

Nanostructured and Self-Assembled Superhydrophilic Bipolar Plate Coatings for Fuel Cell Water Management

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ABSTRACT

Layer-by-Layer (LbL) assembly of silica nanoparticles onto Proton Exchange Membrane Fuel Cell (PEMFC) bipolar plates is demonstrated for enhanced hydrophilicity (contact angle $< 15^\circ$), enabling effective water management and stable low-power operation of a FC stack. Besides superhydrophilicity, the coating nanostructure and thickness are tailored to meet other competing and challenging requirements—including low electrical contact resistance, high electrochemical stability, good wet adhesion, and low costs—by modifying the electrostatic interaction between the anionic silica particles and cationic polymer layer and by selecting the appropriate number of polymer/silica bilayers. Three hydrophilic degradation mechanisms are observed in FC stacks—dissolution, adhesion, and contamination. It's unclear whether superhydrophilicity can be maintained throughout a 10-year stack life, particularly with respect to contamination robustness.

Keywords: hydrophilic, bipolar plates, coatings, fuel cells, water management

1 INTRODUCTION

Liquid water accumulation in bipolar plate flow field channels is detrimental to fuel cell performance. Water slugs obstruct reactant gas flow, preventing gases from reaching the catalyst layer and from participating in the electrochemical reaction. This is particularly prevalent in automotive fuel cell applications where operating conditions (e.g., inlet relative humidity, temperature and pressure) are extremely dynamic and difficult to control, but is required to manage liquid water effectively. The FC polymer membrane needs to be saturated for good conductivity while the channels need to be dry for low mass-transport losses. Channel blockage results in gas flow maldistributions within a given cell and/or from cell-to-cell within a stack. The net result is a significant reduction in cell voltages, which, if severe enough, can potentially result in catastrophic cell reversals and stack shutdowns.

The surface energetics of the plate material can significantly influence liquid water management. Hydrophobic and hydrophilic surfaces have been

investigated and found to impact fuel cell performance either negatively or positively depending on the system operating conditions, plate designs and membrane architectures. This present study assumes a superhydrophilic plate surface (contact angle $< 15^\circ$ by definition) and addresses the concern of maintaining superhydrophilicity throughout the targeted fuel-cell stack life.

The plate surface should also exhibit low contact angle (CA) hysteresis to facilitate water removal from the channels. Hysteresis is defined as $\theta_a - \theta_r$, where θ_a is the advancing contact angle and θ_r is the receding contact angle. According to equation (1), with small liquid-to-solid contact width ω and low hysteresis, little force would be required to remove the imbibed water in the channels,

$$F = \sigma_{lg} \omega (\cos \theta_r - \cos \theta_a) \quad (1)$$

where F is the force (e.g., capillary, gravity, shear, etc.) and σ_{lg} is the liquid-vapor interfacial tension[1].

CA hysteresis depends on surface roughness and surface heterogeneity. Johnson and Dettre simulated the water CA for idealized sinusoidal hydrophobic and hydrophilic surfaces with various roughness and various degrees of chemical heterogeneity[2]. For intrinsically hydrophilic surfaces, if the periphery of a water droplet advances over a surface containing islands of high-CA material, the edge of the liquid is pinned at the boundaries of the islands. Only 5 to 10% of high-CA material with micron-sized dimensions ($> 5 \mu\text{m}$) results in high hysteresis and poor film thinning. Thus, if a low hysteresis and superhydrophilic coating is to be developed for low surface energy plates (e.g., Au-coated stainless steel, graphite-filled polymer composite; $60^\circ < \theta < 80^\circ$) an intrinsically hydrophilic coating ($\theta \ll 90^\circ$) with good spatial surface homogeneity is required. In this work, superhydrophilic amorphous silica coatings derived from particulate sols and applied using a low-cost, layer-by-layer (LbL) conformal coating process were developed for bipolar plates.

The coating must meet other challenging and competing coating criteria such as low electrical contact resistance (CR), high electrochemical stability, good wet adhesion and low cost. Low CR is achieved by enabling the fibers from the GDL to penetrate

through the thin (< 100 nm), porous and soft structure of the silica coating and contacting the underlying conductive bipolar plate surface. Fiber penetration is compromised with increasing silica thickness, thereby increasing the CR. Amorphous silica is electrochemically stable within the PEMFC potential range (-0.4 to +0.6 V, Ag/AgCl), but dissolves chemically via hydrolyzes in water (solubility: 70 to 150 ppm @ 25°C) at relatively low rates (ca. 1 nm/hr @ 80°C) [3]. Adhesion of silica to graphite-filled composite and metallic (e.g., stainless steel) bipolar plate surfaces relies on weak electrostatic dispersion forces, but is normally not a problem in thin (50 to 200 nm) sol-gel—derived films[4]. Silica is inexpensive, particularly at the targeted thin thickness level required for low CR. Hence, thin silica is desired for low CR, good adhesion, and low material and processing costs; while thick silica is desired for sufficient surface coverage (low hysteresis) and for prolonging coating life by offsetting negative dissolution effects.

For the most part, 4 bilayers of LbL silica meets beginning-of-life bipolar plate coating requirements. However, it's questionable whether these desired coating properties can be maintained over a 10-year stack life as three modes of hydrophilicity degradation—dissolution, adhesion, and contamination—are observed and are addressed in this study.

2 EXPERIMENTAL

Materials: Two types of silica nanoparticles are investigated: X-tec 3408 (Nano-X GmbH) has a reported average particle size of 20 nm and comes in a sol containing 10% v/v ethanol in water with a solids content of 5% w/w. Polishing silica (Electron Microscopy Supply – EMS) has a reported average particle size of 60 nm and is obtained in an alkaline (NH₄OH) base at 40% w/w solids content.

The cationic binder that was employed with the colloidal sol is a copolymer of acrylamide and a quaternary ammonium salt (acrylamide/β-methacryloxyethyl-trimethyl-ammonium copolymer). The specific material employed in this study has a charge density of 10% and is available commercially as Superfloc C442 from Kemira Corporation. This is a strong polyelectrolyte with a cationic charge density which is independent of solution pH. The high molecular weight polymer was dissolved in DI water at 21°C for 8 hrs to a concentration of 0.36 g/l. The pH of all suspensions was maintained at a value sufficiently low to prevent rapid dissociation of the hydrolyzed acrylamide groups on the cationic binder (onset at pH 7) while maintaining a strong negative charge in the colloid suspension for stabilization. Note

that although an acidic (pH 1) cationic polymer solution at 21°C was used to minimize polymer de-esterification and hydrolysis of the acrylamide groups in the dipping bath, the adsorbed copolymer will eventually be exposed to higher fuel-cell like pHs (3 to 5) and temperatures (60 to 95°C), and under these conditions, the copolymer is known to hydrolyze slowly[5]. It's unclear whether this cationic copolymer will exhibit long-term thermal and chemical stability in a fuel-cell environment beyond 5500 hrs of operation.

The principal mechanism by which silica surfaces acquire a (negative) surface charge in contact with water is the dissociation of silanol groups. Hence, pH is a critical parameter in suspension stabilization and LbL formation of these particles. Another critical parameter is the dielectric constant of the silica sol as it impacts the zeta potential (ζ) which provides a quantitative assessment of the extent of the electrostatic interaction between nanoparticles in a given suspending medium and subsequent to surface deposition. The relationship between ζ and the nanoparticle surface charge, σ, and the properties of the suspending media such as dielectric constant, ε, and ionic strength, κ, is given by the following expression[6]:

$$\sigma = \frac{-2\kappa kT}{ze} \epsilon \sinh \left(\frac{ze\zeta}{2kT} \right) \quad (2)$$

where k is Boltzmann's constant, T is the absolute temperature, and e is the electron charge. From this equation, we can predict how suspending media composition may alter the multilayer nanostructure. More specifically, we can vary ε via addition of alcohols and σ via pH control.

The substrates used consisted of BMC 940-8695 graphite-filled vinyl ester composite plate material (Bulk Molding Compounds, Inc.) and electroplated Au of 20 to 30 nm thickness on 316L SS plate material.

Processes: Nano-X and EMS were applied to the coupons using an LbL process in which the alkaline-cleaned coupons were: (1) dipped into a cationic C442 polyelectrolyte (0.36 g/li, 1.0 pH) for 3 minutes at room temperature to acquire a positively charged surface, (2) rinsed in DI water with vigorous agitation for 2 minutes to remove non-adhered polymer, (3) dipped into a Nano-X or EMS sol containing negatively charged silica particles for 3 minutes, and then (4) rinsed in DI water with vigorous agitation for 2 minutes to remove unbonded silica particles and to form a monolayer of silica. This produces a single polymer/silica bilayer and the process is repeated to build up the desired thickness.

Characterization Methods: During CR measurements, the coated sample is compressed between two GDLs at predetermined pressures using a force controlling instrument (e.g., Instron machine) and is subjected to a known current through its thickness direction. By measuring the voltage drop across the sample and knowing the sample area, the specific area resistance is calculated using Ohm's Law. In this study, 6.45 A or 1 A/cm² (1 in × 1 in area = 6.45 cm²) was used throughout and the resistance was determined at 200 psi. All voltage drops were measured between gold-coated copper blocks to reduce measurement variations.

X-ray Fluorescence Spectroscopy (XRF) and Electron Probe Microanalysis (EPMA) were used to measure the area weights of SiO₂ in µg/cm². Time-of-Flight Secondary Ion Mass Spectroscopy (TOF-SIMS) was used to map the surface composition of silica-coated materials. Although CA hysteresis is a critical parameter for water removal, static contact angles were measured in this study using a contact angle meter (Kernco Instruments Co, Inc.).

3 RESULTS AND DISCUSSION

Nanostructure Development: An SEM image of 4 bilayers of LbL NanoX silica on gold-plated SS is shown in Fig. 1. NanoX sol (5 pH) was diluted with 50/50 ethanol/water to a solids content of 0.5% w/w.

Fig. 2 illustrates the dependence of electrical CR, silica thickness, and static CA on the number of bilayers for LbL NanoX. Toray TGP-H-1.0T GDL was used in the CR measurements. As expected, the CR/CA increased/decreased exponentially with increasing bilayers. The SiO₂ thickness increased monotonically with the number of bilayers (each bilayer ca. 20 nm), suggesting excellent polymer/silica electrostatic interaction. However, the targeted hydrophilicity (< 15°) was not achieved until three bilayers were deposited. This indicates incomplete surface coverage for one and two bilayers, and a heterogeneous surface of high CA hysteresis consisting of less hydrophilic gold domains surrounded by hydrophilic silica. Note that 0% ethanol (instead of 50% used in Fig. 2) required more than five bilayers to achieve 15° CA (not shown here), indicating a strong dielectric constant effect on surface charge and, in turn, on the extent of LbL adsorption.

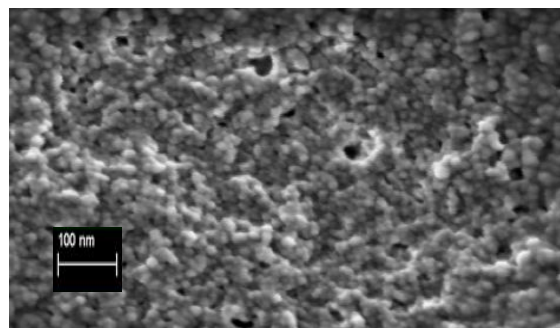


Fig. 1: FE-SEM image at 100 kX magnification of 4 bilayers of LbL NanoX nanoparticles (pH 5) deposited onto electroplated gold with cationic polyacrylamide.

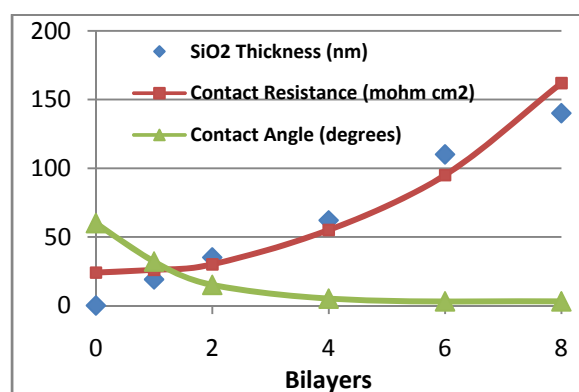


Fig. 2: Contact resistance, contact angle and silica thickness as a function of the number of bilayers for LbL NanoX (pH 5) onto Au-coated stainless steel.

Dissolution and Adhesion: Silica hydrolyzes in water via nucleophilic attack of the oxygen contained in water on the Si atom, thereby breaking the siloxane bond. Polyelectrolyte adsorption (adhesion) results from a combination of van der Waals bonding and coulombic (including polarization) interactions between ionic groups on the polymer and the plate surface[7].

It's difficult distinguishing between dissolution and adhesion effects for silica-based coatings exposed to a wet fuel-cell environment. They are coupled. Poor wet adhesion is attributed to water penetration to the coating-substrate interface followed by displacement and/or dissolution of the adhesive bonds. FC test results confirm that both SiO₂ loss mechanisms are present.

Composite plates were coated with 4-bilayers of LbL NanoX and evaluated in a FC stack for silica durability. Plates were removed from the stack after 700, 1500 and 2500 hrs of operation and their surfaces sectioned for Electron Probe MicroAnalysis (EPMA).

The following was observed:

- 20% and 30% loss of SiO₂ for the cathode and anode plates, respectively, after 2500 hrs.
- A discontinuous silica film after 2500 hrs of FC exposure (see Fig. 3).
- Poor water wicking in channels due to the surface heterogeneity of the discontinuous film (high CA hysteresis).
- Large white silica deposits with thickness (ca. 100 to 140 nm) greater than that of original film. The silica solubility level was exceeded and the silica re-precipitated or the deposits result from coalescence of the silica nanoparticles.

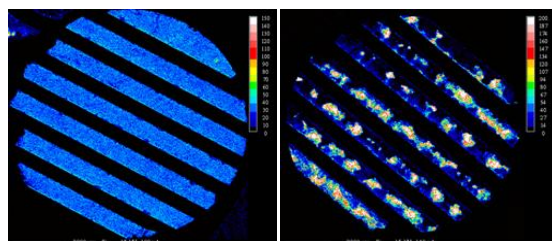


Fig. 3: EPMA images of 4-bilayers of NanoX on composite plates before (left) and after (right) 2500 hrs of FC exposure.

The formation of heterogeneous surface domains and corresponding loss in hydrophilicity was also observed after 1461 hrs of FC operation on Au-plated SS plates coated with 4-bilayers of LbL NanoX. TOF-SIMS chemical mapping was conducted in hydrophobic and hydrophilic regions. Figure 4 illustrates the surface chemical composition of the hydrophobic area of the FC-tested plate. Although the SiO₂ coating is relatively thick, based on almost complete attenuation of the Au signal, SiO₂ loss is observed, evidenced by the exposure of the underlying and less hydrophilic Au coating. These hydrophobic domains (20 to 50 μm in diameter) were not observed on freshly coated plates (before FC testing).

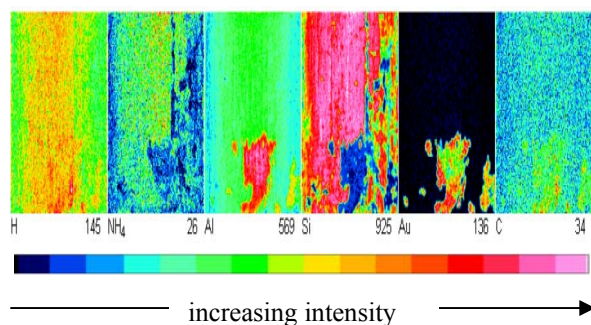


Fig. 4: TOF-SIMS surface chemical composition mapping of 4-bilayers of LbL NanoX on Au-plated plate in hydrophobic cathode channel.

Contamination: The high-energy “residual valences” surrounding a surface Si atom are responsible for the adsorption of foreign atoms or molecules on the surface [8].

LbL silica coatings have performed well in FC stacks for 2500 hrs; however, maintaining a superhydrophilic plate surface over a 10-year stack life is of great concern. Low-energy contaminants (e.g., air-borne hydrocarbons, lubricating oils, plasticizers, etc.) are attracted to high-energy SiO₂ surfaces, particularly under dry conditions in which electrostatic charges are prevalent. The composite plates in Fig. 3 exhibited a severe loss in hydrophilicity near the polymeric gasket. Fortunately, silica-based coatings can rely somewhat on a self-dissolution mechanism to help maintain hydrophilicity.

4 CONCLUSIONS

LbL deposition of silica nanoparticles onto conductive bipolar plate surfaces is an enabler for meeting beginning-of-life plate requirements, including superhydrophilicity. It is unclear, however, whether silica-based coatings are durable enough to meet end-of-life PEMFC targets as hydrophilicity is lost due to dissolution, poor adhesion, and contamination. New nanostructured coating materials and processing developments are needed to mitigate these loss mechanisms, particularly the latter.

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