A conductive and hydrophilic bipolar plate coating for enhanced proton exchange membrane fuel cell performance and water management

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ABSTRACT

Electrically conductive and hydrophilic coatings for proton exchange membrane fuel cell (PEMFC) stainless steel bipolar plates have been developed in order to minimize voltage losses at the plate and gas diffusion layer (GDL) interface and facilitate liquid water transport in plate channels for efficient stack operation. The coatings are based on a multifunctional silane, 1,2-bis(triethoxysilyl)ethane (BTSE), mixed with conductive, hydrophilic carbon black. Vulcan® XC72 carbon black was modified with either polar phenylsulfonic acid (PSA) or carboxylic acid (COOH) groups to increase hydrophilic character and wetting behavior. Wetting and electrical contact resistance performance was compared with coatings based on nano-particle titania and silica. These conductive silane and carbon composite coating precursors are conveniently formulated in alcohol solution for scalable application via spray coating. Cured films exhibit negligible contact resistance increase ($<2\,m\Omega\,cm^2$) at 1.4 MPa when deposited on both physical vapor deposited (PVD) carbon and electroplated gold coated stainless steel. The coatings were tested for hydrophilicity retention under wet and dry fuel cell conditions where the BTSE-COOH coating remained hydrophilic on stamped stainless steel bipolar plate prototypes after greater than 1200 h of simulated fuel cell testing with only moderate loss of hydrophilicity.

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1. Introduction

Liquid water accumulation in proton exchange membrane fuel cell (PEMFC) bipolar plate flow field channels is detrimental to fuel cell performance and durability. Water slugs obstruct flow, preventing reactant gas from reaching the catalyst layer and participating in the electrochemical reaction. This is particularly true at low loads and low gas velocities in which the gas shearing forces are insufficient to purge slugs of water from the channels. Liquid water blockage of anode channels can also lead to starvation of the hydrogen electrode accelerating corrosion of the cathode catalyst carbon support [1]. The overall result is a significant reduction in cell voltage of approximately 200 mV less than the average stack cell voltage under low power operating conditions which can potentially result in undesirable cell reversals and stack shutdowns [2].

Two approaches are used to manage liquid water in fuel cell stacks to enable low power stability. The first involves a passive material approach relying on the use of a hydrophilic treatment or coating to the bipolar plate surface. Water droplets emanating from the gas diffusion layer (GDL) wet along the hydrophilic plate surface forming a thin film that enables reactant gases to readily flow unobstructed to the electrodes. Nano-particulate silica and titania [3–6] are examples of passive materials strategies capable of creating hydrophilic coatings for water management [7] that have the benefit of inexpensive raw materials that are easily applied. These surfaces demonstrate good wetting behavior due to surface composition containing hydroxyl groups along with nano-scale porosity and topography driven capillary flow [8].

Alternatively, system engineering approaches can be employed to the operation of the PEM fuel cell including optimization of plate geometry to enhance water management and system operating conditions such as reactant gas pulsation, high reactant gas velocities, and low relative humidity to mitigate water stagnation [9,10]. However, such system fixes occur at the expense of increased cost and a reduction of ionic conductivity of the membrane at low relative humidity. As a result, surface modifications to the bipolar plate to enhance water management are highly desirable.

Low contact resistance at the bipolar plate and GDL interface is required to minimize power losses and maximize fuel cell

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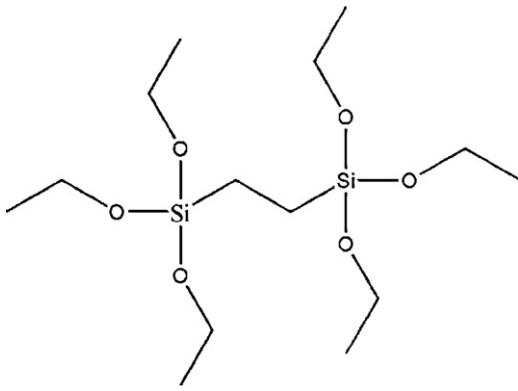[3] Present address: Robert Bosch LLC, Plymouth, MI 48170, United States.

Fig. 1. Chemical structure of 1,2-bis(triethoxysilyl)ethane (BTSE).

Fig. 2. Schematic of the fuel-cell coupon (18 cm × 6.4 cm × 0.3 cm) stamped from 304L stainless steel strip with designated wide (WA, WB) and narrow (NC, ND) land regions representing anode and cathode flow field geometry respectively of larger fuel cell plates.

efficiency. The primary source of ohmic loss comes from contact resistance associated with the oxide layer at the stainless steel surface. As a result, the United States Department of Energy has set the autocompetitive electrical contact resistance target at less than $20\,m\Omega\,cm^2$ at a stack compression pressure of 1.4 MPa. Thin gold (PVD or electroplated) and thin carbon (physical or chemical vapor deposited) are cost effective conductive coating options typically applied to the stainless steel surface to reduce contact resistance to acceptable levels [11–14]. Both maintain stable contact resistance after thousands of hours in the fuel cell environment, but neither gold nor carbon [12–14] is sufficiently hydrophilic to manage water at the bipolar plate surface. Passive coating solutions such as silica and titania are hydrophilic, but have the disadvantage of being electrically insulating and thick layers of such materials create unacceptable electrical loss. When bipolar plate surfaces are treated with such coatings, they must be thin and porous enough to allow micrometer sized carbon fibers from the GDL to penetrate through the soft, porous structure of these top coats and make electrical contact with the underlying conductive coating. Hydrophilicity is achieved with such coatings, but at the expense of significant increases in contact resistance over unmodified gold or carbon coated surfaces. Coatings based on silica or plasma fluorinated carbon that are both hydrophilic and conductive have been reported [7,12], but no details were given on the long term stability of such materials in the fuel cell environment. Ideally, bipolar plate coatings for water management would be hydrophilic, sufficiently conductive to eliminate electrical loss at the plate surface and capable of long term stability in the fuel cell.

In order to create a conductive and hydrophilic coating suitable for the fuel cell environment, the following requirements must be present: (1) a conductive component at a level sufficient to create continuous pathways through the film, (2) a binding element to provide durability and mechanical integrity, and (3) sufficient hydrophilic character over all elements of the coating to produce wetting. Practical methods of application for such coatings are also a concern, and it is advantageous to produce formulations capable of being either dip coated or sprayed onto a surface for scalable production methods. To meet this combination of requirements, a system based on conductive carbon with its surface modified to increase hydrophilicity was combined with a silane based binder element and dispersed in an alcohol carrier solution for convenient application to a surface.

Here we report the development of a durable, hydrophilic and electrically conductive coating for the PEMFC bipolar plate surface. A multifunctional, dipodal silane, 1,2-bis(triethoxysilyl)ethane (BTSE) shown in Fig. 1 is combined with hydrophilically modified carbon. The silane acts as binder surrounding carbon particles in a network that provides electrical conductivity while the hydrophilic surface modification enhances wetting behavior of the film.
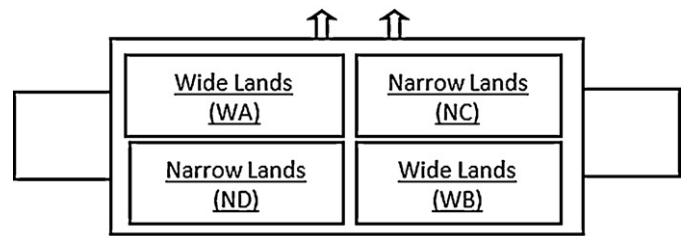
Electrical and wetting behavior of these silane and modified carbon composite coatings is compared with that of passive, insulating silica and titania based coatings. Characterization is focused on changes in contact resistance and the ability of the silane based coating to remain hydrophilic when exposed to a simulated fuel cell environment. Carbon and silane composites were applied to surfaces of gold coated welded stainless steel bipolar plates via spray coating to demonstrate process scalability and generate samples to test performance and durability under extended fuel cell aging conditions. It is found that unlike hydrophilic silica and titania nanoparticle coatings, these composite carbon and silane coatings show minimal increase in contract resistance while maintaining long term wetting behavior up to 1200 h in the fuel cell environment.

2. Experimental

2.1. Materials

Small flat coupons (2.54 cm × 2.54 cm × 0.32 cm) of 304L stainless steel and larger stamped bipolar plates (18 cm × 6.4 cm × 0.32 cm) shown schematically in Fig. 2 were used to evaluate coating durability and performance. The stamped plates contain regions of narrow and wide flow field lands representing those used in larger cathode and anode fuel cell plates respectively. Geometric details of these flow fields are not shown or described since they are proprietary. Coupons consisted of 304L stainless steel uncoated, gold electroplated (Tanury Industries, Inc.), or coated with physically vapor deposited carbon (General Motors). Both gold and carbon thicknesses were approximately 20–25 nm. Silica nanoparticle sol (X-tec 3408) was obtained from Nano-X GmbH. Cationic binder for nanoparticle silica coatings (Cytec C-442) was a product of Cytec Industries. Carbon black (Vulcan® XC72) was from Cabot Corporation. Titania powder, BTSE and all reagents used for carbon modification with the exception of carbon black itself were purchased from Sigma Aldrich and used as received. Toray (0.5 mm, Toray Industries) carbon diffusion paper was used in all ex situ contact resistance measurements and in situ fuel cell evaluations.

2.2. Preparation of functionalized carbon

Functionalization of carbon blacks was carried out using standard diazonium coupling chemistry [15]. A representative functionalization for phenylsulfonic acid (PSA) modified carbon is described as follows: a 500 mL round bottom flask (2 neck) with Teflon coated stir bar was charged with Vulcan® XC72 carbon (10 g), 50 mM nitric acid (250 mL), isopropyl alcohol (15 mL), and sulfanilic acid (5.20 g, 30 mmol). This mixture was cooled to 0 °C with stirring and a 1.1 M solution of sodium nitrite (30 mL) was added drop wise. Following this addition the mixture was stirred for 2 h at 0 °C at which point formic acid (6.91 g, 0.15 mol) was added drop wise

with stirring. The cooling bath was removed and the mixture left to warm to ambient temperature overnight. The following morning the temperature was raised to 70 °C for 1 h. The mixture was then cooled to ambient and the carbon passed through a 2.5 μm filter. Next, the material was washed with deionized water and split into separate portions in centrifuge tubes to be spun down. Centrifugation was repeated once more followed by washing and centrifugation with isopropanol and finally acetone. The carbon material was then dried under vacuum for two days. Carboxylic acid modified carbon (COOH) was made in a similar fashion using identical molar ratios by exchanging sulfanilic acid with 4-aminobenzoic acid.

2.3. Preparation of BTSE sol and carbon suspension

A 40 mL Nalgene container was charged with ethanol (6.0 mL), deionized water (0.72 mL), BTSE (4.65 mL), and 0.5 M sulfuric acid (0.125 mL). The container was capped, gently shaken, and left to age for 20 min to form reactive oligomeric species. This was then diluted with ethanol (270 mL) and the pH of the solution adjusted to approximately 2.0 using concentrated sulfuric acid. The solution was left overnight before combination with carbon. The modified hydrophilic carbon black was then added (432 mg carbon/40 mL BTSE solution) with stirring to the BTSE solution at a concentration of 10.8 g L^{-1}. In order to ensure dispersal and homogenization, the mixture was stirred for 10 min followed by a 10 min sonication. This procedure was repeated three times. Throughout the text, shorthand nomenclature for the silane and carbon composite coatings is indicated by BTSE-PSA and BTSE-COOH for the silane with phenylsulfonic acid (PSA) modified carbon and carboxylic acid (COOH) modified carbon respectively. Coatings exclusively composed of silane are indicated by BTSE.

2.4. Coating protocols

Coupons were degreased by sonication in a 20% aqueous solution of Simple Green® for 10 min followed by two separate 10 min sonications in deionized water. Finally the coupons were sonicated in ethanol twice for 10 min each.

The BTSE carbon solution was applied to coupons or stamped bipolar plates via a spray coating process (Iwata, HP-BC1 Airbrush). The coating was air dried at room temperature and then cured at 120 °C for 30 min. Finally, the hydrophobic coating was activated in deionized water at 80 °C for 12 h to generate a hydrophilic surface. Coating thickness measurements of the pure, transparent BTSE coating were made using an elipsometer (Accurion, EP3-SE). A Surface Profilometer (Veeco Dektak 3) was used to measure the thickness of the BTSE-carbon coatings.

Silicon dioxide nanoparticles were applied to the coupons using a multilayer adsorption (MLA) process [5] in which the degreased coupons were: (1) dipped into a cationic polyelectrolyte (Cytec C442, 0.36 g L^{-1}, 1.0 pH) for 3 min at room temperature to acquire a positively charged surface, (2) rinsed in deionized water for 2 min to remove poorly adhered polymer, (3) dipped into a 10% diluted (50/50, water/ethanol) and negatively charged Nano-X sol for 3 min, and then (4) rinsed in deionized water for 2 min to remove loosely bound silica particles and form a monolayer of silica. The 4-step process is repeated to build up the desired thickness. For example, a 4 dip MLA experiment repeats this 4 step procedure four times and generates a silica thickness of approximately 100 nm based on X-ray fluorescence spectroscopy (Phillip Analytical, PW4202).

The titania coating was prepared using a stock solution of 10% titanium oxide nanoparticles (<75 nm) suspended in water. The solution was applied to the surface of the samples via brush coating and then dried in approximately 20 s using a hot air gun to a thickness of approximately 3–5 μm as measured by electron probe microanalysis (EPMA).

2.5. Contact resistance characterization

Electrical contact resistance measurements were made on small coupons using a 4 point probe method and Toray gas diffusion layers (GDLs). The sample was compressed between two GDLs at predetermined pressures using a force controlling instrument (Instron 5565) and subjected to a known current perpendicular to the surface. Details of the experimental setup can be found elsewhere [16].

2.6. Hydrophilic coating assessment

Static water contact angle (WCA) measurements were made on the small coupons used in ex situ testing with a contact angle meter (Kernco Instruments Co., Model G-II). Hydrophilic retention of the various coatings was assessed by placing a 10 μl drop of deionized water into each channel and measuring the water wicking length before and during in situ fuel cell testing. The fuel cell was operated at 80 °C with 7 psig reactant gas pressures and the wet/dry fuel cell humidity was cycled over the following schedule: 1 day at 100% relative humidity (RH) (wet) followed by 1 day 40% RH (dry).

3. Results and discussion

3.1. Carbon/silane coating

Carbon black was chosen as the conductive component of the films for its known electrical conductivity, robustness to the fuel cell environment, and low cost. Carbon in its native form is insufficiently hydrophilic to adequately wet water at the coating surface based on experience with vapor deposited carbon coated bipolar plates [12–14]. However the carbon particle surface can be chemically modified to introduce polar hydrophilic species using known techniques [15]. Conductive carbon black was made hydrophilic to enhance wetting behavior by grafting phenylsulfonic acid (PSA) or carboxylic acid (COOH) groups onto its surface. Since these moieties are ionic, the modified carbon black should be robust to external contamination, increasing the likelihood that the surface will remain hydrophilic throughout the stack life even under dry fuel cell conditions. Film composition was set at 58 wt% carbon. This level ensured that carbon particle volume fraction was above the critical pigment volume, a level such that it would not be completely encapsulated by silane binder material and produce a percolating network of carbon for high conductivity [17].

Silanes are a natural choice to bind carbon particles to the surface due to their ability to condense under mild conditions and produce a robust network with the potential to withstand the fuel cell environment [18]. Many silanes possess multiple condensable linkages and are used in a variety of applications such as water-repellents, mineral surface treatments, pigment dispersants, anti-fog coatings, release coatings and crosslinkers for silicones. In particular, dipodal silanes have been shown as effective barriers for corrosion protection coating for metals containing surface hydroxyls [19]. A dipodal silane (BTSE) with the structure shown in Fig. 1 was selected as the carbon particle binder due to excellent hydrolytic stability reported as 10^5 times greater than conventional silanes [20]. With six hydrolyzable groups per molecule, the crosslink density of the condensed film is large, creating a strong durable network. Such networks also have the ability to reversibly break and form siloxane bonds in an aqueous environment to produce a mixture of siloxane (hydrophobic) and silanol (hydrophilic) groups at the surface [18]. It was hypothesized that under wet fuel
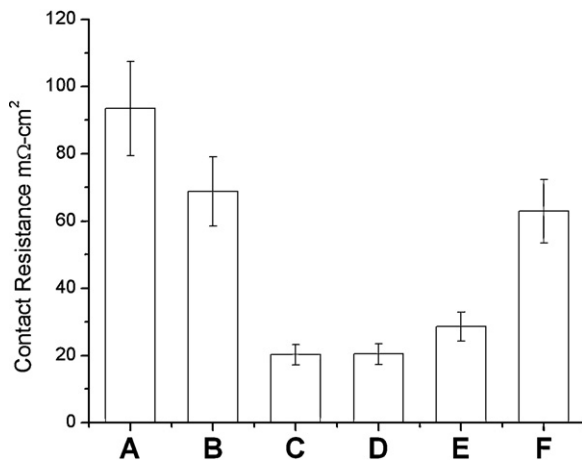
Fig. 3. Comparison of contact resistance values at 1.4 MPa for stainless steel and stainless steel with BTSE-PSA coating for passivated SS surfaces, surfaces with oxide layer removed, and following drying and soaking. Samples: A, passivated SS; B, passivated SS + BTSE-PSA; C, non-passivated (cleaned) SS; D, non-passivated SS + BTSE-PSA; E, non-passivated SS + BTSE-PSA dried at 120 °C for 30 min; F, non-passivated SS + BTSE-PSA water soaked at 80 °C for 18 h. Error bars display ± standard deviation with $n = 5$.

Fig. 4. Contact resistance of gold coated SS with BTSE-PSA coating under different aging conditions at 1.4 MPa. Samples: A, gold coated SS; B, gold coated SS + BTSE-PSA; C, gold coated SS + BTSE-PSA dried at 120 °C for 7 days; D, gold coated SS + BTSE-PSA water soaked at 80 °C for 37 days. Error bars display ± standard deviation with $n = 5$.

cell conditions (80–100% RH), equilibrium would produce a sufficient number of hydrophobic siloxane bonds to maintain a coherent and dense crosslinked film while simultaneously producing a high density of silanol groups that would promote water spreading. This reversibility also enhances wet adhesion as bond breaking and reforming helps to eliminate residual stresses in the film created during condensation [18]. It was also hypothesized that under wet conditions the rate of depolymerization of siloxane linkages would be insignificant in the presence of low levels (0.1–1 ppm) of hydrofluoric acid – degradation product of perfluorosulfonic acid membranes in PEMFCs – due to the high crosslink density of dipodal BTSE. Under dry fuel cell conditions (~40% RH), it was considered highly likely that equilibrium would shift toward siloxane linkages, resulting in a loss of hydrophilicity which would be mitigated by the polar groups on the modified carbon surfaces.

Coatings were prepared by initially dissolving the silane precursor in a mixture of water and alcohol at reduced pH to produce a sol. This solution could then be used to disperse the modified carbon particles that were more readily suspended in the mixture compared to untreated carbon black. These particulate suspensions are easily deposited onto surfaces using conventional spray coating technology giving the advantage of easily controlled film thickness and rapid throughput to enhance scalabilty.

3.2. Electrical contact resistance

The contact resistance at the GDL interface between carbon fiber and untreated stainless steel ranges from 75 to 120 mΩ cm^2 at 1.4 MPa depending on the stainless steel alloy and GDL type [21,22]. This high contact resistance is attributed to the insulating oxide layer on the stainless steel surface that passivates the alloy under cathode side potentials of a PEM fuel cell. Typically, the oxide layer is reduced or removed cathodically, chemically or physically before gold or carbon coatings are applied. In this study, the oxide layer was removed chemically with a 0.1 M HF/1.0 M H$_2$SO$_4$ solution at 80 °C for 10–20 s. Fig. 3 presents contact resistance values of stainless steel surfaces comparing presence of a passivation layer, composite coatings, and aging treatments. The results illustrate the need for an oxide layer removal step to generate a low beginning of life contact resistance. At 1.4 MPa, the contact resistance for passivated 304L stainless steel against either the GDL or the
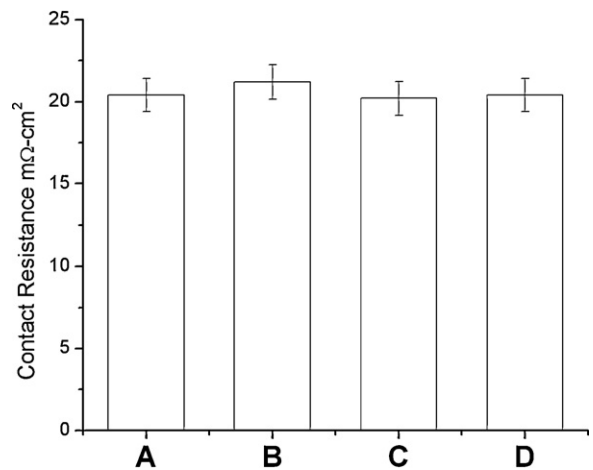
BTSE-PSA carbon coating exceeds 65 mΩ cm^2 and is unacceptable. However, if the stainless steel substrate is first chemically treated in an HF/H$_2$SO$_4$ solution to eliminate the passive film, the contact resistance of the stainless steel with and without the hydrophilic coating meets target levels. Unfortunately, the BTSE-PSA carbon film is not impervious to oxygen and water, and contact resistance increases substantially after only 30 min of drying at 120 °C and <2% relative humidity (RH) or after 18 h of exposure to 80 °C water.

In order to meet contact resistance requirements either gold or carbon undercoats must be used with these films. Fig. 4 shows the result of having a conductive underlying gold coating to produce and maintain low contact resistance when using the carbon and silane composite coating BTSE-PSA. In this situation, the resistive GDL fiber to oxide interface is replaced by a conductive GDL fiber to gold interface. As a result, the samples with underlying gold coating generated and maintained low contact resistance even when exposed to a 120 °C air temperature for 7 days and to 80 °C water for 37 days. Low electrical contact resistances were also maintained with BTSE-PSA top coats on PVD carbon (data not shown).

Hydrophilic coatings deposited on hydrophobic surfaces typically show enhanced wetting with increasing coating thickness. Water droplets on the surface show improved wetting character as increasing film thickness steadily reduces the hydrophobic contribution of the underlying substrate. Fig. 5 shows the contact resistance of stainless steel surfaces that have a hydrophilic and conductive composite coating on top of an underlying gold coat. The combination of modified carbon black and silane binder enables the use of these thicker coatings without sacrificing through plane conductivity. At 1.4 MPa, the thickness of BTSE coatings without carbon black must not exceed 40–60 nm in order to meet the one sided (electrode to sample) contact resistance requirement of less than 10 mΩ cm^2 for a gold plated stainless steel coupon. In contrast, no significant increase in contact resistance compared with gold alone was realized with BTSE-COOH and BTSE-PSA coatings at the maximum thickness tested of 570 and 630 nm respectively.

Gold and carbon with water contact angles (WCA) ranging from 60 to 80° are not sufficiently hydrophilic for water management and require surface modification for hydrophilicity. Excellent hydrophilicity (WCA < 15°) is achieved with silica and titania coatings on gold coated stainless steel, but at the expense of an increase in contact resistance. Fig. 6 presents the contact resistance versus pressure data of these films where the silica coating was applied with four cationic polymer and silica bilayers for a thickness of approximately 100 nm, while the titania top coat on gold was
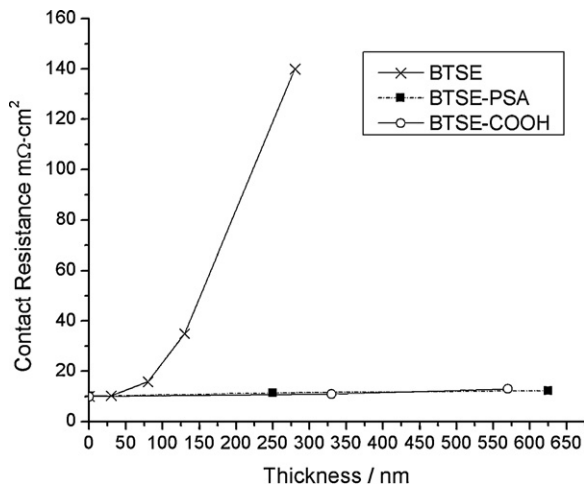
Fig. 5. Effect of coating thickness and composition on the electrical contact resistance of gold plated stainless steel coupons at 1.4 MPa compression pressure. Coupons coated on one side only with BTSE, BTSE-PSA, and BTSE-COOH. Contact resistance of one side of a bare gold plated stainless steel coupon corresponds to 10.1 mΩ cm² as shown at 0 nm thickness in the figure above.

roughly 3–5 μm thick. Both silica and titania based coatings show a significant increase at 1.4 MPa of 16 and 22 mΩ cm² respectively when applied to gold coated stainless steel coupons. In contrast, a contact resistance increase of <2 mΩ cm² is observed with the two hydrophilic BTSE-PSA (260 nm) and BTSE-COOH (330 nm) coatings on gold coated stainless steel surface at the same pressure.

Fig. 7 displays the effects on contact resistance for films when the underlying conductive gold coating is replaced with PVD carbon. An even larger increase in contact resistance is observed at 1.4 MPa for silica and titania on underlying PVD carbon of 101 mΩ cm² and 181 mΩ cm² respectively. In contrast, the BTSE-PSA and BTSE-COOH top coats again show a negligible effect on contact resistance on PVD carbon. In both cases of gold and PVD carbon coatings in contact with the GDL, the conductive BTSE-PSA and BTSE-COOH coatings outperform inorganic films of silica and titania by exhibiting no significant increase in contact resistance while presenting a hydrophilic surface.
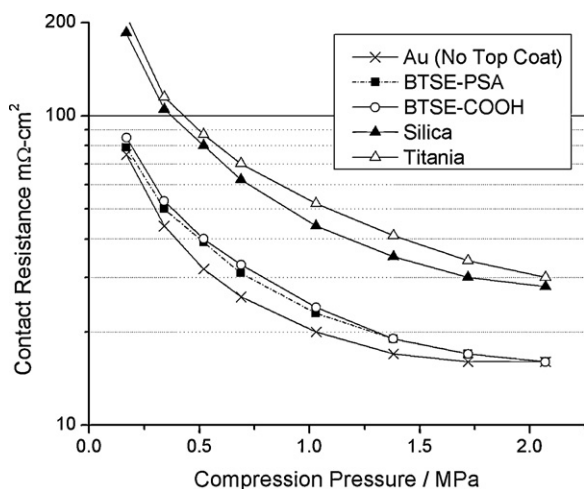

Fig. 6. Electrical contact resistance of gold plated stainless steel coupons coated with insulating silica (100 nm) and titania (3000 nm) along with conductive hydrophilic coatings BTSE-PSA (260 nm) and BTSE-COOH (330 nm).

Fig. 7. Electrical contact resistance of PVD carbon-coated stainless steel coupons coated with insulating silica (100 nm) and titania (3000 nm) along with conductive hydrophilic coatings BTSE-PSA (260 nm) and BTSE-COOH (330 nm).
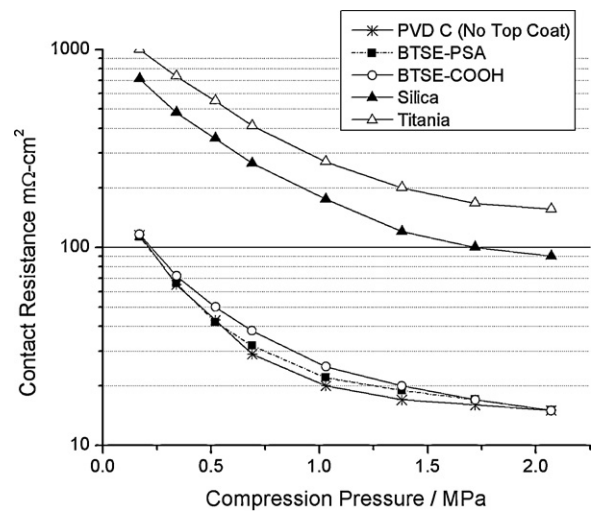
3.3. Hydrophilicity

3.3.1. Ex situ oven testing

For hydrophilic surfaces, lower WCAs can be achieved by increasing the surface roughness, and for a given intrinsic surface energy, there is a critical roughness above which the liquid will spread spontaneously due to capillary forces [8]. The titania sample demonstrates high roughness or surface area as shown in Fig. 8d through primary particles <100 nm associated into a larger aggregate structure. The modified carbon coatings (Fig. 8a and b) possess a similar morphology to that found in the titania coatings creating high surface area porous networks and enhanced wetting. In addition, overall thickness of the coating is important in that wetting predicted by Wenzel's equation will occur only if the surface texture can completely draw up the volume of the deposited droplet. Minimum thicknesses were required for silica and titania to reliably achieve excellent hydrophilicity (WCA < 15°) due to thinner films resulting in exposure of the underlying hydrophobic gold coating and poor wetting. For the titania used in this study, this critical thickness was determined empirically and corresponds to approximately 1 μm which is met with the 3 μm coatings used in our study while silica required at least 100 nm thickness to achieve its maximum wetting performance.

In order to simulate wet fuel cell conditions, coatings were soaked in 80 °C water for extended periods and tested at set intervals to track changes in hydrophilicity. Acceptable wetting was set at a WCA ≤ 15°. Fig. 9 displays the time when hydrophilicity is degraded by the WCA exceeding this target during 80 °C water soaking for hydrophilic coatings on gold coated stainless steel coupons. The coatings include layer by layer deposited silica (100 nm), brushed titania (3000 nm), BTSE (50 nm), BTSE-COOH (330 nm) and BTSE-PSA (260 nm). The silica coating lost hydrophilicity as a result of poor wet adhesion to the gold coated stainless steel surface after roughly 600 h. Likely causes for this behavior are related to the cationic binder used for these coatings being known to hydrolyze in hot aqueous solutions [23]. Hydrophilicity retention is superior for the titania and carbon composite coatings as no increase in WCAs was observed during 2005 h of 80 °C water immersion. The initial WCA for the carbon silane composite coatings ranged from 60° to 80° for BTSE without carbon and 30° to 40° for BTSE-PSA and BTSE-COOH modified carbon and silane composites, indicating exposure of the modified hydrophilic carbon black particles to the surface and efficacy
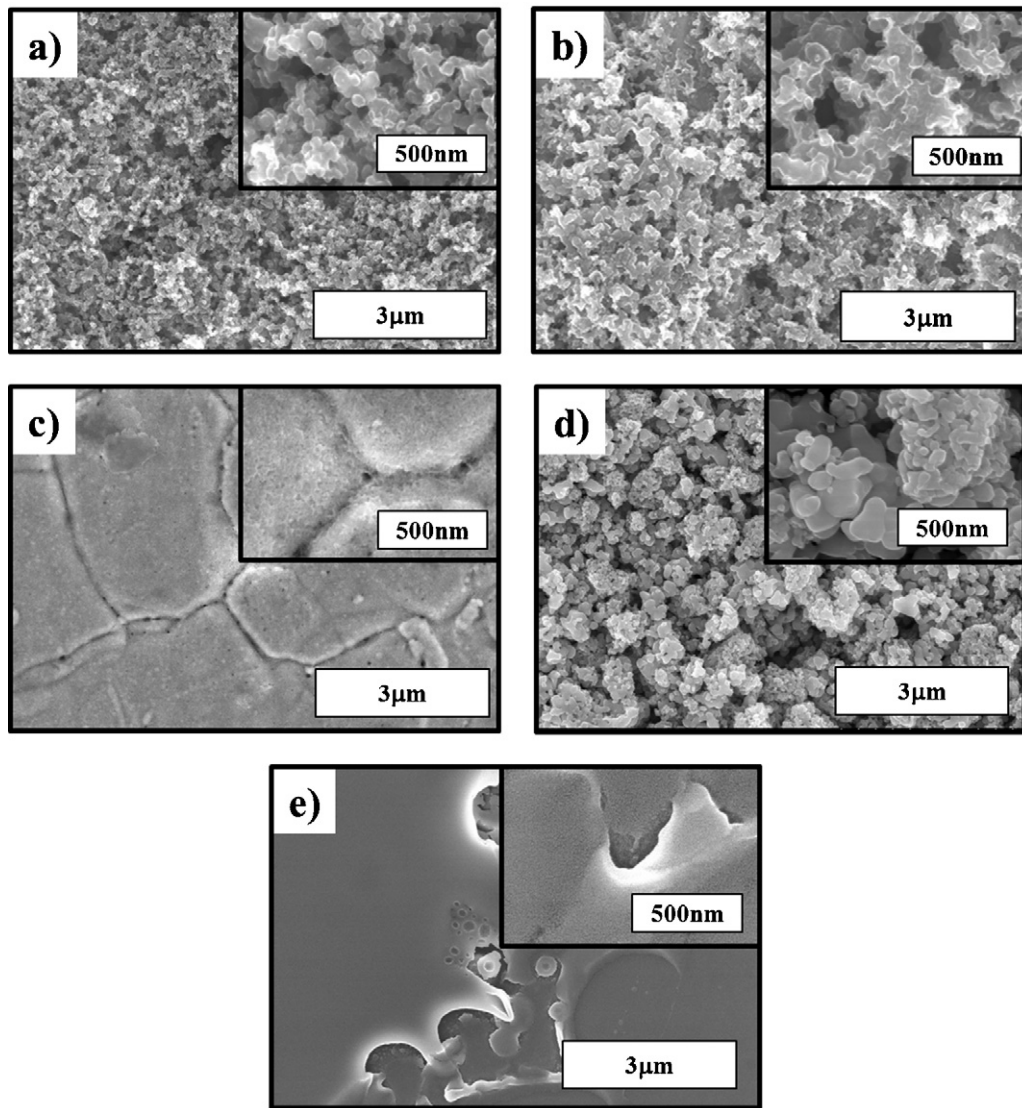
Fig. 8. SEM micrographs of hydrophilic coatings: (a) BTSE-PSA, (b) BTSE-COOH, (c) silica, (d) titania and (e) BTSE.
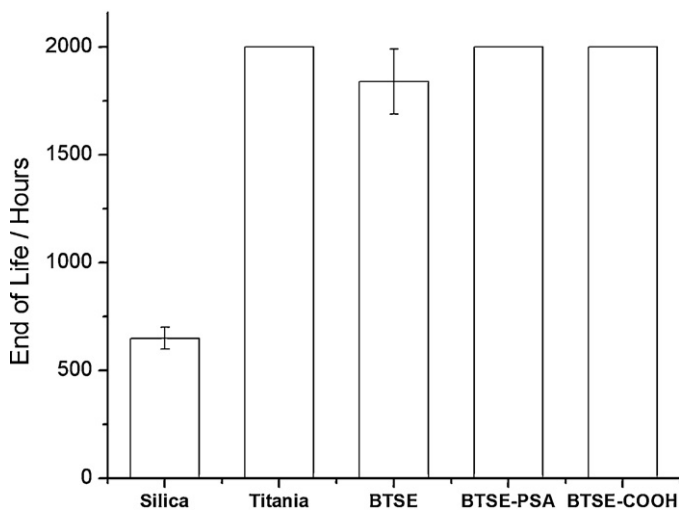

Fig. 9. End of life (water contact angle exceeds 15°) for coatings on gold coated stainless steel coupons water soaked at 80 °C. Test terminated after 2005 h.

at improving wetting. After curing, the WCAs are initially high due to the formation of hydrophobic siloxanes from the condensation of silane functional groups. Following water soaking for 24 h at 80 °C the silane based samples exhibited stable WCA < 10°. This is due to the BTSE based samples undergoing both hydrolysis and condensation during 80 °C water immersion. This soaking produces silanol groups needed for hydrophilicity while condensation generates a crosslinked siloxane matrix needed for adhesion and mechanical integrity. Two of the four pure BTSE samples became less hydrophilic over time with WCAs increasing to 19 and 20° after 1632 h of soaking, while WCAs for all composite BTSE-PSA and BTSE-COOH samples remained strongly hydrophilic due to the additional functionalized hydrophilic carbon component with less than 10° WCA throughout the duration of the test (2005 h).

Over the anticipated 10 year lifetime for an automotive fuel cell, the unit is regularly cycled between wet and dry states. A major concern surrounding the use of PEM fuel cell hydrophilic coatings is their wetting stability upon exposure to dry conditions. Contaminants such as air borne hydrocarbons, lubricating oils, and plasticizers are attracted to high energy silanol containing surfaces such as these. This is particularly the case under dry conditions in which electrostatic attraction forces between the coating surface
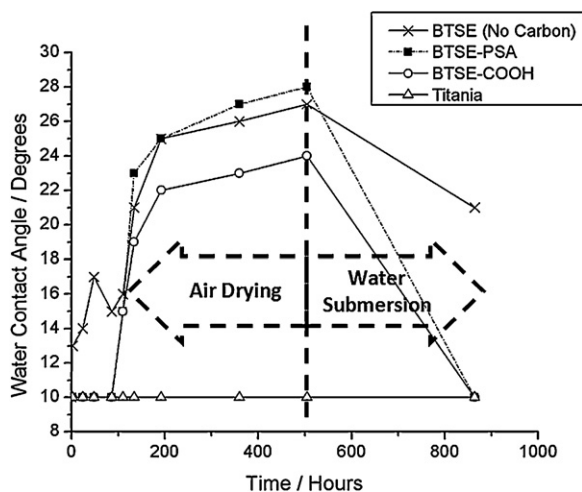
Fig. 10. Water contact angles (WCA) of gold coated stainless steel coupons. Coupons were subjected to 504 h in a dry oven environment (80 °C, 1% RH) followed by 360 h of submerged in water (80 °C).

dry oven conditions. Exposure of these samples to wet conditions at the 504 h point results in the pure BTSE coating regaining some degree of hydrophilicity, but not enough to produce a WCA under 15°. However, after exposure to wet conditions in 80 °C water for 360 h, the BTSE-PSA and BTSE-COOH coatings both recover their initial WCA hydrophilicity of approximately 10°. This reversibility demonstrates potential for successful performance in the fuel cell environment where cycle times between wet and dry states are much shorter and the severity of the dry condition is less than in the above testing.

3.3.2. In situ fuel cell testing

In order to determine how these coatings will behave in a more realistic fuel cell environment where relative humidity ranges from 40% to 100% and wet and dry cycle times are shorter than the conservative ex situ test conditions, coated bipolar plates were fuel cell tested in single cells. At 40% RH, physisorbed and chemisorbed monolayers of water on the coating surface may reduce surface charges and, in turn, electrostatic attraction with oppositely charged contaminants [24]. While the nature and concentration of contaminants in a fuel cell versus those encountered in the ex situ oven testing is beyond the scope of this study, there are many potential sources specific to the fuel cell environment that must be considered. These include contaminants originating from the reactive air stream and from the plastic components of the external gas and coolant delivery system. At 100% RH, liquid water is generated, but the plate only encounters intermittent water droplets as the flow field channels are purged with reactant gases. Hence, if the plate surface is contaminated and becomes less hydrophilic, the amount of liquid water may be inadequate to restore the surface to a hydrophilic state. In order to address these uncertainties, coatings that showed strong hydrophilic durability in ex situ testing including titania, BTSE-PSA, and BTSE-COOH coatings were selected for fuel cell testing.

Carbon and silane composite and $3 \mu m$ thick titania coatings were deposited on a stamped and gold coated stainless steel bipolar plate (Fig. 2) and evaluated in a $50 \, cm^2$ single cell geometry. Hydrophilicity of these coatings was assessed initially and at selected time points during the test by measuring the wicking length of a $10 \mu L$ water drop deposited at one end of each channel. The water wicking lengths for all coatings are reported in centimeters as a function of fuel cell run time as shown in Table 1. A wicking length of approximately 2 cm is considered to be sufficient for good fuel cell performance based on previous stack testing. For comparison, untreated gold coated stainless steel typically shows a value of 0.5 cm with this test. The titania coating showed no drop off of excellent wetting (6–7 cm) and spatial uniformity after 1250 h of fuel cell testing. This is in agreement with short stack test results in which titania coatings retained hydrophilicity after 5120 h of fuel cell testing on large gold coated plates (stack data

and the contaminant are larger and in which silanol groups are less protected with a physisorbed layer of water [24,25].

In order to assess the ability of coatings to withstand dry conditions, samples were placed in an 80 °C (1% RH) oven environment to be exposed to elevated temperatures and hydrocarbon contaminants naturally found in the atmosphere. This is a more aggressive atmosphere than the anticipated dry fuel cell environment (80 °C, 40% RH) to better ensure suitability of screened candidates for extended fuel cell stack testing. Fig. 10 shows WCA data for similarly prepared silane and titania based samples on gold coated stainless steel. In this test, the hydrophilic coatings were first exposed to dry oven conditions (80 °C, 1%RH) for 504 h and then submerged in water (80 °C) for 360 h. Time zero for the carbon silane composites corresponds to the 24 h time period after activation to achieve WCA < 10°. The titania coating was robust to contamination throughout the entire 504 h of dry exposure due to its intrinsic hydrophilicity and surface roughness. Early on during dry exposure, the carbon and silane composite coatings are more contamination robust compared to the pure BTSE coating. The former coatings demonstrated <15° WCA for about 90 h while the pure BTSE exceeded 15° WCA after only 48 h of exposure. The combination of ionic moieties and increased surface roughness found in the composite coatings clearly promote water wetting beyond what BTSE, which lacks surface texture (Fig. 8e) and hydrophilic chemical functionality, is capable of alone. Midway through dry exposure however, the WCAs for the two silane and carbon composite based coatings are similar and exceed the 15° WCA criteria. Neither coating is sufficiently hydrophilically robust under the aggressive 80 °C

Table 1
Wicking lengths (in cm) for $10 \mu L$ water drops in coated channels across regions of the stamped metal bipolar plates as a function of aging time in the fuel cell environment for BTSE-PSA, BTSE-COOH, and titania coatings.

Area	BTSE-PSA			BTSE-COOH			Titania		
	0 h	216 h	937 h	0 h	676 h	1273 h	0 h	720 h	1250 h
Anode									
WA	5.0 ± 0.0	3.4 ± 2.2	0.5 ± 0.0	6.0 ± 0.0	4.4 ± 0.5	3.0 ± 0.0	6.6 ± 0.5	6.0 ± 0.0	6.0 ± 0.0
WB	5.0 ± 0.7	4.8 ± 0.4	4.8 ± 0.4	5.6 ± 0.5	4.4 ± 0.5	3.8 ± 0.4	6.2 ± 0.4	6.4 ± 0.5	6.2 ± 0.4
NC	5.0 ± 0.0	5.0 ± 0.0	4.2 ± 0.4	5.0 ± 0.0	4.8 ± 0.4	4.8 ± 0.4	6.2 ± 0.4	6.2 ± 0.4	6.0 ± 0.0
ND	5.0 ± 0.0	5.0 ± 0.0	5.0 ± 0.0	5.0 ± 0.0	4.6 ± 0.5	4.2 ± 0.4	6.0 ± 0.0	6.2 ± 0.4	6.0 ± 0.0
Cathode									
WA	4.5 ± 0.6	4.6 ± 0.5	2.5 ± 1.7	6.0 ± 0.0	3.2 ± 0.4	3.0 ± 0.0	6.2 ± 0.5	6.0 ± 0.0	6.0 ± 0.0
WB	5.0 ± 0.0	3.0 ± 0.0	0.7 ± 0.3	5.6 ± 0.5	3.8 ± 0.4	3.2 ± 0.4	6.0 ± 0.0	6.4 ± 0.5	6.2 ± 0.4
NC	4.8 ± 0.4	4.8 ± 0.4	3.6 ± 0.9	5.2 ± 0.4	4.8 ± 0.4	4.0 ± 0.0	6.2 ± 0.4	6.0 ± 0.0	6.0 ± 0.0
ND	5.0 ± 0.0	5.0 ± 0.0	2.6 ± 0.5	5.0 ± 0.0	4.8 ± 0.4	4.0 ± 0.0	6.4 ± 0.5	6.2 ± 0.4	6.0 ± 0.0

not shown). In the active area of the plate where the titania is in contact with the carbon based GDL material, the coating exhibited uniform hydrophilicity. Only in the cross flow plate areas, where the titania coating directly contacts polymer subgasket material was hydrophilicity uniformly lost (0.5 cm wicking length). These observations suggest that the titania coating is not completely robust to contamination but with proper selection of fuel cell stack materials, a stably hydrophilic plate surface is possible.

Initially, the BTSE-PSA coating is uniformly hydrophilic with wicking lengths of approximately 5 cm. After 216 h of fuel cell testing, the largest wicking length decreases were at 3 cm and found in the wide land area of section WA of the anode and WB of the cathode, the wide land area of section WA of the anode. After 937 h of testing, water wetting essentially ceased in wide land plate regions WA under anode conditions and land region WB under cathode conditions with length measurements of approximately 0.5 cm, while hydrophilicity was retained in narrow land areas at 2–5 cm wicking lengths. This spatial inhomogeneity in hydrophilicity is attributed to contamination effects and not loss of coating due to poor adhesion since the presence of the black opaque coating was clearly observed upon completion of the fuel cell test. Time points for the BTSE-COOH coating are given at 0, 676 and 1273 h. After 1273 h of fuel cell testing, the anode and cathode plates maintained spatially uniform hydrophilicity, although some loss was observed as wicking lengths decreased from 5–6 cm initially to 3–4 cm at 1273 h. This result is quite promising in that it demonstrates the potential for silane and carbon composite coatings that can display long term wetting behavior under realistic fuel cell testing conditions.

4. Conclusions

A new type of hydrophilic and conductive coating based on a silane compound, 1,2-bis(triethoxysilyl)ethane, combined with modified hydrophilic carbon black was developed to improve water management at the bipolar plate while providing low electrical loss. BTSE and BTSE combined with either phenylsulfonic acid (PSA) or carboxylic acid (COOH) modified carbon were investigated and coatings tested for increase in contact resistance and hydrophilicity retention using ex situ techniques and in situ fuel cell testing. While carbon filled BTSE coatings still required an underlying conductive layer of gold or PVD carbon to maintain acceptable contact resistance, thick coatings (∼600 nm) of BTSE-PSA and BTSE-COOH showed negligible increase in contact resistance on both gold and PVD carbon coated stainless steel. This compares favorably to insulating coatings of silica or titania that begin to increase contact resistance above roughly 60 nm thickness. Wetting performance of thick 3 μm titania films retained excellent

hydrophilicity under both wet and dry conditions due to small particle size and high surface area. BTSE with and without modified carbon retained excellent hydrophilicity during 80 °C water soaking over 2000 h, but did not maintain <15° WCA during overly aggressive oven drying (80 °C). However, unlike BTSE alone, the carbon and silane composite coatings demonstrated the ability to recover hydrophilicity when exposed to water following drying. Under actual small scale fuel cell testing, the conductive BTSE-COOH and insulating titania coating remained hydrophilic after 1200 h with moderate loss of wicking behavior observed for BTSE-COOH due to external contaminants. Based on these promising results, large scale fuel cell testing of BTSE-COOH is warranted to continue assessment of contamination robustness and hydrophilicity retention under realistic vehicle contamination and operating conditions. Future performance could likely be improved through modification of silane and carbon composite coating morphology, particularly increased thickness, to better replicate structural features found in the titania coatings.

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