.

CELD produces ceramic materials and provides their deposition. It is important to see that electrodeposition allows coating formation on atomic scale and is now an important tool in formation of nanostructured materials.^{18,21–23} Owing to use of ionic species instead of ceramic particles the deposits obtained via CELD have lower particle sizes, more uniform and continuous microstructures than those prepared via EPD. Therefore higher sintering activity of CELD deposits can be expected. CELD results in formation of oxide or hydroxide films. Oxide films obtained by thermal dehydration of hydroxides exhibited^{23,32,48} cracking attributed to drying shrinkage. However, it was established^{17,31,49} that the use of additives and multiple deposition allows problems related to drying shrinkage to be diminished. Deposition rate and maximal deposit thickness obtained in EPD and CELD experiments depend on various factors discussed in.^{18,28,34,35,40,42,45} Coating thickness can be controlled by variation of deposition time, voltage or current density. The experimental data presented in Fig. 2 demonstrate a manner in which the deposit diameter can be controlled. The decrease of deposition rate with time is attributed to the increase in voltage drop across the deposited layer.⁴⁰ Turning to experiments on deposition of various materials via EPD and CELD it is seen that deposition rate in electrophoretic process is much faster (by 2–3 orders of magnitude) than that in electrodeposition process, resulting in significantly higher deposit thicknesses. According to³⁵ particle/electrode reactions are not involved in EPD and ceramic particles do not lose their charge on being deposited. In contrast, CELD is based on base generation in electrode reactions and neutralization of ionic species to form deposits. As the coating process progresses, an insulating layer forms, which in turn prevents OH⁻ generation. It was pointed out^{32,49} that coating resistivity is a major limiting factor of the electrodeposition method for development of thick coatings.

The choice of suitable solvent is important for EPD^{34,35} and CELD.^{33,42} It should be noted that non-aqueous solutions enable to decrease porosity of films, resulting from gas bubble evolution. With this fact in mind, EPD experiments were performed

in isopropyl alcohol. It should be mentioned that the adsorbed water in green deposits obtained via CELD leads to cementation of small particles to form aggregates and thus diminishes the advantage of electrodeposition in producing films with nano-size particles.²⁹ However the deposition process needs certain amount of water for base generation and prevention of formation of non-stoichiometric oxides.^{29,42} It is clear that CELD can be performed from aqueous or mixed solutions.

EPD offers advantage in deposition of complex compounds. Indeed, the degree of stoichiometry of the electrophoretic deposit is controlled by the degree of stoichiometry of the powder used.⁴⁵ Problems are associated with control of stoichiometry of electrolytic deposits due to different deposition rates of individual components. However, the possibility of control of the deposit composition by use of specifically designed precursors^{17,22,30,31} opens new perspectives in deposition of important ceramic complex oxide compounds of exact stoichiometry.

The above experimental data coupled with results of previous works^{18,42,44,45} suggest that EPD and CELD enable formation of thick and thin ceramic deposits on fibrous carbon materials. Moreover, EPD and CELD can be used to replicate the carbon structures with ceramic materials to form hollow fibers and microtubes. Obtained results have a significant potential for design of composites. HA, alumina, zirconia and titania are important materials for biomedical applications.⁵⁰ The possibility of formation of hollow fibers of various diameters⁴⁵ is promising for the development of biomedical implants of controlled porosity. The deposition of PZT via CELD and EPD on fibrous substrates can be utilized for development of advanced piezocomposites of desired phase connectivity.^{51–53} The possibility of formation of multilayer coatings on fibrous substrates can be used for design of composites based on coated and laminated fibers.

5 Conclusions

This investigation has shown that various ceramic materials can be deposited via EPD and CELD on fibrous carbon substrates. Ceramic coatings can be obtained as monolayers or multilayers, coating thickness can be controlled by variation of deposition time, voltage or current density. The feasibility of formation of hollow fibers via EPD has been demonstrated. Obtained results pave the way for formation of coated fibers, hollow fibers and microtubes for development of composites for biomedical, piezoelectric and other applications.

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