The ability to manipulate microstructural features and the facileness of the electrophoretic deposition (EPD) technique has attracted considerable attention from academia and industry. Considerable work has been completed to understand the basic particle consolidation mechanism and to develop a wide range of novel applications for EPD in the processing of advanced materials and coatings. A brief history of recent electrophoretic deposition (EPD) developments will be presented and the EPD process will be defined. Basic fundamental aspects of electrophoretic consolidation of fine particles from colloidal suspension will be discussed. The kinetics of the EPD process will be discussed in light of the fabrication of advanced ceramics. It will be shown that the properties of the EPD suspension play a vital role in the manufacture of high performance bulk materials and coatings.

This presentation will discuss the unique capabilities of EPD. The talk will describe applications of EPD to the fields of coatings, nanoscale assembly, micropatterned thin films, near shape ceramics, and others. The fabrication of metal ceramic composite coatings combining EPD with metal electrodeposition technique will also be described.

Figure (a) Sintered microtubular SOFC without cathode, fabricated using sequential EPD technique; (b) Typical SEM fracture surface cross sectional micrograph showing the five layers of the µT-SOFC.

One of the advanced applications of EPD with high potential is the manufacture of ‘Microtubular Solid Oxide Fuel Cell’ (µT-SOFC). The author’s research group in Alberta Innovates - Technology Futures (AITF) was a pioneer in µT-SOFC development using EPD-based technology. Tubular single cell manufacturing challenges and limitations will be discussed along with innovative ways to overcome some of the fabrication issues. This EPD based manufacturing process is capable of fabricating single cells as small as ~10µm in diameter. Due to its thin wall, a µT-SOFC has extremely high thermal shock resistance and low thermal mass. Controlling the defect density of a ceramic is important for fluid separation applications. The strategic application of the EPD technique for targeted repair of membrane defects will also be illustrated.

Bio. Dr. Sarkar received the B.E. degree from College of Ceramic Technology, Calcutta, India, M.S. degree from Indian Institute of Technology Kanpur and a Ph.D. degree in Materials Science & Engineering from McMaster University, Canada. Dr. Sarkar is well known in the world's ceramics/materials scientist community for his outstanding contribution in Electrophoretic Deposition (EPD) and work in Tubular Micro Solid Oxide Fuel Cell. Dr. Sarkar was awarded a visiting scientist fellowship in 1996 by the Tokyo Metropolitan University (TMU) in Japan, to work on its International Joint Research Program. He joined the Alberta Innovates – Technology Futures (AITF) (former name: Alberta Research Council) in November 1997. Dr. Sarkar is a Principle Scientist at AITF. His present main research areas are Solid Oxide Fuel Cell and its innovative applications, Chemical Looping Combustion, solid sorbents for CO₂ capture & tubular structure bed reactor, water harvesting from humid gaseous streams and next generation membrane distillation device for water purification. Dr. Sarkar has over 10 issued patents, over 70 journal publications and has written two book chapters, ‘Electrophoretic Deposition (EPD): Fundamental & Novel Applications in Fabrication of Advanced Ceramic Microstructures’ and ‘Advances in Micro Solid Oxide Fuel Cells’.
EFFECT OF ELECTRODE REACTIONS DURING AQUEOUS ELECTROPHORETIC DEPOSITION ON BULK SUSPENSION PROPERTIES AND DEPOSITION QUALITY

Laxmidhar Besra, Institute of Minerals & Materials Technology (IMMT), India
ldbesra@immt.res.in
Sanjukta Dey, Institute of Minerals & Materials Technology (IMMT), India
Sarama Bhattacharjee, Institute of Minerals & Materials Technology (IMMT), India
Tapan K. Rout, Tata Steel Limited, India
Dilip K. Sengupta, Tata Steel Limited, India
Tetsuo Uchikoshi, National Institute for Materials Science (NIMS), Japan

Non-aqueous solvents have been popularly used as suspending medium in Electrophoretic deposition (EPD) for several applications. The drawbacks of these solvents are that they cause environmental concern and are expensive. Therefore, there is a great interest for the development aqueous EPD, which is low-cost and environmental friendly. There are several problems when using water as the suspending medium in EPD. First, there is gas evolution at the electrodes on application of the electric field. Hydrogen is generated at cathode and oxygen at anode. This results in incorporation of bubbles in deposits and the quality of deposit suffers. Several approaches, such as the use of pulse DC, asymmetric AC, and palladium electrode have been reported in the literature to overcome this problem.

However, the biggest problem concerning aqueous EPD is reproducibility of deposition. As an example, in batch EPD of Al₂O₃ and TiO₂ from aqueous suspension, we observed the best quality of deposition from the first deposit. Invariably, the amount and quality of deposit decreased progressively with increased number of deposition from the same suspension. For prolonged first deposition, the deterioration became severe and no deposition occurred from the second deposition onwards. This occurred even for cases when only a small fraction of the powder suspension is depleted in the first deposit. A closer look showed destabilized suspension and significant change in bulk pH of the suspension. Here, we measured the change in bulk pH as a function of time, starting pH, electrode material during water electrolysis as well as during aqueous EPD of TiO₂ and Al₂O₃. At an applied voltage of 100 V, the bulk pH of water increased rapidly from 3.5 to about 8.9, resulting in destabilization of suspension and no deposition. The extent of pH change for different electrode material (both anode and cathode) was in the order: steel > aluminium > palladium. Use of suitable dosages of cationic dispersant polyethylenimine (PEI) and poly(dially dimethyl ammonium chloride) (PolyDADMAC) in the suspension decreased the extent of bulk pH variation during aqueous EPD. Further work is on to understand the underlying mechanism.
Molecular and ionic liquids are the most common solvents used in electrodeposition (ED) and electrophoretic deposition (EPD). Molecular liquid solvents, including water, organic and inorganic solvents are widely used for such applications. When water is appropriate for a given purpose, it should be used without hesitation. Otherwise, nonaqueous solvents must be considered to obtain desirable solvent properties.

Under the context of a green chemistry approach, efforts are being made to promote the use of environmentally friendly media, i.e., green solvents. Among such solvents, ionic liquids are considered as a good alternative. Ionic liquids have been the focus of research on ED and EPD due to the following advantages: i) availability of a large variety of ionic liquid formulations, ii) ability to better control redox potentials; iii) capability to control the deposition of nanostructures, iv) ability to process water-sensitive species and substrates.

Recent publications show the different efforts made worldwide for the commercialization of deposition systems using ionic liquids. However, up to now, the benefits of using ionic liquids as solvent media are only partially recognized, especially because of their toxicity and high cost, which limits their applicability on a significant scale.

In the present review, we analyze the different requirements and the viability of ionic liquids as green solvents for ED and EPD processes. The analysis takes into account parameters and characteristics of ionic liquids such as purity, chemical stability, biodegradability, toxicity, recyclability coating properties and cost. As a case study, this work shows a technical and economic analysis comparing the use of ionic liquids and molten salts as solvent media in the ED of aluminum on stainless steel.
SUBSTRATE SELECTION AND MANAGEMENT STRATEGIES FOR AQUEOUS EPD

Peter Hope, LVH Coatings Ltd., United Kingdom
Janet Hope, LVH Coatings Ltd., United Kingdom

Classical EPD has typically been conducted in organic solvent media. Many suitable solvents are volatile and highly flammable and this limits the industrial application of the technique on the basis of safety alone. Aqueous EPD may be seen as a safer method, but issues relating to electrolysis and surface energy phenomena become prominent and can create interferences and variability unless the substrate type and its preparation are compatible with the aqueous EPD chemistry and its deposition method. As EPD layers become thinner, factors such as substrate surface structure and wettability become more critical. Industrial processes utilising some principles of EPD for applying paint from water-based preparations are well established in the metal finishing sector. Consequently there is a significant body of practical experience available from this sector that can be of use in translating classical EPD from a solvent to an aqueous technique while avoiding interferences inherent in the use of water as the deposition medium. In this paper, substrate selection is discussed in relation to the electrolyte content of the system where phenomena such as dissolution and micro-arcing can occur. The initial wetting of the substrate must be considered prior to applying voltage. Surface preparation techniques and the methods of introducing the substrate into the EPD dispersion all can have an impact on the final result.
EFFECT OF ELECTRIC DOUBLE LAYER CHARACTERISTICS ON CHAIN FORMATION OF CERAMIC NANO-PARTICLES

Babak Raissi, Materials and Energy Research Center, Iran
babakraissi@yahoo.com
b-raissi@merc.ac.ir
Reza Riahifar, Materials and Energy Research Center, Iran
Maziar Sahba Yaghmaee, Materials and Energy Research Center, Iran
Mahsa Navidirad, Materials and Energy Research Center, Iran
Batool Mehralian, Materials and Energy Research Center, Iran

Key Words: AC electrophoretic Deposition, Chain Formation.

By applying AC electric fields, chain formation of ceramic nano-particles was observed. This phenomenon was seen at low frequencies in organic liquid media. In the present work, effect of Electric Double Layer (EDL) characteristics on chain formation is investigated by considering a two layers model. EDL characteristic was changed by either washing the initial powder to remove impurities or by adding polymeric additives. These results showed that by some modifications at the surface of nano-particles, chain formation phenomenon can be promoted or prevented in a 150 micrometer gap between two planar electrodes.
ELECTROPHORETIC (INFILTRATION) DEPOSITION OF THICK CONDUCTING SUBSTRATES

Aljaž Ivekovič, Jožef Stefan Institute, Slovenia
aljaz.ivekovic@ijs.si
Saša Novak, Jožef Stefan Institute, Slovenia

Key Words: Electrophoretic (Infiltration) Deposition, conducting substrates, fusion

The use of EPD in the infiltration of fibrous preform for the fabrication of ceramic matrix composites has been up to now focused mainly on the fabrication of oxide based composites in particular with 2D reinforcement. Since oxide fibres are non-conductive, they are placed in front of the electrode and the particles migrating towards the electrode with the opposite charge gradually fill the fibrous preform.

In the case of conducting substrates, porous structures or woven fibre preforms are normally used as depositing electrodes, which enables only shallow penetration of particles into the substrate due to electric shielding effect. In order to successfully utilize EPD for fabrication of thick composite structures, the substrate has to be electrically separated from the depositing electrode. Furthermore, the suspensions, as well as fibre electrokinetic properties play a crucial role in infiltration kinetics, determining the rate of particle electrophoresis and electroosmotic flow within the porous substrate. Infiltration of conductive 3D woven fabric preforms was demonstrated using concentrated SiC powder suspensions and constant current deposition in the range from 1-10 mA/cm². Particle infiltration was enhanced by increasing the electrostatic repulsion between the particles and the fibres. Appropriate selection of applied current, particle concentration and particle and fibre potential, together with appropriate EPD cell configuration results in a complete through thickness filling of the porous substrate.

Figure 1 – Schematic representation of EPD cell where a) fibres are in contact with the electrode and b) fibres electrically isolated from the electrode.
INFLUENCE OF LIGANDS ON THE MOBILITY OF NANOPARTICLES DURING THE ELECTROPHORETIC DEPOSITION

Stephan Barcikowski, Technical Chemistry I, University of Duisburg-Essen, Germany
Stephan.Barcikowski@uni-due.de
Sven Koenen, Technical Chemistry I, University of Duisburg-Essen, Germany
Carmen Streich, Technical Chemistry I, University of Duisburg-Essen, Germany

Key Words: electrophoretic deposition, electrophoretic mobility, deposition rate, ligand-free, nanoparticles

Electrophoretic deposition (EPD) of colloidal nanoparticles is used to create nanostructured topographies on 3-dimensional substrates [1]. These substrates are used for a lot of different applications like medicine as one of them. Aspects that are often overlooked during the generation of the desired nanostructure on the substrates are fundamentals that affect the electrophoretic deposition. One of these important aspects is different ligands around the nanoparticles which influence the electrophoretic deposition. Since, the ligands may cause a barrier formation in front of the electrode during electrophoretic deposition, which can hinder the nanoparticles deposition. Due to the importance of the ligands on the electrophoretic deposition mechanism, the aim of this study was to investigate the influence of different ligands on the electrophoretic deposition and also on the electrophoretic mobility. As a reference ligand-free, bare nanoparticles which were generated via laser ablation in liquids were used. The study confirmed that the different ligands cause a different electrophoretic mobility in the electric field due to the steric effect of the ligands and also because of the charge of the molecule. It has to be noted that the ligand-free, bare nanoparticles show a good comparability to the electrophoretic mobility calculated in the literature. It was also proved that a high electrophoretic mobility is not directly transferable into a high deposition rate since the ligands have different effects regarding the barrier formation that hinders deposition. However, the ligand-free nanoparticle control group showed a linear behavior of the deposition rate. This result could not be found in the literature before. Therefore, this study presents a good investigation of the influence of ligands on the electrophoretic deposition, because for the first time a control group, which properties were ideal to characterize the electrophoretic deposition, was used.

Figure 1 – influence of a ligand on the electrophoretic velocity (left) and on the concentration that is deposited

UNDERSTANDING THE COLLOIDAL BEHAVIOR OF BIOGLASS 45S5® TO OBTAIN BIOACTIVE-GLASS BASED SOFT COATINGS BY EPD

Sandra Cabanas-Polo, Institute of Biomaterials, Department of Materials Science and Engineering, University of Erlangen-Nuremberg, Germany
sandra.cabanas@ww.uni-erlangen.de

Aldo R. Boccaccini, Department of Materials Science and Engineering, University of Erlangen-Nuremberg, Germany

Key Words: Electrophoretic deposition, colloidal behavior, Bioglass, coatings.

The increasing interest in the fabrication of composite coatings based on biopolymers and bioactive glasses (or ceramics) for orthopedic applications arises mainly from the potentially improved attachment that can be obtained between the rigid implant (e.g., Ti alloy) and the vascularized "softer" bone tissue. These so called soft coatings should also increase the corrosion protection of the metallic implant and avoid the high temperature sintering of pure bioceramic coatings.

A suitable technique to fabricate this kind of coatings is the electrophoretic deposition where a key parameters to control the final microstructure of the coatings is to understand the interaction between the inorganic particles and the organic polyelectrolytes in the suspension.

In this work, the interaction between Bioglass 45S5® particles and different biocompatible polymers (polyacrylic acid, polyvinyl alcohol, poyvinylpyrroldione, chitosan and alginate) is studied in order to understand the colloidal behavior of the bioactive glass. The stabilization mechanisms with the different polymers are discussed in terms of zeta potential considering both the functional groups and the geometry of the polyelectrolytes. The optimization of the EPD process (voltage and time) is also study in order to develop coatings with each single polymer. The link between the suspension stability and the final microstructure of the soft-coatings will be highlighted.
ADVANCES IN MICROSCALE AND NANOSCALE MECHANISMS OF ELECTROPHORETIC DEPOSITION IN AQUEOUS MEDIA

Guido Falk, University of Saarland, Structural and Functional Ceramics, Germany

The processing of ceramic thick and thin films, nano- and micro-scaled ceramic structures as well as bulk ceramics of high quality and precise dimensions under electrophoretic boundary conditions requires a full understanding of the dynamics of relevant interfacial mechanisms and interactions of colloidal phases at the nano- and micro-scale.

Recent findings and latest insights on the importance of electrokinetic and electrohydrodynamic interfacial processes for electrophoretic deposition in aqueous media are summarized. In this context, the presentation addresses the fundamental importance of surficial charge heterogeneities, electric double layer instabilities, electrokinetically induced micro-vortex dynamics, as well as lateral and medial effective electrial field gradients. These phenomena are evaluated in terms of reasonable correlations and mechanistic coincidences of general EPD deposition principles. The experimental results are based on potentiometry, in-situ videomicroscopy, high-resolution, secondary electron microscopy, as well as total internal reflection fluorescence microscopy. A numerical method for the simulation of the electrophoretic deposition process is suggested based on a multiphysical Finite Element approach given by Nernst-Planck, Poisson- and Navier-Stokes equations. The results of the simulations provide adequate agreement with experimental findings. Possible potential applications, e.g., the EPD based self-organization of submiro- and nano-particles to innovatively designed ceramic structures of high-quality characteristics are questioned and evaluated critically.
The electrophoretic-deposition (EPD) method was tested to fabricate pristine and composite polymer-in-ceramic solid electrolytes for application in planar and 3D microbattery configurations. To gain a phenomenological understanding of the EPD process for a system of charged colloidal particle covered with a polyelectrolyte (PE) we developed a model for the electric potential on the basis of the Poisson-Boltzmann (PB) relation. We simulate a set of scenarios in an attempt to present the influence of the pH, surface potential, PE density, and the PE brush length on the electric potential and charge distribution profiles as a function of distance from the solid-surface/brush interface, where ‘brush’ is one of the possible PE configurations.

TGA, DSC, XRD, TOFSIMS, ESEM and AC-impedance tests were used for the characterization of the films. We found that the relative content of polymer and ceramics in the film depends on the type of solvent and composition of the suspension. Films deposited at 50V are smoother, conformal and more uniform than those prepared at 100, 150 and 200V. The room-temperature ionic conductivity of solid polymer-in-ceramic composites prepared by electrophoretic deposition, followed by impregnation with Li(CF₃SO₂)₂N and LiI salts, was 0.3 and 0.5mS/cm, respectively.
CELL ROTATION UNDER DIELECTROPHORETIC FORCES

Guigen Zhang, Department of Bioengineering and IBIOE, Clemson University, USA
guigen@clemson.edu
Yu Zhao, Department of Bioengineering, Clemson University, USA
Johnie Hodge, Department of Bioengineering, Clemson University, USA
Jozef Brcka, Tokyo Electron U.S. Holdings, Inc., U.S. Technology Development Center, USA
Jacques Faguet, Tokyo Electron U.S. Holdings, Inc., U.S. Technology Development Center, USA
Eric Lee, Tokyo Electron U.S. Holdings, Inc., U.S. Technology Development Center, USA

Key Words: Dielectrophoresis, electric field distortion, cell rotation, rat adipose stem cells

Rotating electrical field is often needed to induce cell rotation by generating a rotating dielectrophoretic (DEP) force. However, the setup for generating a rotating electrical field may be too sophisticated for most practical uses. It is thus desirable to manipulate cells using conventional DEP. With the current prevailing DEP theory, it is impossible to know if it is even feasible to drive cell rotation with conventional DEP. In this study we use COMSOL simulation to reexamine the DEP phenomena by accounting for the field distortion caused by the presence of particles having different permittivity than their surrounding medium. With this new approach, we are able to predict that it is possible to drive cell rotation, provided that the cell body can be regarded as having anisotropic structure. To validate our modeling results, we performed experiments using rat adipose stem cells and achieved cell rotation with parallel interdigitated electrodes biased under alternating current (AC) DEP.

3D COMSOL models were developed. In modeling the cell rotation behavior, we hypothesized that cell rotation is caused by the non-spherical shape of a cell body and the off-centered location of its nucleus, and that rotation direction depends on the relative location of the nucleus with respect to the electrical field. To prove this, we considered an ellipsoid-shaped cell with off-centered nucleus. The cell nucleus was assigned with a higher conductivity value than cell plasma due to greater hydrated free ion content, making the relative permittivity of the cell nucleus higher than that of the cytoplasm. We considered two cases: 1) the nucleus was off centered to the right above the center line and 2) it was off centered to the right below the center line. For experimental validation, a glass slide with etched parallel gold electrodes was used to deliver the conventional DEP forces. Rat adipose stem cells in a glucose/sucrose mixture solution were used. A glass cover slip was used to ensure a uniform height of the liquid layer. A functional generator and an amplifier were used to provide sine wave AC potential.

Fig.1 shows the obtained DEP forces as a function of the cell orientation angle for both cases. As the cell orientation angle changes from 0° to 360°, the x- and y-components of DEP force exerted on the cell follow a sinusoidal wave pattern having a 90° phase delay. This indicates that there exists a net rotation force causing the cell to rotate in the x-y plane. In experimental validation, by sweeping the frequency of the AC biasing from low to high, we noted that some of the cells in the gap region spin either clockwise or counterclockwise as shown in Fig.2. Note that the red-circled cell is rotation counterclockwise and the green-circled cell clockwise.

This validation result confirms our hypotheses are confirmed: the cell rotation is indeed caused by the non-circular shape of the cell body and the off-centered location of its nucleus and that the rotation direction depends on the relative location of nucleus with respect to the electrical field. In essence, cell rotation can be achieved with conventional DEP by taking advantage of the anisotropy of the cell body structure. The off-centered nucleus causes asymmetry, thus affecting the rotation direction. In experimental validation, we observed the predicted cell rotation behavior under normal DEP, and that cells may rotate in the clockwise direction or the counter clockwise direction dependent on the related locations of their nuclei.
HYDRODYNAMIC MODELING OF ELECTROCODEPOSITION ON A ROTATING CYLINDER ELECTRODE

Alexander Vakhrushev, Institute of Mechanics, Ural Branch of the Russian Academy of Sciences, Russia
postmaster@ntm.udm.ru
Eugene Molchanov, Institute of Mechanics, Ural Branch of the Russian Academy of Sciences, Russia

Key Words: Nanoparticles, electrocodeposition, coatings, composite materials,

Metal matrix composite electrochemical coatings (MMEC) prepared from the suspensions, representing electrolyte solutions with additives of certain quantity of a superfine powder. The powder particles are adsorbed on a cathode surface in combination with metal ions during electrocodeposition (ECD) process and the metal matrix composite coating is formed. Metal matrix composite coating consists of the galvanic metal (dispersion phase) and particles of a powder (dispersed phase). ECD process was developed with the intent of increasing the versatility of the electrophoretic deposition process by combining it with electroplating.

The general mechanism of ECD was analogous to that of electrophoretic deposition. There are the following steps of ECD process: i) the particles in suspension acquire a surface charge, ii) the charged particles and metal ions are transported through the liquid by the application of an electric field (electrophoresis), convection and diffusion iii) the particles and metal ions are adsorbed onto the electrode surface, and iv) the particles adhere to the electrode surface through van der Waals forces, chemical bonding, or other forces and, simultaneously, adsorbed metal ions are reduced to metal atoms. Metal matrix are encompassed the adsorbed particles, and thus, the MMEC is formed.

As dispersed phase employ particles of oxides Al₂O₃, ZrO₂, TiO₂, SiO₂ Cr₂O₃, various allotropic form C, carbides SiC, WC, TiC, nitrides Si₃N₄ and number of other materials. Diameter of particles as usual vary within 4-800 nanometers. As dispersion phase employ such metals as Cu, Ni, Co, Cr, Zn, Ag, Fe, Au and their alloys.

Process of ECD finds application in such areas of the industry, as automobile production, building, electric power production, and also in airspace industry along with oil and gas production. It is possible to produce coatings of sensor both from soft magnetic material and from hard-magnetic material. MMEC find wide application as wear-resistant coatings, coatings with a low friction coefficient, coatings for tools with high hardness, coatings for the abrasive tool, and also for dispersion hardening of alloys, and also for protection from oxidation and from high-temperature corrosion.

In this work the mathematical model of ECD process of system Cu-Al₂O₃ on a rotating cylinder electrode is presented. The mathematical model described the mass transfer of electrolyte ions and held in suspension of nanoparticles throughout the volume of the electrolyte, electrode processes, adsorption and desorption of electroactive ions and nanoparticles on cathode and anode and turbulent fluid motion. Turbulent flow of rotating liquid in electrochemical cell is described based on the Reynolds-averaged Navier-Stokes (RANS) equations with the Abe-Kondoh-Nagano (AKN) low Reynolds number modification. The mass transfer of ions and nanoparticles throughout the volume of the electrolyte is described by the convective diffusion equations, which takes into account the convection, diffusion and electrophoresis. The cathodic and anodic processes are investigated using the tertiary current distribution. The adsorption/desorption of ions and nanoparticles on electrode surfaces is described by Langmuir adsorption isotherm. The coupled mathematical model consist of RANS equations, continuity equation, material balance equations for mass transfer throughout the volume of electrolyte and material balance equations for surfaces reaction.

A results of mathematical modeling of ECD process of composite Cu-Al₂O₃ with the various dispersive and concentrations of nanoparticles Al₂O₃ in the on a rotating cylinder electrode were received.

Reference
PARTICLE-PARTICLE INTERACTION UNDER DIELECTROPHORESIS FOR RAPID PATTERNING

Guigen Zhang, Department of Bioengineering and IBIOE, Clemson University, USA
guigen@clemson.edu
Yu Zhao, Department of Bioengineering, Clemson University, USA
Johnie Hodge, Department of Bioengineering, Clemson University, USA
Jozef Brcka, Tokyo Electron U.S. Holdings, Inc., U.S. Technology Development Center, USA
Jacques Faguet, Tokyo Electron U.S. Holdings, Inc., U.S. Technology Development Center, USA
Eric Lee, Tokyo Electron U.S. Holdings, Inc., U.S. Technology Development Center, USA

Key Words: Dielectrophoresis, electric field distortion, particle-particle interaction, pearl-chain formation

Cells and other biological particles will experience dielectrophoretic (DEP) forces when placed in a non-uniform electric field. DEP forces have been widely used to separate and sort micro and nano biological particles including biological cells, bacteria and viruses. While the prevailing DEP theory provides good qualitative predictions of the direction of DEP forces, it does not account for particle-particle interaction, thus it cannot provide any information on particle alignment. To address this crucial problem, we performed integrated experimentation and modeling with an end goal of developing a DEP-based rapid patterning technique for tissue engineering by elucidating the underlying DEP mechanisms governing the particle-particle interaction and the formation of particle alignments.

On the experimental front, to generate DEP forces, we etched electrodes on a thin titanium/gold film coated on a glass slide using conventional photolithographic techniques. Several electrode designs with interdigitated geometries were used. During experiments, the electrodes were insulated using a thin (12µm) polyethylene sheet. Drops of DI water mixed with aliquots of polystyrene bead suspension solution were dispensed on top of the insulation sheet while the electrodes were biased using an AC function generator (0-32V peak-peak and 0-20MHz) and the formed bead alignment patterns were recorded. On the modeling front, we developed 3D COMSOL models to evaluate the underlying driving mechanisms. We hypothesize that the volumetric domains of the particles with different dielectric properties from the surrounding media will distort the electric field and affect the resulting DEP forces. Thus the size and location of a particle and the distance between neighboring particles are all accounted for in the modeling.

As shown in Fig.1, polystyrene beads formed alignment patterns quickly under proper DEP biasing conditions. Moreover, the pattern lines consisted of particles aligned parallel in a pearl-chain manner. Fig.2 shows the x-component of the resulting electrical field when the particle presence is considered (a) and not considered (b). Clearly, the electrical field surrounding the particle is distorted drastically due to the presence of the particle having a different conductivity and permittivity from the surrounding medium. With this field-distortion effect considered, we then examined the process of pearl-chain formation. Of the three particles (Fig.2-c,d) the two outer ones were driven closer to the middle one to form a packed chain, indicating that the DEP force, along with the influence of the distorted electric fields by the neighboring particles, generates a driving force to move the particles closer together in a line that is parallel to the overall electric field. Our new approach of evaluating the DEP forces overcomes the limitation in the current DEP theory by accounting for the effects of particle size, shape and location, and interaction between particles. The obtained results prove to be effective in explaining our experimental observations.
ELECTROPHORETIC DEPOSITION OF COLLOIDAL NANOPARTICLES AND NANOSHEETS
FOR OPTICAL AND ELECTROCHEMICAL APPLICATIONS

Atsunori Matsuda, Toyohashi University of Technology, Japan
Matsuda@ee.tut.ac.jp

Key Words: silsesquioxane, micropattern, hydrated titanate, layered double hydroxide, electrochemical cell

Electrophoretic deposition (EPD) is a simple and cost-effective process that enables us to obtain uniform thick films under ambient pressure and temperature in comparison with conventional physical vapor deposition using vacuum system and aerosol deposition using high-pressure carrier gas. This technique can be widely applied to produce coatings for substrates for use as electrodes of various shapes, and allows us to produce composite materials composed of ceramics, polymers, dyes and metals. EPD is an effective method to prepare nanostructured thick films, and has been widely used for the fabrication of functional coatings of charged colloidal materials such as nanoparticles, nanotubes and nanosheets. In this paper, micropatterning using poly(phenylsilsesquioxane) (PhSiO32) nanoparticles and fabrication of electrochemical cells using titanate and layered double hydroxide nanosheets by EPD are described.

In the micropattering, hydrophobic-hydrophilic (Hphob/Hphil) patterns were formed on the indium tin oxide (ITO)-coated glass substrates, and thick films of PhSiO32 particles, prepared by the sol-gel process, were selectively deposited onto the hydrophilic areas of the substrates by EPD (Fig. 1) [1]. The films composed of PhSiO32 particles became transparent with morphological changes from aggregates of particles to a continuous phase after a heat treatment. After the heat treatment at 200°C, convexly shaped PhSiO32 microlens arrays were formed on the hydrophilic region of the pattern. Moreover, the height, i.e. focal length, of microlens was controlled by the deposition time. This patterning technique has a wide variety of applications such as fabrication of micro- optical components.

In the fabrication of electrochemical cells, anionic hydrated titanate (H,TiO,m HTO) nanosheets, cationic Mg-Al layered double hydroxide (Mg-Al LDH) and Ni-Ti layered double hydroxide (Mg-Al LDH) nanosheets were electrophoretically deposited on ITO- or F-doped tin oxide (FTO)-coated glass substrates (Fig. 2) [2]. The HTO, Mg-Al LDH and Ni-Ti LDH nanosheets obtained were identified as H2Ti4O9, [Mg0.75Al0.25(OH)2] 0.25+ and [Ni0.8Ti0.2(OH)2]0.4+, respectively. Dense and smooth HTO, Mg-Al LDH and Ni-Ti LDH films with layered structures were prepared by EPD from the colloidal nanosheets. EPD HTO and LDH films showed elasticity because of their layered laminate structures. The HTO thick films demonstrated large adsorption properties and high photocatalytic activity with ultraviolet light irradiation. The Mg-Al LDH thick films showed relatively high ionic conductivity of 10−5 Scm−1 at 80°C and 80% relative humidity. In addition, Ni-Ti LDH thick films showed photovoltaic power with visible light irradiation. The EPD processes of these hydrated oxides and hydroxides with nanosheet structures are useful for the fabrication of thin film electrochemical devices.

References

Fig. 1. Micropatterning using PhSiO32 nanoparticles by EPD; (a) EPD on a Hphob/Hphil patterned ITO substrate, (b) after takeoff, and (c) heat treatment.

Fig. 2. Fabrication of electrochemical cells using titanate (HTO) and layered double hydroxide (LDH) nanosheets by EPD.
PIEZOELECTRIC ELEMENTS FOR MULTI-ELEMENT LINEAR-ARRAY TRANSDUCERS PREPARED BY ELECTROPHORETIC DEPOSITION

Danjela Kuscer, Jožef Stefan Institute, Slovenia
danjela.kuscer@ijs.si
Mara Bernardo, Jožef Stefan Institute, Slovenia
Andre-Pierre Abellard, François-Rabelais University, France & Jožef Stefan International Postgraduate School, Slovenia
Franck Levassort, François-Rabelais University, France
Silvo Drnovšek, Jožef Stefan Institute, Slovenia
Barbara Malič, Jožef Stefan Institute, Slovenia

Keywords: lead zirconate titanate, piezoelectrics, thick films, electrophoretic deposition, transducers

We have investigated the processing of piezoelectric elements for high-frequency linear-array transducers. Such devices consist of a set of rectangular elements juxtaposed and aligned along an axis that can each be independently driven. The elements were processed by electrophoretic deposition process (EPD) followed by sintering.

Niobium-doped lead zirconate titanate powder (Pb(Zr_{0.53}Ti_{0.47})_{0.98}Nb_{0.02}O_3, PZT-Nb), prepared by solid state synthesis at 1100°C, was stabilised in ethanol by the addition of a polyelectrolyte. The zeta-potential of the particles of about -50 mV and the electrical conductivity of the dispersion of about 20 µS/cm were appropriate for depositing the particles on an alumina substrate with patterned gold electrode at a constant current density. The deposits were sintered in a temperature range between 850 and 950°C in a PbO-controlled atmosphere.

Structure with six aligned piezoelectric elements with the width of about 1 mm and the edge-to-edge distance of about 0.5 mm were fabricated and tested. The influence of the geometry of the counter electrode, the distance between the electrodes, the deposition time and the sintering temperature on the morphology and geometry of the as-deposited and sintered films were studied. The thickness and the density of the sintered films were measured. By optimising the deposition parameters and the sintering process, uniform elements with П-shaped geometry, a thickness of about 20 μm and a density of about 85% of the theoretical density were obtained. The elements had a dielectric constant at a constant strain of 370 and a longitudinal velocity of about 2800 m/s. These values were slightly lower than that of a bulk ceramic with identical composition but the electromechanical performance (thickness coupling factor) was sufficiently high for the application. The resonance frequency of around 70 MHz (in free mechanical conditions for the thickness mode) of the elements indicated that they can be used for fabricating the linear-array high-frequency transducers for medical applications.
NICKEL OXIDE/ NICKEL COMPOSITE AS SUPERCAPACITOR ELECTRODE VIA ELECTROPHORETIC DEPOSITION

Zoilo González, Instituto de Cerámica y Vidrio (CSIC), Campus de Cantoblanco, Spain
zgonzalez@icv.csic.es
Begoña Ferrari, Instituto de Cerámica y Vidrio (CSIC), Spain
Antonio Javier Sánchez, Instituto de Cerámica y Vidrio (CSIC), Campus de Cantoblanco, Spain
Álvaro Caballero, Inorganic Chemistry Department. University of Córdoba, Spain
Julian Morales. Inorganic Chemistry Department. University of Córdoba, Spain
Lourdes Hernan, Inorganic Chemistry Department. University of Córdoba, Spain

Key Words: Electrophoretic Deposition, Nickel Oxide, Electrochemical Capacitors, Nickel Foam

Nanostructured materials are leading to the development of new energy storage technologies. Due to the high power demand of electronic devices, electrochemical capacitors that deliver high power density, long cycling life and fast recharge ability, are being studied.

Nickel oxide has received great attention due to its high theoretical specific capacitance of 2573 F/g, multiple reversible electrochemical reactions, high surface-to-volume ratio, ready availability and cost effectiveness. On the other hand, the use of the foam structures as electrodes support demonstrates a clear improvement in electrochemical properties. Nanoparticles incorporation on the 3D network allows obtaining of excellent porous platforms that enhance the connectivity between particles.

EPD method is a good via for the practical application of foam-like as supercapacitor electrodes providing numerous advantages: non-vacuum method, room-temperature processing, short processing time, low cost, scalable, additive free and suitability for mass production. In addition, thickness of the films can be easily controlled by the concentration of the suspension, applied potential, and deposition time.

In this work, a NiO/nickel foam composite as supercapacitors electrode has been processed by a simple, green and cost-effective electrophoretic deposition method directly from the post-reaction medium in a one-pot synthesis and its later heat treatment.

FESEM Images of NiO/NiFoam Composite
NICKEL-COBALT DOUBLE HYDROXIDE AND OXIDE DECORATED CARBON NANOTUBES VIA AQUEOUS ELECTROPHORETIC DEPOSITION TOWARDS CATALYTIC APPLICATIONS

Anirudh Balram, The University of Texas at Arlington, USA
Moisés Hernández Fernández, Universidad de León, León, Spain
Dennis Desheng Meng, The University of Texas at Arlington, USA

Key Words: Double hydroxide, MEC, catalyst, superhydrophilic, EPD

In this work, we present a co-deposition of transition metal double hydroxide decorated carbon nanotubes (CNT) using facile aqueous electrophoretic deposition (EPD). We specifically explore the performance of nickel-cobalt hydroxides given their higher activity, conductivity and stability as compared to the individual hydroxides. Metal salts have been typically used in EPD as charging agents to primarily improve electrophoretic motility of suspended nanomaterials. We focus our work here on obtaining functional and conductive deposits upon electrochemical reduction of these charging ions on CNTs. We concentrate on the performance of these deposits in catalytic applications such as glucose detection and hydrogen evolution reaction in microbial electrolysis cells. Upon contact with the electrode during EPD process, the charge-providing ions typically reduce into metals or their corresponding hydroxides depending on the conditions at the electrode interface. The high localized pH at the electrodes during water-based EPD gives rise to conditions that promote hydroxide formation. These deposits can be further annealed at 300°C to convert hydroxides into corresponding oxides. Electrophoretic co-deposition of this nature to yield double hydroxides on CNTs has not been studied. We find that the crystal structure of the co-deposited alloy is highly dependent upon the order in which the charging salts are introduced to the CNT suspension. X-ray diffraction data indicates that the initially adsorbed metal ion tends to dominate the crystal structure of the co-deposited hydroxide. We use this phenomenon to produce a wide range of nickel-cobalt hydroxides and oxides. With increasing interest in double transition metal hydroxides due to their superior properties, we believe our work will contribute to the understanding and formation of functional double hydroxide deposits using EPD. Additionally, owing to the surface energy and porosity, these deposits exhibit superhydrophilicity. This should facilitate removal of gas bubbles, allow for effective access to electrolyte, and help to improve performance even with thicker deposits.
NANOMANUFACTURED HYBRID CARBON NANOMATERIALS FOR IMPROVED ENERGY STORAGE DEVICES USING ELECTROPHORETIC ASSEMBLY

Landon Oakes, Vanderbilt University, USA
Adam P. Cohn, Vanderbilt University, USA
Rachel Carter, Vanderbilt University, USA
Andrew Westover, Vanderbilt University, USA
Cary L. Pint, Vanderbilt University, USA

We demonstrate electrophoretic assembly as a powerful nanomanufacturing tool for the development of pristine, freestanding materials composed of carbon nanostructures that can support the development of next-generation energy storage systems. In particular, the ability to electrophoretically assemble pristine carbon nanostructures from polar solvents without the use of surfactants enables the formation of materials with electrical and electrochemical properties not compromised by excess surfactant that can inhibit performance in device applications. Furthermore, the ability to perform electrophoretic assembly uniformly into three-dimensional sacrificial metal foam templates enables us the capability to develop flexible, freestanding all-carbon hybrid materials with controllable nanostructured morphology. Employing this approach with both single-walled carbon nanotubes and graphene, we develop 3-D freestanding all-carbon energy storage electrodes exhibiting superior performance across a broad range of platforms including supercapacitors, lithium-ion batteries, and lithium-air batteries. In particular, we emphasize materials with up to 340 F/g specific capacitance in electrochemical supercapacitors, and over 2600 mAh/g specific capacity in lithium-ion battery anodes. We demonstrate such extraordinary performance as a result of the clean assembly approach and the controllable nanoscale morphology that is achievable in electrophoretic deposition. Our work builds the intersection between the emerging area of nanomanufacturing and liquid electrophoretic assembly routes that could play a pivotal role in the development of advanced materials across fields of energy storage and conversion, sensing, catalysis, and other areas.
ELECTROPHORETIC DEPOSITION OF APATITE TYPE LANTHANUM SILICATES FOR SOFC HALF-CELL PRODUCTION

Omer Van der Biest, Dept. MTM K U Leuven, Belgium
Omer.vanderbiest@mtm.kuleuven.be
Ezhil Jothinathan, Dept. MTM K U Leuven, Belgium
ezhil.jothinathan@gmail.com
Jef Vleugels, Dept. MTM K U Leuven, Belgium

Key Words: Electrophoretic deposition, Apatite, Solid oxide fuel cell, SOFC, Sol–gel processing.

Apatite type lanthanum silicates (ATLS) are a new class of electrolyte materials exhibiting good oxygen ion conductivity in the intermediate temperature range (600-800°C). In this range their ionic conductivity is higher than that of yttria stabilized zirconia (YSZ). This makes them suitable candidates for electrolytes for intermediate temperature solid oxide fuel cells (SOFC). The flexibility of the apatite structure allows a wide range of doping possibilities both on the rare earth and silicon site. Therefore most research has focused on increasing the ionic conductivity (by doping) and on understanding the conduction mechanism.

The use of EPD for half-cell fabrication with yttria-stabilized zirconia as electrolyte has been demonstrated. However, there are no reports on the EPD of lanthanum silicates. This contribution reports on the EPD of an apatite type lanthanum silicate with aluminum doping on the silicon site (LASO-La$_{9.83}$Si$_{4.5}$Al$_{1.5}$O$_{26}$) prepared by a modified sol-gel procedure. We have chosen aluminum doped ATLS as this electrolyte is reported to have higher oxygen ion conductivity and transport number. The EPD related characteristics such as the iso-electric point, zeta potential and stability of the LASO powder suspension were determined. A range of organic solvents with different charging agents were studied and the most reliable solvent-charging agent combination to realize homogeneous crack-free deposits on a conductive polymer substrate was determined.

Although ATLS is established as a good electrolyte, the development of suitable compatible electrode materials remains a challenge. In this study, we selected a simple and most frequently used NiO–ATLS mixture as the anode substrate. This substrate consisted of a coarse powder mixture which was pre-sintered at a low temperature so that it remained porous as required. In this stage of processing the substrate was also not electrically conductive. For the preparation of half cells, it needs to be covered by a thin electrolyte layer. For the EPD cell a modified electrode was designed and built which enabled the deposition of a thin and uniform electrolyte layer on the non-conductive porous substrate. The combined use of optimized suspension along with the modified electrode configuration enabled successful production of green half –cells as shown in Figure 1.

Figure 1 – Scanning electron micrograph of a cross-sectioned as-deposited half cell with the LASO electrolyte layer on the right and the porous LASO-NiO anode substrate on the left
ELECTROPHORETIC METHOD FOR FABRICATING POROUS CERAMICS – APPLICATION TO DIFFERENT OXIDE MATERIALS

Kirsten Moritz, Technische Universität Bergakademie Freiberg, Germany
Christos G. Aneziris, Technische Universität Bergakademie Freiberg, Germany

Electrophoretic deposition (EPD) with controlled gas evolution by electrolysis is a suitable method for producing ceramic green bodies with unidirectionally aligned pore channels. Aqueous suspensions containing appropriate amounts of electrolyte are used for this purpose. The method was successfully applied to yttria-stabilized zirconia in previous experimental studies. In the present work, its application to further oxide materials - including alumina, alumina-toughened zirconia, mullite, and hydroxyapatite - has been investigated. Whether the desired pore structure can be obtained or not depends on several factors. First of all, an adequate electrophoretic mobility and suspension stability are required. Secondly, the electrolyte content has to be optimized in order to provide the right intensity of gas bubble formation. Furthermore, the porous structure is influenced by the EPD parameters.

A suitable suspension composition had to be found for each of the powders differing in the chemical properties of the particle surfaces, in the inherent pH value, and in the initial conductivity of the slurry without additives. Electrokinetic and rheological measurements were used for choosing kind and amount of deflocculant. The influence of the electrolyte content and the applied voltage on the pore structure was investigated in EPD experiments.

A commercially available carboxylic acid formulation in combination with ammonia was found to be suitable for forming green bodies with channel-like pores. The required amounts depended on the kind of powder. The pore size could be varied by the ammonia content. Lower voltages led to more homogeneous porous structures than higher ones because of the lower velocities of deposition and gas generation. When the applied voltage was too high, many fine pore channels were formed at the bottom of the deposit, but only few large pores reached the surface. By contrast, small tubular pores reaching over the whole sample thickness (typically a few millimeters) were obtained at low voltages.
This talk is about the electrophoretic deposition of Sr₄Nd₂Ti₄Nb₆O₃₀ tungsten bronze thick films for temperature stable dielectric applications.

Tungsten bronze oxides are the largest dielectric family just after perovskites, and their interesting dielectric, ferroelectric properties have attracted systematic research activity towards gathering understanding on the structural and physical properties. The tetragonal tungsten bronze structure consists of layers of distorted BO₆octahedra sharing corners in such a way that three different types of interstices (pentagonal A1, square A2 and trigonal C) are available for cation occupancy (A1)₄(A2)₂(C)₄(B1)₂(B2)₈O₃₀. Research has been devoted to the characterization of single crystals and ceramics. So far, no research has been carried out on the tungsten bronze thick films. However, the layered and anisotropic structure of tungsten bronzes and our previously knowledge on the role of constrained sintering on development of anisotropic microstructure, allows us to expect behavioral differences between ceramics and thick films. Therefore, preparation and characterization of tungsten bronze thick films is important both for applications and for physical understanding of the relaxor and ferroelectric behavior of this family of materials.

In the present work 10 μm-thick Sr₄Nd₂Ti₄Nb₆O₃₀ films were fabricated by electrophoretic deposition on Pt foils under different processing conditions. Contrary to the microstructure of bulk ceramics anisotropy of the grain growth is detected (as shown in figure 1). The observed anisotropic grain growth is facilitated by the constrained sintering of Sr₄Nd₂Ti₄Nb₆O₃₀ films on the Pt foils. The increase of the sintering temperature affects markedly the microstructure of the thick films and, subsequently affects the dielectric properties. The value of the dielectric constant measured in the out of plane direction decreases from ~300 to ~150 with increasing sintering temperature from 1200°C to 1400°C, while the low temperature dielectric relaxation increases (see figure 2). The relationship between the microstructure and the dielectric properties is discussed. With increasing sintering temperature, the grains grow along the c axis, and the orientation increases with sintering temperature. The decreasing dielectric constant confirms the main contribution of the c axis vibration to the dielectric constant in tungsten bronze Sr₄Nd₂Ti₄Nb₆O₃₀ and also the relation between the low temperature relaxation with polarization on ab plane.

![Figure 1](image1.png)  
**Figure 1:** Top view SEM images of Sr₄Nd₂Ti₄Nb₆O₃₀ thick films sintered at different temperatures: (a) 1250°C; (b) 1300°C; (c) 1350°C; (d) 1400°C. As the temperature increases the elongation of the grains increases, being maximized for the films sintered at 1400°C.

![Figure 2](image2.png)  
**Figure 2:** Dielectric constant of Sr₄Nd₂Ti₄Nb₆O₃₀ bulk ceramics and thick films sintered at different temperatures.
Fabrication and characterization of 3-D photonic crystals of various microspheres by electrophoretic self-assembly

Rong-Fuh Louh, Feng Chia University, Taiwan
rflouh@fcu.edu.tw
Yi-Jui Huang, Feng Chia University, Taiwan
Ya-Chih Tsai, Feng Chia University, Taiwan
Danny Ho, Feng Chia University, Taiwan
Doris Liao, Feng Chia University, Taiwan

Fabrication of high sphericity, monodispersed microspheres (100~600 nm) of various oxides (SiO₂, TiO₂, ZnO, In₂O₃, SnO₂) via sol-gel process and polystyrene (PS) microspheres (200~300 nm) via emulsion polymerization is presented. A high colloidal stability suspension was obtained by carefully adjusting the zeta potential of such microspheres and pH of the colloid. The 3-D photonic crystal (PhC) templates of opaline structure on indium-tin oxide (ITO) glasses and silicon wafers were easily formed under electrophoretic self-assembly (EPSA) behavior of microspheres under the influence of exerting electrical forces in EPD tank, where different setups of counter-electrode were attempted to establish a non-uniform electrical field. The lattice constant of an ordered opal structure by EPSA can also be tuned by the applied electrical field gradient. Interestingly various self-assembled 3-D structures of silica microspheres in either symmetrical curvilinear profile or triangular ridges can be produced through the proposed EPSA route using specific counter-electrode setups. The measured optic properties of such 3-D PhC templates manifest photonic bandgap (PBG) based on our planar-wave expansion (PWE) simulation to verify the existence of real PBG in our tunable nanostructures PhC samples. To acquire pronounced PBG effect for photonic applications in developing LEDs or solar cells of high conversion efficiency, most of PS microsphere templates are currently used due to its material flexibility to avoid introduction of structural defects or voids during the drying and to easily transform into inverse opal structure (IOS) by infiltrating sol of other oxides with high dielectric constant (e.g. ZnO or TiO₂) and filled with metallic nanoparticles (Ni or Cu) by electrochemical deposition and chemical bath deposition (CBD).

Key words: photonic crystals, electrophoretic self-assembly, opal structure, inverse opal structure, microspheres, colloidal crystals, SiO₂, TiO₂, ZnO, In₂O₃, SnO₂, polystyrene, plane wave expansion simulation, photonic bandgap.
MULTILAYERED CERAMIC CONSTRUCTS CREATED BY EPD

Carolina Mochales, Dental School, “Charité” Universitaetsmedizin Berlin, Germany
carolina.mochales-palau@charite.de
Stefan Frank, Dental School, “Charité” Universitaetsmedizin Berlin, Germany
Rolf Zehbe, Materials Engineering, Berlin Institute of Technology, Germany
Claudia Fleck, Materials Engineering, Berlin Institute of Technology, Germany
Wolf-Dieter Müller, Dental School, “Charité” Universitaetsmedizin Berlin, Germany

Key Words: Ceramics, multilayers, dental crowns, electrophoretic deposition.

Ceramic materials are known for their high compressive strength which is usually accompanied by brittleness. In this regard, ceramic layered structures are a route to combine crack bifurcation and interface delamination mechanisms in architecture with improved failure resistance. The interest in electrophoretic deposition (EPD) for ceramics production has widely increased due to the versatility of this technique to effectively combine different materials in unique shapes and structures. We therefore established the layered deposition of alternating ceramic materials via EPD with the underlying goal to produce ceramic constructs with improved mechanical response; and studied the properties and mechanical response of their interface. Moreover, EPD has been pointed out as an effective technique to obtain complicated 3D shape structures. In this sense, EPD appears to be a potential technique to be used in the production of 3D shaped ceramic constructs with interest for the medical field, e.g. ceramic dental crowns and bridges. In our research group, we have developed an EPD set-up to obtain ceramic dental crowns and we are currently investigating different technical variations, as well as the use of different ceramics and structures (i.e. layers and, or pores) to increase the final reliability of the ceramic construct.

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INFLUENCE OF FORMULATION ADDITIVES ON THE ELECTROPHORETIC MOBILITY AND CORROSION RESISTANCE ENAMEL VITREOUS COATING OBTAINED BY ELECTROPHORETIC DEPOSITION

Josemari Muñoz, Fundación CIDETEC, Spain
jmunoz@cidetec.es
José Antonio Diez, Fundación CIDETEC, Spain
David Vélez, Fundación CIDETEC, Spain
Mónica del Rincón, Fundación CIDETEC, Spain

Key Words: Electrophoretic deposition (EPD), enamel vitreous coating, high corrosion resistance, characterization, electrophoretic mobility.

Electrophoretic deposition (EPD) of ceramic vitreous enamels is one of the most advantageous methods to protect different metal surfaces and geometries from corrosion, considering that it allows obtaining very smooth surfaces with precise control of their thickness, porosity, chemical and mechanical properties. The selection and stabilization of ceramic compounds, through the correct choice of formulation additives, is the first requirement before the EPD process is carried out to guarantee an optimal result. The basic phenomena involved EPD can be explained in two-step process. In the first step, charged particles stabilized in an organic/aqueous medium move under the effect of an electric field, and finally the deposition of those particles on the oppositely charged electrode takes place.

In this study, a non-commercial ceramic compound with high corrosion resistance based on SiO₂, Al₂O₃, CaO, TiO₂… was developed and stabilized with polymeric and ceramic additive agents in an aqueous solvent previous deposition process over carbon steel metal substrate. The influence of the constitution of formulation additives on the electrophoretic mobility of ceramic particles was evaluated measuring the thickness of the coating obtained, keeping others parameters constant. On the other hand, the effect of EPD process parameters such as deposition voltage, deposition time, pH and suspension composition were also investigated. Finally, EPD parameters, electrophoretic mobility and thermal treatment were optimized in order to obtain a ceramic coating with high quality and resistant to different corrosion systems applied to a wide range of technical applications.

The corrosion resistance of these coatings was evaluated using selected chemical methods and electrochemical impedance spectroscopy. Microstructure characterization was performed using scanning electron microscopy (SEM) and X-ray diffraction analysis (XRD). Specific mechanical features of the coatings were measured by pin-on-disk and micro-hardness techniques and surface properties using confocal microscopy.
Electrophoretic deposition (EPD) has been applied for depositing phosphors for a “remote phosphor” configuration in a near UV-LED-based light source for improved white light extraction efficiency. It was demonstrated that EPD could be used to deposit red, green, blue, yellow and orange phosphors to generate white light using a near UV-emitting LED by either depositing a phosphor blend or layer-by-layer in a sequential method [1]. Individual and phosphor blend coatings were prepared by EPD of red, green, blue, yellow and orange emitting phosphors. The phosphor coverage was excellent, demonstrating that EPD is a viable method to produce phosphor layers for the “remote phosphor” white light design. The deposition rates of the individual phosphor films were \( \approx 1-5 \ \mu \text{m/min} \). The blend depositions composed of both three and four phosphor compositions emit white light located on or near the black body locus on the CIE chromaticity diagram. Phosphor films were also prepared by sequential deposition of red/orange and green/blue compositions, to generate white light. When the layered films were flipped over and illuminated in this orientation, they showed approximately the same luminescence characteristics. No change in the reabsorption ratio of green/blue emission by the red/orange phosphor was found regardless of the deposited order of the layered films. These applications of EPD of phosphor for white solid state lighting are promising and effective due to easy tuning of emissive color by varying the phosphor blend compositions.

Reference

ELECTROPHORETIC DEPOSITION OF PHOSPHOR MATERIAL FOR WHITE LIGHT CONVERSION IN LEDS

Ion Stoll, OSRAM Opto Semiconductors GmbH, Germany
Ion.Stoll@osram-os.com
Kirstin Petersen, OSRAM Opto Semiconductors GmbH, Germany
Martin Mandl, OSRAM Opto Semiconductors GmbH, Germany
Tilman Schimpke, OSRAM Opto Semiconductors GmbH, Germany
Martin Strassburg, OSRAM Opto Semiconductors GmbH, Germany
Barbara Huckenbeck, OSRAM GmbH, Germany
Daniel Bichler, OSRAM GmbH, Germany
Franz Zwaschka, OSRAM GmbH, Germany
Xue Wang, Institut für Halbleitertechnik, Germany
Johannes Ledig, Institut für Halbleitertechnik, Germany
Frederik Steib, Institut für Halbleitertechnik, Germany
Andreas Waag, Institut für Halbleitertechnik, Germany

Solid state lighting based phosphor converted LEDs evolved as the driving force in the general illumination market. It has become one of the most important lighting technologies in the recent years. Essential for white light conversion is to place phosphor material in the ray of light of a blue light emitting semiconductor chip. Several process technologies are employed to place phosphor in an LED and an important one is electrophoretic deposition of phosphor material. Aim is to give a survey of material and process requirements for white light conversion and electrophoretic phosphor deposition in particular. The challenges and advantages of the phosphor deposition in regard to device de-heating and ageing, different chip technologies, and application requirements will be reviewed.

Fig. 1: Phosphor particles deposited onto a 3D-microrod chip structure

Recently, 3D-chip nano- and microrods structures have been proposed as a possible route to overcome some of the limitations solid state lighting currently is facing. Since the active layer is wrapped around the entire structure it scales with the rod’s aspect ratio. Therefore, a tremendous increase of active region can be achieved by controlling the density, diameter and height of the rods. For these structures completely new requirements to the phosphor material and the method of conversion are arising. Conventional methods to apply phosphor converter encounter problems to fill the areas between the light emitting rods. The placement of the phosphor close to the facets of the rods is highly beneficial to the white LED device performance since it supports the light coupling between semiconductor and phosphor material, increases the scattering of light in forward direction and improves the de-heating of the phosphor. It will be presented that EPD is a feasible method to implement novel phosphor material into 3D GaN structures.
ULTRA-LOW-POWER ELECTROPHORETIC DEPOSITION OF SILICA POWDER USING NONFLAMMABLE ORGANIC SOLVENT

Hideyuki Negishi
National Institute of Advanced Industrial Science and Technology (AIST), Japan
h-negishi@aist.go.jp

Key Words: Hydrofluoroether, Nonflammable, Low Power Consumption, Specific Gravity, Silica Powder

Although conventional organic solvents are used in electrophoretic deposition (EPD) owing to several advantages, such as high electrical resistance, no bubble formation, and feasibility of high-voltage application, they are hazardous because of their inflammability or ignition properties. In contrast, hydrofluoroether (HFE) is nonflammable, and possesses excellent electrical insulation properties. It is also a polar solvent. In this study, HFE was used as the solvent to prepare a suspension for the EPD of silica powder, which was selected as the deposition material. Because the specific gravity of HFE is higher than that of conventional solvents, which include aqueous solutions and organic solvents such as acetone and/or alcohol, sedimentation of inorganic particles is slow in the former solvent. The deposition behavior in HFE was similar to the EPD in conventional solvents, and was controlled by tuning the applied voltage, deposition time, and particle concentration. A uniform coating was obtained. Notably, the power consumed to deposit the same amount of particles in this process was significantly lower than that in the EPD using conventional solvents. The current density observed in this process was in the order of 10 nA/cm²; therefore, the electric power consumption for EPD using HFE was less than 0.1% of those using conventional solvents. In addition, the quantity of electric charge required to deposit each particle was estimated. Therefore, HFE can be used as an effective solvent for EPD because it is nonflammable, allows the application of high voltage, and enables the deposition of particles with low power consumption.
Keywords: Alternating Current Electrophoretic deposition (AC-EPD); Biomolecules; Proteins; Albumin; Coatings

Abstract. Prevention of biofouling is one of the biggest challenges spanning several branches of the biosciences, including the food processing and biomaterials research. Hence in all these fields there is a large interest in new techniques which allow application of antifungal and/or antibacterial coatings on sensitive surfaces. This included both permanently active coatings as releasing systems. Furthermore the spectrum of active antibacterial and antifungal materials used in such coatings is being expanded continuously. Amongst others, naturally occurring and synthetic peptides are being investigated because of their reported strong antibacterial activity.

In the past 5 years the use of electrophoretic deposition by means of unbalanced AC-fields has been demonstrated for both the deposition of inorganic material and living matter in the form of yeast, bacterial cells. In this work we investigate this technique can be used for generating coatings of biomolecules permanently attached onto titanium alloy substrates. Proof of concept that biomolecules can be deposited in an adhering coating is achieved using Bovine Serum Albumin (BSA) as cheap model molecule. Subsequently the deposition of a peptide, selected for its activity against bacterial attachment, is explored.
Implant failure remains a serious complication for both orthopedic and dental implants leading to painful and costly revision surgery. Two major causes of implant revision are loosening and infection. Therefore, today’s implantology research is focusing on strategies to both improve implant fixation and reduce the incidence of infections. A key requirement for a long-term implant fixation is osseo-integration, i.e. a direct implant/bone contact maintaining a rigid fixation of the implant during functional loading. Hereby, porous coatings are of special interest, because of the possibility to establish a firm interlocking with the surrounding tissue by ingrowth of bone into the porous structure. However, porous coatings typically present an increased surface roughness and the concomitant large surface area renders the implant extremely susceptible to bacterial colonization and subsequent biofilm formation.

Recently, we reported on a new powder metallurgical processing route for the application of porous Ti coatings on Ti alloy substrates by electrophoretic deposition (EPD) of TiH2 powder suspensions followed by dehydrogenation and sintering in vacuum. Different grain sizes of TiH2 starting powders (~ 10 µm for grade VM and ~ 40 µm for grade P, Chemetall GmbH) were used to engineer porous titanium coatings with varying surface roughness ($S_a = 1.6$ to $4.9$ µm) and pore morphology (open porosities ranging from 35 - 51% and an average interconnective pore channel (IPC) size of 2 to 9 µm). Using the same powder grades, additional spherical pores could be introduced into the coatings by EPD of a combination of a TiH2 (grade Vm) stabilized emulsion, of which the droplet size acts as a template for the final pores in the sintered coating, in combination with a grade Vm or P TiH2 powder based suspension which is used to engineer the interpore struts. The use of TiH2 powders resulted in a higher sinterability as compared to pure Ti powders allowing reducing the sintering temperature below the β-transus ($975 \pm 15^\circ$C) of the Ti-6Al-4V substrates. Additionally, EPD was shown a valuable tool in controlling the coating thickness within the range of 80 – 200 µm, which allowed upscaling of the coating process to complex shaped dental implants.

To functionally validate these coatings for potential clinical applications, a biological screening in comparison to several clinically relevant reference surfaces was performed, addressing in vitro bacterial attachment, in vitro cytocompatibility and in vivo bone response.

Multiple linear regression analysis indicated that surface roughness and hydrophobicity were the main determinants for the in vitro staphylococcal adherence on the experimental EPD Ti coatings. Accordingly, the novel coatings displayed a significant reduction of up to five times less bacterial colonization when compared to a commercial vacuum plasma sprayed (VPS) Ti coating.

In vitro biocompatibility testing did not show any cytotoxic effects for the experimental EPD Ti coatings. Additionally, a study with loco specific cell types relevant for bone formation revealed that adhesion and cell spreading was substantially better for EPD Ti coatings than for VPS Ti. Moreover, when compared to both Ti-6Al-4V and VPS Ti, the EPD Ti coatings showed an advanced expression of osteoblast markers, indicating an improved cell differentiation into osteoblasts.

In order to assess the feasibility of bone ingrowth into these predominantly microporous Ti coatings, the early peri-implant bone response was evaluated in an in vivo rabbit model. After 4 weeks, bone with osteocytes encased in the mineralized matrix was found throughout the porous Ti coating up to the coating/substrate interface, highlighting that osseointegration of microporosities (< 10 µm) was achievable, as opposed to the minimum pore size of 50-100 µm commonly claimed in literature. The bone trabeculae interwove with the pore struts, establishing a large contact area which might enable an improved load transfer and stronger implant/bone interface. Furthermore, there was a clear interconnection with the surrounding cortical bone, suggesting mechanical interlocking of the coating in the host bone on the long-term is possible. Overall, EPD Ti coatings thus present an advantageous surface when envisaging osseointegration in combination with a reduced risk on bacterial adherence.
ELECTROPHORETIC DEPOSITION OF HYDROXYAPATITE AND BIOACTIVE GLASSES COATINGS ON THE Ti6Al4V ALLOY SUBJECTED TO SURFACE MECHANICAL ATTENTION TREATMENT

J. Faure, Reims University, France
R. Drevet, Reims University, France
N. Ben Jaber, Reims University, France
S. Potiron, Reims University, France
C. Demangel, CRITT-MDTS, France
D. Retraint, Troyes University, France
H. Benhayoune, Reims University, France

Ti6Al4V alloy is used for the manufacturing of dental and orthopedic prostheses due to its well-established biocompatibility, corrosion resistance and mechanical behavior. Moreover, increasing the fatigue and wear resistance of Ti-6Al-4V through modification of its surface microstructure may be a solution to reduce the failure rate and to increase the lifetime of such medical devices. Surface mechanical attrition treatment (SMAT) is an innovative technique that enhances the mechanical properties of a material by transforming its original large grained surface into nanograins without alteration of the material composition [1]. SMAT is carried out in a cylinder chamber where steel balls will impact the surface of a sample, achieving large plastic deformation that will gradually refine the sample microstructure. Otherwise to improve the bioactivity and osteoconductivity of Ti6Al4V alloy a coating is generally made with hydroxyapatite (HAP) which is able to form a real bond with the surrounding bone tissue ‘in vivo’ [2]. However when the Ti6Al4V alloy is subjected to SMAT the classical techniques used to produce HAP coatings (plasma spray and electrodeposition [3]) are not suitable. These techniques not also allow producing Bioactive Glasses coatings. Therefore, we demonstrate that Electrophoretic Deposition (EPD) proved to be a solution to these problems. Indeed, we obtain homogeneous HAP and Bioactive Glasses coatings on a SMATed Ti6Al4V alloy by performing EPD from suspensions in ethanol. The Bioactive Glasses powders (58S and 45S5) were obtained by sol-gel method. From the characterization point of view, MEB observations clearly showed that all coatings are uniform and compact with a good link to the SMATed Ti6Al4V surface. XRD and EDXS revealed that coatings composition were not altered by EPD.

Chitosan (CS) is a versatile biopolymer whose morphological and chemico-physical properties can be designed for a variety of biomedical applications. Taking advantage of its electrolytic nature, cathodic polarization allows CS deposition on electrically conductive substrates, resulting in thin porous structures with tunable morphology. Here we propose an easy method to obtain CS thin scaffolds with highly oriented micro-channels for tissue engineering applications, relying on simple control of process parameters and cathodic substrate geometry. Cathodic deposition was performed on different aluminum grids in galvanostatic conditions at 6.25 mA cm\(^{-2}\) from CS solution [1g L\(^{-1}\)] in acetic acid (pH 3.5). Self-standing thin scaffolds were cross linked either with genipin or epichlorohydrin, weighted, and observed by optical and electron microscopy. Swelling properties at pH 5 and pH 7.4 have been also investigated and tensile tests performed on swollen samples at room temperature. Direct and indirect assays have been performed to evaluate the cytotoxicity at 24 and 72 hours. In vivo preliminary test have been performed to evaluated neoangiogenesis.

Thin scaffolds with two different level of porosity have been successful fabricated. The first level of porosity depends on cathode geometry and determines an oriented porosity; the other one depends on the H2 development at the cathode surface, determining a random porosity. Both cross-linking agents did not affect the mechanical properties and cytocompatibility of the resulting structures. Depending on the pH, these structures show interesting swelling properties that can be exploited for drug delivery systems. Moreover, thanks to the possibility of controlling the porosity and the micro-channel orientation, they should be used for the regeneration of tissues requiring a preferential cells orientation. The in vivo investigation, using mice model, showed no inflammatory reaction and revealed high tissue ingrowth in all constructs; in turns, neo-vascularization, evaluated by immunofluorescence and semi-quantitative analysis, resulted enhanced in presence of oriented porous scaffolds.
ELECTROPHORETIC DEPOSITION OF \textit{n}TiO$_2$-\textit{n}BG/ALGINATE COMPOSITE COATING FOR BONE REPLACEMENT APPLICATIONS

Luis Cordero-Arias, Institute of Biomaterials, University Erlangen-Nuremberg, Germany
luis.cordero@studium.uni-erlangen.de
Sandra Cabanas-Polo, Institute of Biomaterials, University Erlangen-Nuremberg, Germany
Sannakaisa Virtanen, Institute for Surface Science and Corrosion, University Erlangen-Nuremberg, Germany
Aldo R. Boccaccini, Institute of Biomaterials, University Erlangen-Nuremberg, Germany

Key Words: alginate, bioactive glass, titania, coating, bone replacement

Bioactive glasses (BG) are well known biocompatible materials with osteinductive properties that are being increasingly used in the orthopedic field to promote bone repair and regeneration [1]. Bioactive glasses improve the bone-implant contact promoting bone in-growth through the formation of a hydroxyapatite layer where osteogenic cells can attach and differentiate [2]. Moreover, bioactive glasses of silicate specific compositions, e.g. Bioglass®, show antibacterial, anti-inflammatory and angiogenic effects [3]. On the other hand, titania (TiO$_2$) is also a biocompatible ceramic material used to develop biomedical coatings. It has been reported that titania enhances the implant integration with host tissue when used in bone tissue replacement applications [4]. Titania also presents antibacterial properties, what increases its possible benefits in the biomedical field. Titania coatings on metallic surfaces have been produced by different techniques, such as spray plasma technique, micro-arc oxidation (MAO), sol-gel or electrophoretic deposition (EPD). In the case of EPD, to avoid the sintering step a new approach is being investigated in the last years: the production of an organic/inorganic composite coating where the polymer assumes the function of a binder (glue) but also can be used as drug and biomolecule carrier [5]. In this work, biocompatible alginate (2g/l) was co-deposited with bioactive glass nanoparticles (1,5-3g/L, 30-50nm) and titania nanoparticles (1,5-3g/L, 21nm) from a water/ethanol suspension. The voltage used was in the range 5-7 V and deposition time was 1 min, as the optimal deposition parameters. Compared with previous work using micron-size particles, coatings produced from nanoparticles were more homogeneous with effective integration of titania and bioactive glass nanoparticles. Different characterization techniques were applied to characterize the coatings, namely: $\zeta$-potential measurement, bending strength test, FTIR, XRD, roughness determination, thermal analysis, SEM and potentiodynamic polarization curves. To test the bioactivity, samples were immersed in SBF according to Kokubo's protocol.

ELECTROPHORETIC DEPOSITION AS A BIOFABRICATION TECHNIQUE

Sigrid Seuss, University Erlangen-Nuremberg, Germany
Aldo R. Boccaccini, University Erlangen-Nuremberg, Germany

The use of biological entities in biotechnology and the biomedical field is of great interest as the biocompatibility and the functionality of naturally occurring materials is higher compared to other currently used biomaterials. As natural biomolecules, including proteins like collagen, as well as living cells and bacteria, are very sensitive to changes in environmental (processing) conditions as pH, temperature or the surrounding medium (e.g. solvents), the development of medical devices, bioactive coatings, functionalized implants, tissue scaffolds or biosensors by biofabrication technologies is challenging. In this context, electrophoretic deposition (EPD) is acquiring increasing attention and delivering outstanding results, thus becoming an attractive biofabrication tool. EPD is a low-temperature process, which gives the possibility to manipulate a wide range of biomolecules and biological entities [1]. The present contribution will highlight key applications of EPD as a biofabrication tool to manipulate numerous biomolecules, natural materials and biological entities, including proteins, polysaccharides, bacteria cells, hyaluronic acid, peptides and therapeutic drugs. It will be shown that EPD is a suitable method to deposit and fixate biological entities on a variety of devices and substrates. As the processing parameters can be easily adjusted, it is possible to preserve the activity of biological entities, which could be otherwise lost by conventional processing, e.g. at high temperatures. Significant interest is also placed on the use of aqueous suspensions to process biological entities. In most cases organic solvents must be replaced by aqueous suspensions as organic solvents are always problematic in relation to environmental aspects and due to the fact that they can denaturate proteins and destroy the functionality of cells. Parts of the studies also have been conducted using AC EPD instead of depositing under a direct current field. The use of aqueous suspensions in DC fields can lead to electrolysis of water resulting in bubble formation and in the functionality loss of the biological entity. It will be also shown that AC EPD gives the possibility to use higher electric fields and thus to effectively obtain biological deposits. The range of possible applications of EPD in biofabrication is wide, ranging from biosensors to orthopedic implants, tissue scaffolds and drug delivery devices. Specific examples will be presented and discussed highlighting possible research avenues for the broader application of EPD in biofabrication approaches.
Chitosan-graphene oxide (CS-GO) nanocomposite coatings were prepared on titanium foils by cathodic electrophoretic deposition (EPD) process. Different concentrations of GO nanosheets (0.05, 0.5 and 1 g L\(^{-1}\)) at a fixed chitosan concentration (0.5 g L\(^{-1}\)) were utilized for EPD. Composite coatings containing 30-55 wt.% GO were obtained. X-ray diffraction analysis of the films revealed that the GO nanosheets are well exfoliation in the chitosan matrix. Fourier-transformed IR spectrometry also confirmed polymer attachment to the carboxylic bonds of GO, providing a strong interaction and exfoliation of the nanosheets. Both atomic force microscopy and electron microscopic studies showed that co-deposition of CS-GO films increases the surface roughness of the composite films remarkably. In vitro cytotoxicity tests by human MG63 osteoblast-like cells demonstrated that the films containing 30 wt. % GO possess a high biocompatibility while at higher GO concentrations a slight cytotoxicity to osteoblast-like cells was observed.

**Figure 1** - (a) Concentration of GO nanosheets in CS-GO nanocomposite coatings as a function of GO content in the EPD suspension. (b) Cell viability of MG63 osteoblast-like cells incubated on the prepared films for 1, 5, and 10 days (* represents p<0.05 when compared with the negative control group and # when compared to CS coatings).
This paper presents a study on the possibility of separating nanoclays from aqueous synthetic slurry of two clays by EPD. Na-Montmorillonite (NM) from Southern Clay Products and kaolinite (K) from Source Clays Repository were used at 2:1 weight ratio at 3.5% solid loading for the synthetic slurry. Effect of applied potential (E), 2 and 4V, and electrode gaps, 1- and 2-centimeters, was investigated on the yield and on the NM/K ratio of the deposit. Stainless steel was used for working and counter electrodes. AUTOLAB potentiostat/galvanostat (Nova version 1.8) was utilized in EPD. Open circuit potential of the slurries was used as reference potential for EPD. Slurries were stirred at constant rate of 60 rpm during EPD for twenty minutes. Wet deposits on electrodes were scraped by nylon thread and were oven dried below 60°C for twenty four hours. Shimadzu XRD-7000 was used to determine NM/K ratio of the dried deposit. ANOVA of two-factor fixed effect Model was employed with F-test at 5% significance level.

NM slurries have negative bulk potential (163 -170 mV), contrary to kaolinite slurries. NM slurries had higher bulk conductivities (1.616 mS) and pH (~10.2) than kaolinite slurries. These distinct slurry properties could lead to their differential electrophoresis during EPD.

Effect of the interaction of applied potential and electrode gap for the yield and the NM/K ratio (Figure 1) was significant. High potential (4V) - low electrode (1cm) gap had the highest yield of deposit. NM/K ratios of the deposits were compared to the clay ratio of the synthetic slurry (Figure 2). High potential (4V) – high electrode gap (2cm) showed highest NM/K ratio at an average of 5.2 :1 from 2:1 (Figure 1b). This means Na-MMT has been successfully separated from kaolinite from aqueous synthetic clay slurry by EPD at specific potential – electrode gap combination.
In our mobile society, we heavily rely on portable energy sources leading to driving improvements in battery technology. Although lithium-ion batteries offer the highest energy density among present commercial rechargeable batteries, the technology is still evolving and improving. The improvements are particularly important for the wireless network systems and implantable devices, which need rechargeable microbatteries with dimensions on the scale of 1–10mm³, high energy-density storage and high power capability. 3D concentric on-Si-chip architecture developed by our group, enables the fabrication of 10,000-30,000 microbattery units connected in parallel that minimizes the ion-path length between the electrodes and provides high capacity per footprint area. This is achieved by the insertion of thin films of active battery materials in the high-aspect-ratio microchannels of the perforated chip. Special attention is paid to the membrane, since it must have high ionic conductivity (either by intrinsic ion-conducting pathways or by soaking in the electrolyte) and electrochemical compatibility with anode and cathode materials.

In this work, we report on recent achievements in the development of thin-film composite polymer-in-ceramic membranes (electrolytes) for applications in 3D-battery configurations by electrophoretic deposition (EPD) combined with mechanochemistry. We tested electrophoretic co-deposition of several types of composite ceramics and polymers. It was found that with increase in concentration of ceramic powder in the suspension, the deposition of polymer occurs predominantly between the agglomerates of ceramics. The ionic conductivity of the polymer-in-ceramic electrolytes plasticized by 0.3M LiTFSI-PYR14TFSI ionic liquid electrolyte is 0.2-1mS/cm. The membrane follows the complex 3D contours of the electrodes conformally and provides strong mechanical integrity of the microbattery. The experimental data of the study of the effect of magnetic field on the structure of PEO confined in ceramic pores will be presented.

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BIOACTIVE GLASS-BIOPOLYMER MULTILAYER COATINGS FABRICATED BY ELECTROPHORETIC DEPOSITION COMBINED WITH LAYER-BY-LAYER ASSEMBLY

Qiang Chen, University of Erlangen–Nuremberg, Germany
qiang.chen@ww.uni-erlangen.de
Aldo. R. Boccaccini, University of Erlangen–Nuremberg, Germany

Key Words: Electrophoretic deposition, Bioactive glass, Alginate, multilayer, Layer-by-Layer.

A variety of research efforts are being dedicated on the modification of orthopaedic implants with biological coatings containing bioceramics, biopolymers/biomolecules and their combinations, in order to enhance the biocompatibility and bone-to-implant contact as well as to reduce risks associated with infections [1].

Electrophoretic deposition (EPD) is a well-known coating technique which enables the consolidation of suspended solid particles and polymer molecules into deposits on bulk and complex shaped substrates with high microstructural homogeneity and controlled thickness [2]. Moreover, low-cost fabrication of nanocomposite coatings, laminates, functional gradient materials, as well as manipulation of biological entities through EPD have significantly enhanced the application potential of the technique in the biomaterials field [3,4]. A robust and homogeneous composite coating, containing 45S5 bioactive glass (BG), alginate and polyvinyl alcohol (PVA), were successfully co-deposited on stainless steel by a single step EPD process. Cationic chitosan and anionic alginate polyelectrolytes were alternatively deposited (Layer-by-Layer assembly) on the surface of BG-alginate-PVA bottom coating with the aim of retarding the excessive decomposition of BG in-vitro. In addition, biological entities, e.g. antibiotics, proteins and growth factors, can be incorporated along with the deposition of polymer layers for the bio-functionalization purpose. The preparation of suspensions and the parameters of coating techniques (EPD and Layer-by-Layer assembly) were optimized in order to form robust and homogeneous multilayer structures. The degradation and bioactivity properties of the multilayer coating were evaluated. The incorporation of antibacterial agents during the deposition as well as its release behavior in PBS will be investigated and discussed in the next step.

ELECTROPHORETIC DEPOSITION OF COMPOSITE BIOACTIVE COATINGS BASED ON CHITOSAN AND SOL-GEL DERIVED BIOACTIVE GLASSES

Luis Cordero-Arias, Institute of Biomaterials, University Erlangen-Nuremberg, Germany
luis.cordero@studium.uni-erlangen.de

Sannakaisa Virtanen, Institute for Surface Science and Corrosion, University Erlangen-Nuremberg, Germany

Saša Novak, Department for Nanostructured Materials, Jožef Stefan Institute, Slovenia

Aldo R. Boccaccini, Institute of Biomaterials, University Erlangen-Nuremberg, Germany

Key Words: Chitosan, bioactive glass, coating, bone replacement, implant

Metallic materials (e.g., stainless steel and titanium alloys) are the only real choice to produce robust implants for bone replacement applications. Issues related to the lack of surface bioactivity of these materials remain a significant problem which can lead to lack of suitable bone bonding and deficient integration of the device [1]. The body tends to encapsulate the implant with a fibrous tissue, inducing micro-movements of the implant, migration and possible loosening [1]. Bioactive glasses have emerged as attractive biomaterials that induce bone formation [2], with also antibacterial, anti-inflammatory and angiogenic effects. In this work two different sol-gel derived silicate based bioactive glasses (70S: 70wt.% SiO2+30wt%CaO and 66S: 66wt.% SiO2+20wt%CaO+10wt.%Na2O) were mixed with biocompatible chitosan to produce an organic/inorganic composite coating for bone replacement applications via EPD. Polymer/ceramic composites negate the need of a high temperature sintering process which could lead to a negative influence on the structure of the coating and on the quality of the interface, e.g. due to differential shrinkage and thermal expansion mismatch.

A suspension based on a solvent mixture of ethanol and water (in a 80:20 proportion) was used to reduce hydrogen evolution and to increase the deposit stability. Chitosan (0.5g/l) was chosen as the organic filler due its biocompatibility, exhibiting also antibacterial activity, film forming ability and drug delivery potential [3]. The content of bioactive glass studied was 1-2g/L. Optimal deposition conditions were 50-70V deposition potential and 1min deposition time, leading to homogeneous and crack free coatings. Results were compared with those of a previous investigation involving melt-derived bioactive glass [4]. Different characterization techniques were applied: ζ-potential measurement, bending strength test, FTIR, XRD, contact angle measurement, roughness determination, thermal analysis, SEM and potentiodynamic polarization curves. To test the bioactivity, samples were immersed in SBF according to Kokubo’s protocol and the results showed the formation of HA after 1 day of immersion proving the high bioactivity of the coatings.

Electrophoretic deposition (EPD) from colloidal suspensions was utilized for the preparation of composite magneto-dielectric films on a conductive substrate. The present process is developed as a convenient forming process for the development of devices based on thick magneto-dielectric films. The deposition parameters - using EPD - such as colloidal parameters, deposition voltage and deposition time and the post process parameters, such as drying velocity and sintering will be controlled.

This work aims to control the fillers/matrix ratio during the deposition and obtain a good adhesion, compaction and functionality of the composite film after the heat treatment. Measurements results for the current transients during constant-voltage deposition and the correlated deposited mass are presented.

Presenting author: Carmen Galassi carmen.galassi@istec.cnr.it


This study presents experimental results on the electrophoretic deposition (EPD) of chitosan/halloysite nanotubes/titanium dioxide composite coatings based on the Taguchi design of experiments (DOE) approach. The influence of (EPD) parameters including halloysite nanotubes concentration, electric voltage and deposition time on deposition yield was studied by an orthogonal Taguchi array of L18 type with mixed levels of the control factor. For identify significant factors that effect the deposition yield, Multivariate analysis of variance (MANOVA) and regression analysis based on partial least-square method were used. The coatings were characterized by scanning electron microscope (SEM). It was found that the applied voltage and deposition time have significantly influence on the deposition rate but the presence of halloysite nanotubes have the smallest effect on the deposition. It was found that the optimum condition for high yield of deposition with low standard deviation is achieved when the concentration of halloysite nanotubes is 0.4 g/L and the applied voltage is 30 volt with 5 min as a deposition time. The predicted conditions for optimal EPD were verified by experiments and good qualitative agreement was obtained.

References
The treatment of neurodegenerative diseases gains more and more importance in today’s medicine due to a longer life expectancy of human beings. One of these diseases is Morbus Parkinson which causes tremor in limbs and also the loss of fine motoric skills. Since, there is no cure known for Morbus Parkinson disease, the most important goal is to improve the quality of life for these patients. One method to achieve a better quality of life is the deep brain stimulation. In this application electrodes and a pulse generator are implanted into specific brain regions to stimulate these areas which surpresses the tremor [1]. The main problem that arises during deep brain stimulation is the formation of glia-scars that can occur around the implant. This leads to a reduced current flow inside the brain which causes a shorter lifetime of the pulse generator. Thus the system has to be replaced after a few years. A solution to the problem may be the nanostructuring of the implant surface. Since the aforementioned implants are 3-dimensional the electrophoretic deposition presents an ideal method for the structuring of the implant surface [2]. Experiments proved that the coating of the implant surface with nanoparticles has a positive effect on the current flow leaving the electrode. Also the contact angle at the surface changed because of the generated structure. The long term aim is to use the coated electrodes to improve the treatment of the Parkinson disease. Therefore, as a first step an in vivo study with rats will be performed in 2014. This study is one example that electrophoretic deposition can be a huge opportunity in medical application.

Surface modification of Ti alloys towards improved osteoinductive behaviour is one of the major challenges in orthopaedic implant technology nowadays. One way to achieve this is by applying a bioactive ceramics coating which can increase the rate of osseointegration and chemical bonding of surrounding bone to the implant. Calcium silicate (CaSiO₃, CS) ceramics are promising bioactive materials for bone tissue engineering. In the present work, we report a simple method for the synthesis of novel calcium silicate/reduced graphene oxide (CS/rGO) composites using a hydrothermal approach followed by coating on flat Ti alloys by electrophoretic deposition is demonstrated. The coatings are applied by cathodic deposition from non-aqueous suspensions followed by sintering in vacuum, avoiding uncontrolled oxidation of the Ti substrates. The CS/rGO coating was analyzed with field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), Fourier transform infrared (FTIR) and Raman spectra. Moreover, the effect of rGO concentrations on the crystallinity, morphology, adhesion strength, hardness, elastic modulus was evaluated. Additionally, a feasibility study demonstrated the potential of electrophoretic deposition as a coating technique for commercial dental implants. The formation of bone-like apatite on CS/rGO coating has been investigated in simulated body fluid (SBF). The presence of a bone-like apatite layer on the composite surface after soaking in SBF was demonstrated by X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM). The biocompatibility of the CS/rGO coating was characterized using methyl thiazole tetrazolium (MTT) assays in vitro. The cell adhesion results showed that human osteoblast cells (hFOB) can adhere to and develop on the CS/rGO composites. In addition, the proliferation rate and alkaline phosphatase (ALP) activity of cells on the CS/rGO coating was improved compared with the pure CS ceramic coating. These results suggest that calcium silicate/reduced graphene oxide coating are promising materials for titanium dental implants.
DISPERSION AND ELECTROPHORETIC DEPOSITION OF TIN AND TIC NANOPARTICLES

Carlos Mendoza, Consejo Superior de Investigaciones Científicas, Spain
cmendoza@cv.csic.es
Begoña Ferrari, Consejo Superior de Investigaciones Científicas, Spain
Yolanda Castro, Consejo Superior de Investigaciones Científicas, Spain

Key Words: TiN, TiC, Dispersion, Nanoparticles, Electrophoretic Deposition.

Titanium carbide (TiC) or titanium nitride (TiN) has been extensively studied due to its attractive properties such as high hardness, good electrical properties, thermal stability, etc. The fabrication of dense and well adhered thin coatings based on TiN/TiC for cutting technologies and barriers against corrosion, for instance to improve hardness and wear resistance in surgical tools and implants, is still challenging. Among the processes to obtain TiC or TiN coatings, such as physical or chemical vapor deposition methods or nitridation of TiO₂ can be highlighted. In those processes, it is necessary extremely high pressure and temperature conditions. Recently, chemical routes in liquid media especially sol-gel technology have been considered, where the addition of nanopowders to the sol should improve the mechanical properties of the coatings.

During the sol-gel processing of TiN or TiC, non-oxide materials, the alkoxides can be attacked by nucleophiles such as NH₂⁻. The replacement of alkoxy groups by non-oxygen nucleophiles during the synthesis allows obtaining non-oxide gels. In this sense, the stability/dispersion of TiC and TiN nano-powder suspension has to be adjusted to be compatible with the stability of the sol. In this work, the stability as well as the electrophoretic deposition has been evaluated in terms of zeta potential and particle size in isopropyl alcohol when NH₂⁻ is added. The surface of TiC and TiN nanoparticles (Figure 1) has been modified to improve the dispersion in isopropyl alcohol adding a cationic polymer (polyethylenimine) as dispersant. The structure of the coatings has been optimized varying the EPD conditions: current density and deposition time (Figure 2). The influence of NH₂⁻ over the suspension also has been evaluated to reach the most efficient EPD process.

Figure 1. TiN nanoparticles

Figure 2. EPD coating
ELECTROPHORESIS DEPOSITION OF ZnO NANOSTRUCTURES: Au NANO-CLUSTERS ON THE SUBSTRATES INDUCE NANOWIRE GROWTH

Silvina Real, Universidad Nacional de Tucumán, Argentina
sreal@herrera.unt.edu.ar
Claudia Sandoval, Universidad Nacional de Tucumán, Argentina
Oscar Marín, Universidad Nacional de Tucumán, Argentina
David Comedi, Universidad Nacional de Tucumán, Argentina
Mónica Tirado, Universidad Nacional de Tucumán, Argentina
mtirado@herrera.unt.edu.ar

Key Words: EPD, ZnO, nanowires, Au nano-clusters, photoluminescence.

The present work reports the growth of ZnO nanowires on silicon substrate with nanometer sized Au clusters using electrophoresis deposition technique at room temperature.

The ZnO nanostructures were grown from a low concentration of ZnO nanoparticles colloidal suspension in 2-propanol. The size of the nanoparticles obtained in the colloidal suspension was estimated from absorbance and photoluminescence measurements, which yielded an average diameter of 5 nm with a narrow size distribution, between 4 and 7 nm. The gap energy of synthetized nanoparticles was 3.47 eV. Chemical properties of the resultant colloidal suspension were measured: conductivity, pH, zeta potential, density and viscosity in order to calculate relevant parameters in EPD like electrophoresis mobility.

In order to find the best way to obtain homogeneous and reproducible deposits, a careful design of the cell was performed. This allowed the engineering of the directionality and intensity of the applied electric field, which is one of the main parameters determining the effectiveness of the EPD method in producing complex nanostructures with controlled thickness and morphology. The effects of the electric field intensity and distribution on the properties of the nanostructures obtained were studied and discussed. Also, the effect of other process parameters, such as deposition time and adding zinc nitrate to colloidal suspensions at two different concentration 5% and 20 %, were analyzed.

The substrates used were commercial Si wafer, and Si wafer covered with Au nano-clusters deposited by sputtering. To determine the quality of the ZnO nanostructures obtained by EPD, measurements of scanning electron microscope (SEM), energy-dispersive X-ray spectroscopy and photoluminescence were performed.

The results show that the deposition of Au nano-clusters on the silicon substrate induces a vertical alignment of the ZnO nanoparticles which allows the formation of nanowires without the use of templates (see Fig.1). This particular growth is probably due to increased electric field intensity near the Au nano-cluster.

The growth of semiconductors nanowires at room temperature is of a great industrial interest because it minimizes the production costs compared with conventional techniques and enables the growth on substrates that cannot withstand high temperatures, such as polymers.
DEPOSITION OF ALUMINUM-CARBON COMPOSITES ON ALUMINUM SUBSTRATES BY ELECTROPHORETIC DEPOSITION PROCESS: EFFECT OF PULSED ELECTRIC FIELD

Rodríguez Christian, Ingeniería Cerámica, Cinvestav Unidad Saltillo, México
rdz_christian@yahoo.com
Vargas Gregorio, Ingeniería Cerámica, Cinvestav Unidad Saltillo, México
Pech Wilian, Ingeniería Cerámica, Cinvestav Unidad Saltillo, México
Rodríguez Francisco Javier, Ingeniería Cerámica, Cinvestav Unidad Saltillo, México

The aqueous deposition of metal and oxide metal films by electrodeposition or by electrophoretic deposition process (EPD) is economically attractive, however coatings of oxygen sensitive particles and/or substrates are particularly difficult. An example of this case is the aluminum, where an oxide layer is easily formed on its surface. Recently, a novel class of liquids named deep eutectic solvents (DES) based on mixtures of choline chloride and hydrogen bond donors has been developed. These liquids are able to solubilize many different metal salts or metal oxides and show air and moisture stability offering economically viable liquids when aqueous medium is not suitable.

In this work, aluminum-carbon composites were deposited on aluminum substrates by EPD. The deposition was studied at different duty cycles and deposition time. The aluminum was electrochemically polished, then the EPD of Al-C composites were carried out by using functionalized carbon and DES, in order to improve the adhesion and conductivity of the films. The porosity, electrical resistance and corrosion of deposited layers were characterized by Electrochemical Impedance Spectroscopy in acid media and the morphology of the films was studied by Scanning Electron Microscopy. The results have shown that the low duty cycle and the pulsed current lead to more homogeneous and dense coatings.

Key Words: EPD, Al-C composites, Al substrates, pulsed dc, DES.

Bibliografía

AN ENVIRONMENTALLY FRIENDLY SOLUTION PROCESSING OF EARTH-ABUNDANT AND NON-TOXIC MATERIALS FOR PHOTOVOLTAICS

Stephen E. R. Tay, Department of Materials, Imperial College London
en.tay10@imperial.ac.uk
Xuemei Zhang, Department of Materials, Imperial College London
Fatemehsadat Pishbin, Department of Materials, Imperial College London
D. Jason Riley, Department of Materials, Imperial College London
Sandrine E. M. Heutz, Department of Materials, Imperial College London
Mary P. Ryan, Department of Materials, Imperial College London

Key Words: CZTS, kesterite, earth-abundant, non-toxic, photovoltaics

Renewable photovoltaic energy generation has received widespread research attention as an alternative to fossil fuel sources which are limited and environmentally damaging. Among the various photovoltaic materials, CZTS (Cu, Zn, Sn, and S) consists of earth-abundant and non-toxic elements. This is in contrast to rare indium in Cu(In,Ga)Se and toxic cadmium in CdTe photovoltaics. Since the first reported efficiency of 0.489% in 1997,\(^1\) CZTS technology has developed rapidly, reaching an efficiency of 12.6% at the end of 2013.\(^2\) Currently, vacuum and non-vacuum techniques exist for CZTS solar cell fabrication. Among these techniques, electrochemical and electrophoretic deposition provides a cost-effective deposition method for CZTS films.\(^3\) However, current techniques employ toxic sulfurization with H\(_2\)S. In this study, we propose three differing approaches for an environmentally friendly deposition of CZTS films without H\(_2\)S use. They are: 1) hybrid electrochemical and electrophoretic deposition; 2) electrophoretic deposition of metal sulfides; 3) electrophoretic deposition of CZTS nanoparticles. In each of these studies, deposition parameters such as deposition potential and additives were varied and their effects on film morphology and electrical properties investigated. To the knowledge of the authors, this study is the first to compare electrochemical and electrophoretic deposition for earth-abundant and non-toxic CZTS. We believe that this study will be of interest to the scientific community attending this conference, especially in the topics covered under the theme "Novel Applications". Furthermore, this study will aid in the understanding of electrophoretic deposition of multiple particle systems.

Figure 1 – Sulphur content in films deposited at -4 V (hybrid deposition) with increasing sulphur loading in the solution.

ALIGNMENT OF ZIRCONIA DURING ELECTROPHORETIC DEPOSITION IN A STRONG MAGNETIC FIELD

Despoina Vriami, KU Leuven, Belgium
Despoina.vriami@mtm.kuleuven.be
Jef Vleugels, KU Leuven, Belgium
Omer Van der Biest, KU Leuven, Belgium

Key Words: EPD, Zirconia, Magnetic alignment, Reactive sintering, Toughness

It has been shown in literature that the mechanical properties of ceramic materials can be tailored by crystallographic texturing i.e. by giving the ceramic grains a preferred orientation. One method to achieve ceramic texturing is during colloidal processing by aligning the suspended particles in a strong magnetic field and retaining this alignment in the green body. The alignment is possible for equiaxed particles with a pronounced anisotropy in the magnetic susceptibility. It is most effective at high fields and for the larger particles. As the microstructure coarsens during sintering the aligned large particles will gradually consume the smaller ones and thus the texture in the material is enhanced by this grain growth process. In the current work, electrophoretic deposition (EPD) of zirconia in a high field of 17.4 T was investigated. When EPD is performed in a strong magnetic field, the charged particles, before deposition, rotate to an orientation to minimize the system energy. Attempts to align tetragonal zirconia particles have not proven successful, not even in the highest fields. However, monoclinic zirconia was successfully textured with significant alignment in the green samples. Monoclinic zirconia was aligned with its (100) plane perpendicular to the magnetic field direction.

Textured tetragonal zirconia was developed by reactive sintering of undoped pure monoclinic zirconia and co-precipitated 8 mol% yttria-stabilized zirconia. The tetragonal zirconia inherited the alignment of the monoclinic zirconia used as a precursor and aligned with its (001) plane perpendicular to the magnetic field direction. The (001)-oriented 3Y-TZP showed anisotropic toughness with a high value along the [001] direction. In other words, the cracks generated at the Vickers indentation tips do not propagate equally parallel and perpendicular to (001) direction, as shown in Fig.1.

![Figure 1](image_url)

*Figure 1 – Vickers indentations and crack propagation in a tetragonal zirconia deposited outside (a) and inside (b) a strong magnetic field.*
**IN VITRO AND MECHANICAL PROPERTIES EVALUATION OF NANO-WIRE CALCIUM SILICATE COATING ON TITANIUM SUBSTRATE VIA EPD METHOD**

F.S.Shirazi1, University of Malaya, Malaysia  
F.shirazi@siswa.um.edu.my  
M.Mehrali, University of Malaya, Malaysia  
H.S.C. Metselaar, University of Malaya, Malaysia  
N.A. Abuosman, University of Malaya, Malaysia

**Keywords:** EPD, Nano-wire calcium silicate, Titanium, *In vitro*, Mechanical properties

Nano-wire calcium silicate (NWCS) was synthesized using hydrothermal technique and characterized by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) enabling confirmation of the NWCS synthesis. Electrophoretic deposition (EPD) method was carried out for the deposition of NWCS on a titanium (Ti) substrate followed by sintering the Ti specimens coated NWCS in order to enhance mechanical properties. The coating morphology and adhesion observation were analyzed with field emission scanning electron microscopy (FESEM). Mechanical properties including adhesion, hardness and fracture toughness were improved significantly. *In vitro* tests confirmed that NWCS coating layer increased the biological properties of Ti implants dramatically.
Lanthanum-Magnesium HexaAluminate (LMHA) is a promising material to replace the widespread zirconia as a Thermal Barrier Coating (TBC) in gas turbines applications, because LMHA possesses better thermal stability, electroisolation properties, lower Young’s modulus and thermal expansion coefficient. [1]

In the present work, experiments on the Electrophoretic Deposition (EPD) of LMHA are described. EPD was chosen as a cheap and relative simple deposition method. The powder for deposition was synthesized according to Pechini procedure, with ethylene glycol and citric acid as complexants and additionally annealed. The final composition was controlled by XRD. For suspension preparation single-phase powder was mixed with isopropanol in 10g/l ratio with preliminary ultrasonication and shaking of the powder in a small amount of medium. As substrates for the deposition NiCr-alloy plates were used. The deposition was carried out in an EPD-set-up as shown in (Fig. 1) with 10mm electrode distance in galvanostatic and potentiostatic modes, varying current or voltage and deposition time. First results of the most successfully coated plates are presented in the present contribution. In Fig.2 SEM micrograph of a sintered layer and its cross-cut is presented, which showed that the components of substrate and the deposited layer diffuse into each other during sintering. Further experiments and equipment tests are needed to clarify these phenomena.


Fig. 1

Fig. 2

Acknowledgments: Financial support by the European Commission in the frame of the TheBarCode is gratefully acknowledged
ELECTROPHORETIC DEPOSITION AS A ROUTE TO FORMATION OF HIGHLY ORDERED SEMICONDUCTOR NANOROD ASSEMBLIES ON SUBSTRATES

Kevin M. Ryan, University of Limerick, Ireland
Pai Liu, Shalini, Singh, University of Limerick, Ireland
Ajay Singh, University of Limerick, Ireland

In this paper, we describe the formation of vertically aligned nanorod assemblies over several multilayers using CdS, CdSe, alloyed CdSe$_{1-x}$S$_x$ and compound copper chalcogenides CuIn$_x$Ga$_{1-x}$S$_2$ by electrophoretic deposition$^{1-5}$. Remarkable order is obtained extending to centimetre scale areas and over several multi-layers by rod deposition from non polar solvents. The presence of both charge and dipole on the rods allows both field driven deposition and orientational order to occur. We also compare the process of assembly formation in electrophoresis to spontaneous assembly in solution, which gives important insights into nanorod organization by these different mechanisms. We show the influence of ligand environment on net charge (zeta potential) and its influence on assembly formation in CdSe nanorods that have long chain alkyl ligands (low charge) or pyridine ligands (high charge). The experimental observations show that highly charged rods deposit too quickly to allow close packing to occur with perpendicular alignment only occurring with a lower net charge. We further show the effect of controlled drying on the ability to attain crack free thin-films of perpendicularly aligned nanorod layers.

Figure 1: Cross-section SEM images of perpendicular aligned CdSe$_{1-x}$ nanorods deposited by EPD

Figure 1 (A, B) shows as-deposited CdSe$_{1-x}$ closed packed films of different film thicknesses and of different rod dimensions. The obtained closed packed films have CdSe$_{1-x}$ nanorods vertically aligned, with the c-axis parallel to electrical field. These films could be achieved over several centimeter scale areas. The multiple factors that affect the EPD results, such as concentration, field strength, zeta potential, aspect ratio, will be discussed.. The resolute order that is retained over device scale areas and over several multilayers combined with inherent scalability of electrophoretic deposition makes this approach highly attractive for large-scale nanorod integration in electronic, photonic or photovoltaic devices.

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The film microstructure plays a key role in the electrochemical, detection or catalytic activities of inorganic films. For a microstructure made of a specific particle, main reactions under working conditions, as well as side reactions, can be tuned through the processing of an adequate film packing. The colloidal processing offers alternative routes to achieve micro-architecture challenges in the devices manufacture. However, the specific morphology or the surface chemistry of the manipulated entities: from nanoparticle to suprastructures (bi- and tri-dimensional nanostructures, core-shell particles, organically-modified surfaces, etc.), could determine the packing as well as the shaping of a film. In EPD, both process the electrophoresis and the deposition can be tuned to store particles in a controlled, organized and ordered way. In this work, the effect of phenomena such as the hydrodynamics and/or the partial surface modification, etc., in its storage under the influence of an electric field is discussed. The nature, crystallography, shape factor and dimensions of the deposited platelet-like nanostructures/nanoparticles have been specially considered as well as the counterpart: the structure and surface of the working electrode, namely the substrate.
Electrophoretic deposition (EPD) is one of useful methods for the thin film preparation with homogeneous microstructure on a conductive substrate. In EPD method, the structure of the particle film could be controlled by electric operating conditions. Titania nanoparticle (NPs) film which is used for an electrode of dye sensitized solar cells (DSSCs), need not only the homogeneous microstructure but also pore size control for the high electron transport leading to the high photoelectric conversion efficiency of DSSCs.

In this study, titania NPs films were prepared by EPD with DC constant current condition using commercial nanoparticles (P-25, Evonik) dispersed in ethanol. The deposition behavior of titania NPs was drastically changed by the water content in ethanol. We measured the weight of a titania NPs film by chemical treatment and the film thickness using a laser microscopy. The porosity of the titania NPs thin film was evaluated from the measured those values. The film thickness increased almost linearly with EPD operation time, but the increase rate of the weight of the film slightly decreased. From those results, the porosity of the film increased slightly with EPD operation time. We expected that the electric resistance became larger and then the deposition force to the substrate became weaker when the EPD operation time increased. To improve the porosity distribution, three-layer thin film was made as repeating EPD (120 s) and drying (393 K, 180 s) operations. The film porosity was kept almost constant. We also tried to make the so-called buffer layer, which was effective to prevent the recombination reaction of electrons in DSSCs, using single-sized nanoparticles synthesized through the hydrothermal reaction. When adding this buffer layer of about 600 nm thickness before P-25 layers, the voltage during EPD increased with the number of the cycle increased, although the same thickness was obtained with the same applied current density and EPD period as those without the buffer layer. We also found the surface roughness of the thin layer with the buffer layer was smoother than that without the buffer layer.
ELECTROPHORETIC DEPOSITION OF NANOPARTICLES AS ELECTROCATALYSTS FOR ELECTROLYSIS IN THE SOLAR SULFUR AMMONIA HYDROGEN PRODUCTION CYCLE

Jan B. Talbot, University of California, USA
Nicole Shellhammer, University of California, USA
Neil Verma, University of California, USA
Komail Haider, University of California, USA

The solar sulfur ammonia (SA) thermochemical cycle is a potential process for splitting water to produce hydrogen. The hydrogen production sub-cycle in the SA cycle consists of the electrolytic oxidation of ammonium sulfite to ammonium sulfate. The anodic reaction is kinetically slow and nanoparticle catalysts are being investigated to improve this reaction rate. For this purpose, nanoparticles were coated onto graphite substrates by electrophoretic deposition (EPD). Synthesized nanoparticles of cobalt ferrite (20 nm) and purchased platinum cobalt on graphite (50 nm) were mixed into either 100% ethanol or 90% water/10% isopropanol with hexadecyltrimethylammonium bromide (CTAB). Then the nanoparticles were deposited onto either graphite paper or felt using EPD. Linear sweep voltammetry in 2 M ammonium sulfite was performed to test electrocatalytic activity of the deposits compared to blank graphite substrates. The morphology of deposits was examined by scanning electron microscopy.

Nanoparticles were deposited on graphite felt using EPD from ethanol and CTAB bath at a concentration of 1 mM or 0.05 mM. The EPD conditions were an applied voltage of 21 - 40 V for 1 or 2 min. The measured current ranged from 14.5 to 110 mA/cm² with deposit weights ranging from 0.5 mg to 1.2 mg/cm². A much larger amount of nanoparticles could be deposited on the 3-dimensional felt than graphite paper. All deposits showed electrochemical activity greater than the blank graphite felt. The cobalt ferrite deposit from low concentration CTAB bath showed the highest electrochemical activity. From the SEM micrographs, it was concluded that deposits with minimal exposed substrate, as a result of thick depositions with slight cracking, tended to have better electrocatalytic activity compared to sparse, thin deposits.
EPD AS A POWERFUL TOOL TO CONTROL THE DEPOSITION PROCESS OF DENSE AND POROUS FILMS USING SOL-GEL TECHNOLOGY

Yolanda Castro, Instituto de Cerámica y Vidrio (CSIC), Campus de Cantoblanco, Spain
castro@icv.csic.es
Begoña Ferrari, Instituto de Cerámica y Vidrio (CSIC), Campus de Cantoblanco, Spain

Key Words: sol-gel, thick coatings, nanostructured coatings, porous coatings

Nanotechnology for coating has largely developed due to its applications in strong industrial sectors, such as building, automation, aircraft, electronics, and more recently, in the development of films with high specific surface area for heterogeneous catalysts, separation process, host guest chemistry or energy storage or generation. Sol-Gel technology is a powerful route to obtain transparent glass-like coatings, which can be applied upon different substrates (ceramic, metals, polymers, glasses, alloys, etc.) providing a good adherence of coatings. Sol-gel major restriction is the low thickness attainable through mechanical deposition techniques, such as dipping or spinning. However, particles dispersed in a sol can be forced to migrate towards an electrode, where they coagulate to form a deposit. The sol gelling takes place after the deposition of particles leading to a dense and thick coating. Consequently, coatings on demand can be shaped from particulate and stable sols combining sol–gel and Electrophoretic Deposition (EPD). This methodology provides to a cheap and fast process, such as EPD, with sol-gel features, leading to inorganic thick films at low temperature, strongly adhered to the substrate and chemical and thermally stables. This methodology has been proved for the fabrication of homogeneous and transparent coatings on AISI 304 substrates using particulate hybrid sols prepared under basic conditions. The results demonstrated that the fast EPD kinetic allows obtaining highly dense Silica-based films which act as an effective barrier against electrolytic corrosion.

Recently, the sol-gel processes which combine the interaction between organic molecules and inorganic species, through a no-covalent interaction between species, have been gained great interest. In this case, the organic molecules can self-assembly forming micelles (namely templates), and then nanostructures with hierarchical order can be prepared. The elimination of the surfactant by calcination, extraction or other techniques, leads to stable and microporous films with high specific surface area. The micelles suspended within the sol can be moved by EPD. Therefore, this route constitutes the extension of a successful methodology adapted to the assembly of mesoporous structures, controlled by the application of an electric field, with a strong implication in the development of filters, catalyzers and bioactive materials.
This study investigates the electrophoretic deposition (EPD) of dispersed nanoparticles (SiO2, TiO2, SiC) for the formation of submicron coating as a surrogate of selective solar absorbers [1]. The colloidal dispersion is analysed by laser Doppler velocimetry coupled with small angle X-rays and dynamic light Scatterings. This latter, resulting mainly from Van der Waals and electro-steric interactions, is a key factor in order to obtain some uniform and crack-free films. Indeed, it not only affects the particle migration, but also influences the green coating density. Besides, some additives as carbon precursors are also embedded during the EPD in order to modulate the optical properties of the coating. The deposition yield is studied relative to the nature of the working electrode (Platinum, Silicon wafer, ITO) implying de facto some different applied voltage range, deposition time values and nanoparticle and additive concentrations. The composition and the thickness of coatings are analysed by X-ray spectroscopy [2]. Finally, their optical selectivity thresholds are determined by reflectance spectroscopy and the associated optimal film thickness range is discussed.

TOWARD DYNAMIC CONTROL OF NANOPARTICLE MONOLAYERS FABRICATED BY ELECTROPHORETIC DEPOSITION

James Dickerson
Center for Functional Nanomaterials, Brookhaven National Laboratory, USA
jdickerson@bnl.gov

Key Words: directed assembly, nanoparticle, electrophoretic deposition, magnetic, dipole.

Studies of nanoparticle monolayer formation have been motivated by potential applications of the films in magnetic storage, surface-enhanced Raman scattering coatings, ceramic joining, and biosensors, among others. Potential applications of nanoparticle monolayers rely on fabrication techniques that are facile, rapid, and site selective. Electrophoretic deposition (EPD) of nanoparticles from colloidal suspensions stands as an equally powerful and versatile liquid-phase process to fabricate inexpensively films and coatings of materials. A wide assortment of materials, from macroscopic crystals to nanoparticles and including luminescent, magnetic, and ceramics materials, can be cast by EPD onto field-emanating conducting, semiconducting, and insulating substrates. Many potential commercial and industrial applications of nanoparticle ensembles rely on fabrication techniques that are facile, rapid, and site-selective which create homogenous, densely packed, defect-free thin films. EPD is a technique that meets all of these criteria.

In this presentation, we discuss the development of a new technique for fabricating locally-ordered arrays of NPs, electrophoretic deposition (EPD). EPD is a rapid, safe, and facile method for depositing suspended nanomaterials on a large scale. In one minute of deposition, we can fabricate homogeneous NP monolayers on macroscopic surfaces as large as square centimeters. Colloidal suspensions of magnetic nanoparticles [iron oxide (FeO/FeO core/shell, FeO, and CoFeO NPs] have been employed to fabricate nanoparticle monolayers by EPD. The rate of deposition and the total particle deposition were controlled by varying the concentration of nanoparticles and the deposition time, respectively. Using scanning electron microscopy and transmission electron microscopy, we observed tight, hexagonal packing of the nanoparticles, indicating strong particle-particle interactions. Evidence of ordered monolayer films and the ease of creating multilayers based on said monolayers provide substantial promise for future device applications, ones for which the facile assembly of macroscopic, tightly packed, ordered casts of nanoparticles, i.e., a crystal of nanoparticles, could be transformative.
Electrophoretic Deposition at the Interface of Immiscible Liquids

Cullen R. Buie, Massachusetts Institute of Technology, USA
crb@mit.edu

Key Words: electrophoretic deposition; hydrogel; interface; nanomaterial

In this work, we present a novel method to fabricate composite nanomaterials in hydrogel membranes using electrophoretic deposition at the interface of two immiscible liquids. Hydrogels have been widely employed for bio-materials due to their outstanding bio-compatibility, high porosity, and notable swelling capabilities. Thin hydrogel membranes are highly desired because diffusion and mass transfer effects across the films can be improved. Further, conductive hydrogel films have been intensively investigated because they can provide a critical methodology to sense and diagnose biological systems or be used in energy storage applications. To date, vacuum filtering techniques and electrochemical deposition have been utilized to fabricate conductive polymer films. However, the filter textures and pressure gradients distort the polymer structures; especially when mechanically weak hydrogels are used. Here, we propose a novel process employing electrophoretic deposition (EPD) at the interface of immiscible liquids to create composite hydrogel films. During interfacial EPD, nanoparticles such as carbon nanotubes (CNTs) electromigrate to an oil/water interface, where polymer cross-linking is induced to form composite hydrogel membranes. The key aspect of this method is that polymerization occurs away from a solid substrate while surrounded by both polar and nonpolar media, allowing for the integration of CNTs or other nanoparticles into the hydrogel. Properties of the composite hydrogel films are controlled by the deposition parameters and polymerization time, facilitating mass production without the need for complex machinery. This fabrication method is cost-effective and scalable for composite hydrogels with tunable electrical, mechanical, and biological properties. Potential applications include fabrication of doped hydrogels for drug delivery and conductive hydrogels for biological sensing.

Figure 1. Schematic of the interfacial electrophoretic deposition process (a) and scanning electron micrograph of a hydrogel infused with carbon nanotubes created with interfacial electrophoretic deposition (b). Scale bar in (b) is 200 nm.
ELECTROPHORETIC DEPOSITION OF POLY-ETHER-ETHER KETONE (PEEK) FROM AQUEOUS SUSPENSIONS

Saša Novak, Jožef Stefan Institute, Ljubljana, Slovenia
Sasa.novak@ijs.si
Aljaž Iveković, Jožef Stefan Institute, Ljubljana, Slovenia
Marko Lukek, Jožef Stefan Institute, Ljubljana, Slovenia
Mitjan Kalin, Laboratory for Tribology and Interface Nanotechnology, University of Ljubljana, Slovenia

Key Words: poly-ether-ether ketone, PEEK, aqueous suspensions, conductivity, density

Although poly-ether-ether ketone (PEEK) polymer is hydrophobic by nature, aqueous electrophoretic deposition can be employed as efficient technique for shaping bulk parts and coatings. In this paper, the development of the suspension, processing parameters and the properties of the PEEK deposits are described. The mechanisms that took place to form a deposit are suggested and discussed.

Aqueous PEEK suspension with high surface charge and low conductivity was successfully prepared by addition of dodecyl-benzene sulphonic acid (DBSA) and NaOH to adjust pH. The nonpolar DBS- ion attached to the hydrophobic surface of PEEK resulting in hydrophilisation of the PEEK particles as well as in highly negative surface charge favourable for EPD process. During the deposition, the DBS- appear to remain attached at the particles in the deposit. H+ ions produced at depositing electrode through the decomposition of water replaced Na+ ions, which migrate toward the negative electrode where after reduction to Na0 and reaction with water increase the pH of the remaining suspension.

The aqueous electrophoretic deposition from suspensions with 50 wt.% of solids loading was rather fast and resulted in large homogeneous PEEK deposits with density of up to 557% TD. The deposit resistance is greatly affected by the behaviour, amount and concentration of the ions within the interparticle electrolyte within the deposit.

Figure 1 – Density of PEEK deposits as a function of starting suspension

Figure 2 – An image of as-prepared PEEK deposit between the electrodes separated for 5 cm
ELECTROPHORETIC DEPOSITION OF LIGNIN REINFORCED POLYMER COATINGS

M. Federica De Riccardis, ENEA-UTTMB, Italy
federica.dericcardis@enea.it
Daniela Carbone, ENEA-UTTMB, Italy
Virginia Martina, ENEA-UTTMB, Italy
Daniela Cuna, ENEA-UTTMB, Italy

Key Words: Coatings, PEEK, Lignin, Suspensions

As an abundant non-toxic amorphous natural polymer, lignin is an important renewable resource and it is the second most abundant biopolymer after cellulose. Due to its very complex structure, lignin has had historically a limited industrial use but the study of its properties has showed its potentiality in new value-added applications. As an example, the functional groups determine the high polarity of the macromolecular structure and make it an extremely promising material as a chemical component in polymer blends or as an organic filler. Moreover, lignin helps to lower the cost of the finished product, since it is an inexpensive by-product of the paper industry. In this work, lignin has been used as filler in Electrophoretic Deposition (EPD) polymer coatings based on Poly-ether-ether-ketone (PEEK). PEEK is a high performance thermoplastic with an excellent toughness–stiffness combination, good mechanical properties, high temperature resistance, good chemical resistance and high wear resistance. Due to its properties it is used also as a coating material on industrial, oil and gas, automotive, food processing or electronics parts. However, PEEK is uneconomical, so the addition of a low-cost filler as lignin, could increase its dissemination.

EPD has been recently used to obtain polymer coatings, also based on PEEK [1-3]. In this work the optimisation of the EPD suspensions based on PEEK and lignin powders, the deposition of polymer coatings by varying the deposition parameters, and the characteristics of the obtained deposits are described. After deposition and densification, the polymer coatings have been studied from morphological, structural and electrochemical points of view, in order to investigate their functional properties.

Cu$_3$TeO$_6$ THICK FILMS: PROCESSING BY ELECTROPHORETIC DEPOSITION AND ELECTRICAL CHARACTERIZATION

Paula M. Vilarinho, University of Aveiro, Portugal
paula.vilarinho@ua.pt
Xiaoli Zhu, University of Aveiro, Portugal
Zhonghua Wang, University of Aveiro, Portugal

This talk is about the fabrication and characterization of thick films of Cu$_3$TeO$_6$ by electrophoretic deposition.

Te-based compounds have been investigated as possible dielectric candidates for BME-MLCCs and LTCC applications due to their low synthesis and sintering temperature and good dielectric properties. However, research and relevant data on compounds of CuO-TeO$_2$ system are rather scarce. Among the existing compounds, Cu$_3$TeO$_6$ is known as the most stable composition in the CuO-TeO$_2$ system. It is known that Cu$_3$TeO$_6$ single crystal undergoes an antiferromagnetic phase transition at $T_N$ (Neel temperature) = 61 K, but the dielectric characterization is almost absent. Recently, we reported the phase formation of Cu$_3$TeO$_6$ and preliminary dielectric data of Cu$_3$TeO$_6$ ceramics. Cu is an attractive potential electrode for the future development of microelectronic industry due to its low cost and high conductivity. Therefore, fabrication and characterization of Cu$_3$TeO$_6$ ceramics and thick films are of interest in view of not only the possible applications in BME-MLCCs, LTCC and related technologies, but also for the possible compatibility with Cu electrode.

In the present work, single phase Cu$_3$TeO$_6$ powders were synthesized by conventional solid-state reactions and Cu$_3$TeO$_6$ thick films were fabricated by electrophoretic deposition on different substrates under different processing conditions. Effects of applied voltage and depositing time on the thickness of green films were studied. The thickness of green film increased rapidly with deposition time in the initial stage. The electric field exhibited a linear relationship with the thickness at fixed time. However, the quality of the films deteriorated under high voltages (>300V). Sintering of the films was carried out from 800 ºC to 860 ºC. The compatibility with the electrodes is discussed. The dielectric properties of Cu$_3$TeO$_6$ thick films are presented and the relations with the processing established.
Keywords: electrophoretic deposition, anodic porous film, boehmite particles, suspension conductivity

Because of its low density and good mechanical properties, aluminium alloys (AA) are widely used in aircraft industry. Nevertheless their low corrosion resistance requires surface treatments such as anodizing [1] followed by a sealing involving hexavalent chromium [2]. But a new European standard, called Reach, makes these chemical solutions forbidden. Consequently, new processes must be developed taking into account economic and environmental concerns. The electrophoretic deposition answers many expectations and enables to form thin coatings on substrates showing complex geometry, e.g., anodic porous film on AA parts.

In the present work, the insertion of boehmite particles, prepared from Yoldas process [3], from aqueous suspensions into anodic porous film by electrophoretic deposition is investigated. The purpose is to study the influence of colloidal suspensions conductivity to control the water electrolysis. In fact, in aqueous media, the water electrolysis, as soon as an electric field is applied, is observed and induces a local pH increase that destabilises boehmite sol and induces an agglomeration on the film surface. In this work, it was especially studied the influence of the particle size as well as the conductivity.

Conductivity measurements and voltamperometry showed that the electrolysis depends on the conductivity, namely the conductivity must be low enough to limit the electrolysis. However when the conductivity is too low, the electric double-layer fills pores and avoids the particles migration [4], [5]. Thus a compromise on the conductivity value, so on the particle concentration, has to be found in order to perform impregnation of particles only into the pores, rather than the electro-agglomeration of particles on film surfaces.

Figure – Anodic film supported on 1050 aluminium alloy a) without and b) with boehmite deposited on surface by electrophoretic process

Conductivity measurements and voltamperometry showed that the electrolysis depends on the conductivity, namely the conductivity must be low enough to limit the electrolysis. However when the conductivity is too low, the electric double-layer fills pores and avoids the particles migration [4], [5]. Thus a compromise on the conductivity value, so on the particle concentration, has to be found in order to perform impregnation of particles only into the pores, rather than the electro-agglomeration of particles on film surfaces.

PZT FILM ON SILICON BY ELECTROPHORETIC DEPOSITION

Pietro Galizia, CNR-ISTEC, Italy
Carlo Baldisserri, CNR-ISTEC, Italy
Carmen Galassi, CNR-ISTEC, Italy

In recent times direct integration of ferroelectrics on silicon wafer has been attracting interest [1]. Electrophoretic deposition (EPD) was investigated in this laboratory [2] as an alternative mean to produce lead zirconate titanate (PZT) film on silicon wafers followed by sintering at 850-950°C. EPD is an easily implemented deposition technique that requires only basic laboratory gear and a sufficiently stable colloidal suspension to produce ceramic and electroceramic films with thickness in the 100 nm – 10 mm range [3]. It has been found that the EPD of niobium-doped lead zirconate titanate (PZTN), performed in ethanol-based suspensions of PZT on bare silicon wafers on which Al/Si alloyed ohmic contacts were made, produced smooth green films that strongly pinned to the silicon substrate after sintering.

Thick and well-adhered sintered PZT films on silicon having thickness about 50 µm were thus obtained. Such structures could be the core of novel on-chip sensors/actuators. The results of the production of thick PZT films by EPD and sintering and some characterizations of the same are reported.

Presenting author: Carmen Galassi carmen.galassi@istec.cnr.it

The uniformity of surface-charging of the powder affects the deposition characteristics and deposit quality; however, the control of the surface-charging uniformity is often difficult for complex oxide powders because they have several different surface-charging sites. In this study, the surface modification of two kinds of complex oxide powders with polyelectrolytes was performed by the Layer by Layer (LbL) method. The deposition characteristics were then investigated by using the polyelectrolytes-modified powders. Commercially available Gd doped ceria (GDC) and La0.8Sr0.2Ga0.8Mg0.2O1-δ (LSGM) powders were separately dispersed in ethanol. Poly (diallyl dimethyl ammonium chloride) (PDDA) and polyacrylic acid (PAA) were used as polycation and polyanion for the LbL modification, respectively. The PAA was first adsorbed on the GDC and LSGM powders, and then the PDDA was adsorbed on the powders. Finally the PAA and PDDA-coated powders were dispersed in ethanol to prepare the suspensions for the following EPD process. Fig.1 shows the zeta potential change of the GDC and LSGM powders. By the alternate coating of PAA and PDDA, the zeta potential of the particles was changed from positive to negative and then to positive again. Using the surface-modified powders, the tri-layer of GDC/LSGM/GDC was deposited on a polypyrrole coated porous NiO-YSZ substrate by sequential EPD. Fig.2 shows a cross-sectional SEM picture of the layered structure after the co-sintering at 1400 °C. The polypyrrole at the NiO-YSZ/GDC interface is disappeared and the inter-layers between the electrolytes are well bonded. The interfacial adhesion between the LSGM electrolyte and the GDC inter-layer was fairly good; no cracks and no peel-off of the layers were observed.
PARTICLE ASSEMBLY OF MICRON AND NANO SCALE MATERIALS WITH PARTICLE-TO-PARTICLE PRECISION BY ELECTROPHORETIC DEPOSITION

Tammy Y. Olson, Lawrence Livermore National Laboratory, USA
Olson43@llnl.gov
Fang Qian, Lawrence Livermore National Laboratory, USA
Mihail Bora, Lawrence Livermore National Laboratory, USA
T. Yong-Jin Han, Lawrence Livermore National Laboratory, USA
Andrew J. Pascall, Lawrence Livermore National Laboratory, USA
Marcus A. Worsley, Lawrence Livermore National Laboratory, USA
Joshua D. Kuntz, Lawrence Livermore National Laboratory, USA

Key Words: assembly, programmable, nanoparticle, mesoscale, surface plasmon

Precise positioning of particles has wide implications for a variety of applications such as in device fabrication, controlled crystallization, and tuning of materials properties. We have developed a versatile particle assembly technique with precision down to the single particle level, allowing fabrication of limitless particle configurations. Micron sized polystyrene beads were assembled by electrophoretic deposition (EPD) with high reproducibility onto pre-designed, hole-patterns where single, dimers, and higher ordered particle array assemblies were fabricated. Nanometer sized gold nanoparticles were similarly assembled and their surface plasmon resonance (SPR) were precisely manipulated due to its high sensitivity to metal shape and geometry. Voltage and pattern effects on the electric field during EPD allowed for multi-material deposition, enabling this technique to produce mesoscale materials of compositions that are not possible by conventional methods. Numerical simulations of particles during deposition onto a patterned electrode were also performed. This technique can be used with a wide range of particles to fabricate materials such as negative-index optical metamaterials, plasmonic waveguides, antennas, superlens, and data storage devices.

Hole patterns with subsequent particle deposition using EPD.

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FABRICATION OF C-AXIS-ORIENTED ZEOLITE L SEED LAYER ON POROUS ZIRCONIA SUBSTRATE BY ELECTROPHORETIC DEPOSITION IN STRONG MAGNETIC FIELD

Chika Matsunaga, National Institute for Materials Science, Japan
MATSUNAGA.Chika@nims.go.jp
Tetsuo Uchikoshi, National Institute for Materials Science, Japan
Tohru S. Suzuki, National Institute for Materials Science, Japan
Yoshio Sakka, National Institute for Materials Science, Japan
Motohide Matsuda, Kumamoto University, Japan

Key Words: Zeolite L, strong magnetic field, c-axis orientation, seed layer

Zeolites are microporous crystalline solids with well-defined pore channels depending on framework structures. Orientation of zeolites is promising to improve their properties such as gas separation, adsorption and ion exchange. Secondary growth is one of the fabrication methods for zeolite films: Fine seed crystals are applied on a substrate, and then the seeded substrate is hydrothermally treated in a reaction sol. The microstructures of the resultant zeolite films are generally dominated by the seeding process. The electrophoretic deposition (EPD) process has the advantage of high deposition rate and thickness control for the depositing layer by altering the applied voltage and the deposition time. In this study, fabrication of oriented seed layer of zeolite L, which has a one-dimensional large pore channel along the c-axis, on porous zirconia substrates were attempted by EPD in a strong magnetic field.

A commercial zeolite L powder was dispersed in ethanol and agglomerated secondary particles were removed by sedimentation. Well-dispersed zeolite L particles in the supernatant suspension were consolidated on porous zirconia substrates by EPD in or out of a static magnetic field of 12 T. The surfaces of the zirconia substrates were coated with polypyrrole to make them electrically conductive. The obtained samples were evaluated by XRD measurements and SEM observations.

Fig. 1 shows the XRD patterns of the zeolite L layer applied on a porous zirconia substrate by EPD in and out of the perpendicularly-applied magnetic field against the surface of the substrate. The XRD pattern of the zeolite L layer deposited out of a magnetic field showed that the layer had a random orientation. In contrast, the c-axis oriented zeolite L was observed by applying a static magnetic field. Fig. 2 shows the surface view and SEM images of the cross-section for the zeolite L layer. Homogeneous deposit was obtained in the magnetic field. The thickness of the deposit layer was approximately 3 μm. As the results, homogeneous zeolite L layers with the c-axis orientation were successfully deposited on porous zirconia substrate by EPD in a strong magnetic field.

References

Figure 1 XRD patterns of the zeolite L layer on a porous zirconia substrate deposited by EPD (a) in and (b) out of the perpendicularly-applied magnetic field against the surface of the substrate.

Figure 2 Surface view (a) and SEM image of the side (b) surfaces for the layer deposited by EPD for 10 min. in a 12 T strong magnetic field which is parallel to the deposition direction.
CRYSTALLINE-ORIENTED $\beta$-SiAlON:Eu$^{2+}$ PHOSPHOR DEPOSITS FABRICATED BY ELECTROPHORETIC DEPOSITION WITHIN A STRONG MAGNETIC FIELD: PREPARATION PROCESS AND PHOTOLUMINESCENCE PROPERTY DEPENDING ON ORIENTATION

Chennng Zhang, National Institute for Materials Science, Japan  
zhang.chennning@nims.go.jp  
Tetsuo Uchikoshi, National Institute for Materials Science, Japan  
Lihong Liu, National Institute for Materials Science, Japan  
Yoshio Sakka, National Institute for Materials Science, Japan  
Naoto Hirosaki, National Institute for Materials Science, Japan

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Electrophoretic deposition (EPD) assisted with a strong horizontal magnetic field (12 T) was utilized to fabricate the phosphor deposits of the $\beta$-sialon:Eu$^{2+}$ (Figure 1). The direction of the magnetic field was perpendicular to that of the electric field of the EPD. Under the influence of the electric field, the positively charged colloidal particles of the $\beta$-sialon:Eu$^{2+}$ in the suspension were deposited onto the cathodic substrate; simultaneously, the horizontal magnetic force contributed the phosphor particles rotate along the c-axis with higher magnetic susceptibility to form an oriented deposit, therefore made the oriented deposits consist of the phosphor particles having dominant appearances of the side faces (hk0) (Figure 2). Particularly, longer depositing time, higher orientation degree, and, larger particle size, easier alignment. Photoluminescence (PL) intensities of the oriented deposits were improved by comparing with those of the randomly oriented samples; especially, the improvement of 12.4%-fold PL intensity was obtained at 150 s depositing time. This technique of the EPD process proceeded within the strong magnetic field to fabricate the oriented phosphor deposit may be potentially used to prepare the flat LEDs, instead of conventional method.

Figure 1 – Schematic of the deposit fabricated by the EPD process within the horizontal magnetic field. E and B denote the direction of electric field and magnetic field (B), respectively.

Figure 2 – XRD patterns of the $\beta$-sialon:Eu$^{2+}$ deposits: (a) in horizontal magnetic field and (b) in perpendicular magnetic field.
ELECTROPHORETIC DEPOSITION AS AN ADDITIVE MANUFACTURING TECHNIQUE

Andrew Pascall, Lawrence Livermore National Laboratory, USA
Pascall1@llnl.gov
Kyle Sullivan, Lawrence Livermore National Laboratory, USA
Marcus Worsley, Lawrence Livermore National Laboratory, USA
Luis Zepeda-Ruiz, Lawrence Livermore National Laboratory, USA
Joshua Kuntz, Lawrence Livermore National Laboratory, USA

Key Words: additive manufacturing, 3D printing, modeling, near net shaping, light directed EPD

Electrophoretic deposition (EPD) has for many years been viewed merely as a coating process. Recently, some have begun to exploit EPD’s key advantages, such as its wide materials set and conformal coating behavior, to form complex composite and functionally graded parts to near net shape[1]–[3]. In this presentation, we will discuss our efforts to develop EPD into an additive manufacturing technique. Specifically, we will present light directed EPD[4], a technique that allows precise placement of materials in three dimensions and it application to microarchitected materials. We will also detail our progress in developing models of EPD, both continuum and particle based, and their contribution to understanding the morphology, degree of order, and other properties of interest in the final deposit.

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