Carbon-polymer composite coatings for PEM fuel cell bipolar plates

Hans Husby¹, Ole Edvard Kongstein², Anders Oedegaard² and Frode Seland¹,*

¹Department of Materials Science and Engineering, Norwegian University of Science and Technology, 7491 Trondheim, Norway

²SINTEF Materials and Chemistry, 7465 Trondheim, Norway

*Corresponding author. Department of Materials Science and Engineering, Norwegian University of Science and Technology, 7491 Trondheim, Norway, e-mail: frode.seland@ntnu.no, tel: +47 73594042, fax: + 47 73591105.

Abstract

A carbon-polymer composite coating on stainless steel 316L substrates was investigated for the use as bipolar plate material for polymer electrolyte membrane fuel cells. The coating consisted of 45 vol % graphite, 5 vol % carbon black and 50 vol % epoxy binder. The coating was applied by a spraying technique followed by hot-pressing while the binder cured. An interfacial contact resistance of 9.8 mΩ cm² at a compaction pressure of 125 N cm⁻² was measured. Ex-situ electrochemical tests showed that the carbon-polymer composite coated plates had smaller increases in the interfacial contact resistance after polarization than bare stainless steel plates at potentials of 0.0191 and 0.6191 V_SHE. At 1.0 V_SHE, the resistance increased similarly for both the coated plate and the bare stainless steel plate, and reached unacceptable values. The porosity of the coating was estimated with scanning electron microscope imaging of the cross-section of the coating to be about 50 %.

Keywords
1. Introduction

Polymer electrolyte membrane (PEM) fuel cells are pursued as a replacement for the internal combustion engine in vehicles, but cost, performance and durability are critical challenges to commercialization [1]. The bipolar plate is a source of durability constrains, and accounts for up to 75 % of the volume and 11 - 45 % of the total cost of a fuel cell stack [2]. The bipolar plate performs important tasks like collecting current, separating the individual cells, distributing fuel and oxidant within the cells, carrying water out of each cell, and cooling the cells [3].

Metallic bipolar plates are desired due to good physical properties like high strength, no brittleness, no permeability to reactant gases, and especially the possibility for low cost mass production by e.g. hydroforming or stamping. The U.S Department of Energy (DOE) has put forward a set of technical targets for year 2020 with respect to the bipolar plate [1]. The relevant, and challenging, targets for metallic bipolar plates are i) a corrosion rate below 1 µA cm\(^{-2}\), and ii) an interfacial contact resistance (ICR) below 10 mΩ cm\(^{-2}\) at a compaction pressure of 140 N cm\(^{-2}\). These must be achieved while keeping the cost below 3 $kW\(^{-1}\).

Stainless steel has been investigated as a bipolar plate material in numerous works. Some have reported that fuel cell output was stable for thousands of hours with satisfyingly low corrosion rates [4, 5], but the majority concludes that if stainless steel is to be used, it must be protected by a coating [6-8]. This is either due to a too high corrosion rate, or because of unacceptable ICR values as a result of formation and growth of an oxide surface film with poor electrical
conductivity. A coating can prevent corrosion as well as oxide formation while facilitating electrical conductivity.

Carbon-polymer composite bipolar plates are well-established as a commercial product and have been subject for extensive research [9-11]. Protecting the metallic substrate by a carbon-polymer composite coating has been done on previous occasions [12-16]. The coating mixtures and the method for coating application have varied, resulting in reported contact resistance values ranging from around 12 and up to above 100 mΩ cm² at compaction pressures around 140 N cm⁻².

In this work we apply a carbon composite coating to 316L stainless steel substrates (SS 316L) with a spraying technique, and improve the density and quality of the coating by a subsequent hot-pressing step during the epoxy curing stage. The ink composition used has previously been optimized for injection molding [9, 17, 18] and adapted for this work. The coating is evaluated with scanning electron microscopy (SEM) imaging, interfacial contact resistance measurements of bulk electrical conductivity and conventional electrochemical testing. The resulting interfacial contact resistances and apparent currents with this way of preparing a carbon based coating are promising with respect to reaching the targeted goals put forth by the department of energy for 2020.

2. Experimental

2.1. Preparation of substrate, mixing of coating and coating application

SS 316L plates (length: 13.13 cm, width: 1.25 cm, thickness: 0.08 cm, rounded corners, no flow field) were used as coating substrates. To prepare the substrates for coating application, they were etched in 12.5 vol % hydrochloric acid for 15 minutes and rinsed in distilled water before they were dried in air. The exposed geometric surface area was 16 cm² and limited to one side of the
bipolar plate. The back side and edges of the plate were made electrochemically inactive by applying a complete layer of electroplaters lacquer. This lacquer was removed chemically with acetone prior to any ICR measurements.

The coating consisted of 45 vol % graphite (KS6, TIMCAL), 5 vol % carbon black (Super P-Li, TIMCAL) and 50 vol % epoxy (Carbomastic 18 FC, Carboline Norge AS). The epoxy was thinned with xylene to consist of 95 vol % solvent. The suspension was put in an ultrasonic cleaner bath to disperse the carbon particles before it was applied to the substrate with a spraying technique. The coated plates were pressed in a hot press at 1210 N cm⁻² at 110 °C for three hours immediately after spraying, and subsequently cured for 16 hours in a heating furnace at 100 °C. Four different coating thicknesses were prepared in this work. Furthermore, a low alloy structural steel (ST52) was used as a substrate material instead of the SS 316L material for comparison.

2.2. Characterization of coating and coated plates

Electrochemical measurements were performed in a standard three electrode setup, where the working electrode consisted of a bipolar plate connected with a wire from the back side of the plate. The counter electrode was a large area Pt mesh, and a mercury-mercurous electrode (Hg/Hg₂SO₄/SO₄²⁻ in saturated K₂SO₄ solution) functioned as the reference electrode. The reference electrode was separated from the working electrode compartment with a salt bridge. A Gamry Ref600 potentiostat was used to apply the desired potential sequence between the working and reference electrode, and all potentials reported here are given with respect to the standard hydrogen electrode (SHE). To simulate PEM fuel cell environment, the electrolyte in the working
The electrode compartment consisted of a 1 mM H$_2$SO$_4$ solution at 75 °C, bubbled with nitrogen for at least 20 minutes to remove any dissolved oxygen. Even though oxygen gas will be present in an operating fuel cell it was found to have insignificant impact on the current at relevant operating temperatures. It is unlikely that oxygen plays a role in the corrosion reactions and the reason for oxygen removal is thus to avoid any contribution from oxygen in the measured currents (see also ref [19]). Furthermore, the electrode potential is kept within the region where water or sulphuric acid can’t react electrochemically, and oxygen is removed from the electrolyte. The only reactions that can occur are degradation processes involving the electrode/coating components.

Slow linear sweep voltammograms were performed from a starting potential of -0.26 V$_{SHE}$ and up to 1.04 V$_{SHE}$ with a sweep rate of 2 mV s$^{-1}$. Potential hold experiments were performed for a total duration of one or 16 hours at potentials of 0.0191, 0.6191 and 1.0 V$_{SHE}$ on both coated and bare SS 316L plates. Electrochemical measurements (polarization or chronoamperometry) were never performed more than once on each plate.

ICR values of the coated plates were measured before and after the linear sweep voltammetry experiments. In experiments where the current response was measured, the side of the plates without coating was covered with an electrically insulating lacquer.

Ex-situ ICR values were found using the same measuring principles as described by Davies et al. [4], and illustrated in Figure 1. A total current of 2 A was applied, and resulted in a voltage drop due to through plane and contact resistances. Calibrating and controlling the measurement set-up allowed for separating out the contact resistances, which were measured as a function of increased compaction force.
A thin disk of ZrO$_2$ was coated in the same way as the stainless steel plates, and both surface and cross-sectional studies were done with a SEM (Hitachi S-3400N). To obtain a cross-sectional surface, the coated ceramic disk was immersed and broken in liquid nitrogen. The bulk electrical conductivity of the coating (in-plane) was measured on a coating deployed on a thin Teflon film by a square array four-point probe technique as first described by van der Pauw, [20].

3. Results and discussion

3.1. Microstructure and bulk electrical conductivity of coating

The theoretical thickness of the coating was estimated from weight difference before and after coating and density of the ingredients in the ink. In a cross-sectional image shown in Figure 2a the coating thickness after hot-pressing was measured to 21 µm. However, the actual thickness of the coating was almost twice the theoretical value (Figure 2a). Some local variations over the coated surface area exist, but the cross-sectional line that was examined by SEM showed a quite uniform thickness. This means that the porosity of the coating is usually around 50 % after the hot-pressing procedure. Figure 2 b) gives a representative SEM picture of the cross-section of a coating that was sprayed, but not hot-pressed. Comparing the thickness seen in this picture with the theoretical thickness of 5.6 µm, it is clear that the porosity is large. Hot-pressing of the coating after spraying can significantly reduce the porosity and surface roughness of the coating.
Figure 3 shows a SEM image of the surface of a coated plate. What is probably both carbon black (CB) and graphite (Gr) particles are seen in the image (pointed out by arrows). The CB particle clusters seem to be gathered in voids formed by the graphite network to create paths for electrical conductivity, in addition to the routes between graphite particles, thereby increasing the electrical conductivity of the composite as described in literature [21, 22].

The bulk electrical conductivities of carbon composite bipolar plates reported in literature primarily range from 1 to 1000 S cm⁻¹ [23]. Here, the electrical conductivity of the coating (in-plane) was measured twice with the resulting values 17 and 36 S cm⁻¹. Using the average value of the measured conductivities (26.5 S cm⁻¹) the contribution to the ICR from ohmic loss through a 15 µm coating was calculated to be as low as 0.06 mΩ cm². The ohmic loss through this coating is negligible compared to the ICR, but increasing the electrical conductivity in the coating by e.g. increasing the graphite content may however largely affect the ICR by increasing the contact area for charge transfer between carbon filler in the coating and the gas diffusion backing layer.

3.2. Linear sweep voltammetry

Figure 4 shows the polarization curves for the coated and bare SS 316L plates. The bare plate exhibited a normal “active/passive” behavior with a current peak at a potential of about 0 V_{SHE}, before it entered a passive state at higher potentials giving a low current density. The coated plate had a steady increase in current density with increasing potential and experienced no passivating region. The coated plate had a lower current density than the bare plate up to a potential of about
0.9 \text{ V}_{\text{SHE}} \text{ where the two current curves cross. The coating seems to protect the substrate from corrosion, at least at lower potentials. Corrosion of carbon allotropes to form CO and CO}_2 \text{ is known from literature to occur at elevated potentials [11, 24, 25], and might be a reason for the higher current density from the coated plate compared to the bare plate.}

<Figure 4>

The corrosion potential (where the net current density goes to zero) was more positive (more noble) for the coated plate than for the bare plate. Due to the low kinetic currents observed, the open circuit potential is strongly depending on all current generating processes between the working and reference electrode. For instance, the presence of small amounts of dissolved oxygen, or even oxygen gas trapped within the porous coating, would give rise to a reduction current yielding a higher open circuit potential. If there is a cathodic contribution to the current density from oxygen reduction, the current density will be larger than the recorded total current density.

ICR values before and after linear sweep polarization as a function of compaction pressure for coated and bare SS 316L plates are given in Figure 5. The bare plate experienced an increase in ICR from 21 to 47 mΩ cm\(^2\) with a compaction pressure of 125 N cm\(^{-2}\), while the coated plate had literally no change in ICR with a value of about 14 mΩ cm\(^2\). This indicates that the coating improves the ICR and possesses good chemical stability in PEM fuel cell environment. It is worth noting that the time spent at the high potentials are limited and thus can not be directly compared with the measurements performed over longer time periods. The bipolar plate flow field structures applied in this study were prepared by etching prior to each measurement, thus
giving the relatively low ICR for the bare stainless steel. Among all the plates that were coated in this work (about 25), the ICR values were primarily distributed between 10 and 20 mΩ cm². The lowest ICR value that was measured was 9.8 mΩ cm² at a compaction pressure of 125 N cm⁻², thus satisfying the DOE target for year 2020. Plates that were prepared in the same way, but without the hot-pressing step prior to the epoxy curing period, obtained ICR values of about 400 mΩ cm².

3.3. 16 hour potential hold experiments

Figure 6 shows the ICR values at a compaction pressure of 125 N cm⁻² before and after polarization of coated and bare SS 316L plates at various potentials for 16 hours. The coated plates suffered only a minor increase in ICR after polarization at potentials of 0.0191 V_SHE and 0.6191 V_SHE. Both the coated and the bare SS 316L plates had a large increase in ICR after holding the potential at 1.0 V_SHE, with an increase from 14.3 to 114.3 mΩ cm² and 17.9 to 123.6 mΩ cm², respectively. No visual degradation of the coating was observed. The degradation of the coated plates seemed to be more dependent on the hold potential than what was the case for the bare plates. A potential of 1.0 V_SHE is a harsh test and the Department of Energy (DOE) suggests holding the potential at about 0.83 V_SHE when testing for cathode environment [1].

Figure 7 gives the current densities during the 16 hour potential hold at 1.0 V_SHE for both coated and non-coated SS 316L plates. The current density was highest for the coated plate in the
beginning, until it decreased to zero for both plates after about eight hours, thus satisfying the DOE target for year 2020. The higher current density from the coated plate could possibly be explained by pinholes in the coating causing pitting corrosion of the SS behind the coating, but such corrosion has a tendency to increase or fluctuate over time rather than to give a steady decay in current. Corrosion of carbon material in the coating is a more reasonable explanation.

Bipolar plates prepared in the exact same way as described in the experimental section here were also tested in a single cell fuel cell test rig at temperatures up to 70 °C. The experimental test routine is described in Lædre et al [26]. These tests showed only a small change in contact resistance during the operation of the fuel cell to 16.2 mOhm cm$^2$ at 150 N cm$^2$ after testing.

3.4. Effect of coating thickness

Table 1 presents the current densities from four coated plates with different coating thicknesses and one bare SS 316L plate after one hour polarization at a potential of 1.0 V$_{SHE}$. The current density increased with increasing coating thickness with the bare stainless steel plate having the lowest corrosion rate. This linear increase in current can not be explained by dissolution of the substrate material alone, and is therefore an experimental proof of carbon corrosion in the coating. Due to the rather high porosity of the coatings, as estimated from the SEM images, the actual surface area will increase with increasing coating thickness causing the current density to increase as well. Carbon will also oxide at the steel-carbon interface, and when more carbon is removed more of the steel surface is exposed. This steel surface is then susceptible for oxide formation and subsequently leads to an increased interfacial contact resistance.

<Table 1>
3.5. Effect of substrate material

To examine how successfully the coating protected the substrate material, the SS 316L material was exchanged with a low alloy structural steel ST52 which is more prone to corrosion when exposed to the electrolyte. The current densities for coated and bare plates of SS 316L and ST52 when polarized at a potential of 1.0 $V_{\text{SHE}}$ for one hour are seen in Figure 8.

The current density from the coated and the bare ST52 material was orders of magnitude larger than the current density from the plates with SS 316L substrate material, as shown in Figure 8. The initial current density from the coated ST52 plate was similar to that from the bare ST52 material. Such large current densities are not due to corrosion of the carbon fillers, but corrosion of the substrate itself. Thus the coating does not seem to protect the substrate from the corrosive conditions.

Another coated ST52 plate was polarized at a potential of 1.0 $V$ for 16 hours and had an increase in ICR from about 9.0 to 43.5 mΩ cm$^2$ at a compaction pressure of 125 N cm$^{-2}$. This is a less severe increase than what was experienced for the coated SS 316L plate after the same polarization procedure, and suggests that growth of oxide on the surface of the stainless steel material is a reason for the degradation in performance for those plates.

Lædre et al. [19] showed that the oxide layer thickness increased with decreasing pH for 316L stainless steel in sulphuric acid. Ohtsuka et al. [27] investigated growth of oxide layers on SS 304 in 0.1 M H$_2$SO$_4$ solution and found that the thickness increased with increasing potential. This
can mean that an oxide film more easily can grow underneath the coating at high potentials compared to low potentials. Additionally, this process can be facilitated by increased corrosion of carbon fillers at elevated potentials, causing the coating to become even more porous and exposing more of the substrate material to the oxide forming conditions of the electrolyte.

Further work is required to develop a coating that successfully impedes the underlying stainless steel substrate to form less conductive oxides while maintaining a good electronic contact between the layers and possess a high corrosion resistance.

4. Conclusions

A carbon-polymer composite coating for SS 316L bipolar plate substrates was investigated. The coating consisted of 45 vol % graphite, 5 vol % CB and 50 vol % epoxy binder. The coating was deployed by a spraying technique followed by hot-pressing while the binder cured. A contact resistance of 9.8 mΩ cm$^2$ was measured for a coated SS 316L plate with a compaction pressure of 125 N cm$^2$. The same coating deployed without the subsequent step of hot-pressing obtained contact resistance values of about 400 mΩ cm$^2$.

Coated plates were electrochemically tested in a 1 mM H$_2$SO$_4$ solution at 75 °C, with measurements of contact resistance before and after polarization experiments. The coating seemed to protect the substrate from degradation at potentials of 0.0191 and 0.6191 V$_{SHE}$, but not at a potential of 1.0 V$_{SHE}$. At 1.0 V$_{SHE}$ the current density from the coated plates was higher than for the bare SS 316L plates, most likely due to corrosion of carbon fillers. Increase in contact resistance for the coated plates after 16 hours of polarization was equally large as for the bare SS 316L plates.
The coating was found to have a porosity of about 50% and not to protect the substrate sufficiently from the electrolyte. Improvement in the coating is required in the protection of the underlying substrate; the coating process presented here may emerge as a competitive coating solution for metallic bipolar plates.

Acknowledgements

This work was financially supported by SINTEF, Norwegian University of Science and Technology (NTNU), Nordic Innovation (NORCOAT, project 09051) and the European Commission (STAMPEM, FCH JU project 303449).

References


List of Tables

Table 1.
Current density observed for five plates after one hour at a potential of 1.0 \text{V}_\text{SHE}. The plates had coating thicknesses ranging from 0 (bare SS) to 78.6 µm. The electrolyte was 1 mM H$_2$SO$_4$ solution without oxygen at 75 °C.

<table>
<thead>
<tr>
<th>Coating thickness [µm]</th>
<th>Current density after one hour [µA cm$^{-2}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>78.6</td>
<td>53.21</td>
</tr>
<tr>
<td>19.3</td>
<td>15.39</td>
</tr>
<tr>
<td>7.3</td>
<td>5.42</td>
</tr>
<tr>
<td>3.7</td>
<td>2.69</td>
</tr>
<tr>
<td>0</td>
<td>2.04</td>
</tr>
</tbody>
</table>
Figure captions

Figure 1. Schematic of experimental setup used to measure ICR.

Figure 2. Cross sectional SEM images of a) hot-pressed coating b) non-hot-pressed coating

Figure 3. SEM image of the coating surface (top view). Graphite (Gr) and carbon black (CB) particles are visible.

Figure 4. Linear sweep polarization curves starting at -0.26 V_{SHE} and sweeping at 2 mV s^{-1} up to 1.04 V_{SHE} for coated and bare SS 316L plates. The electrolyte was 1 mM H_{2}SO_{4} solution without oxygen at 75 °C.

Figure 5. ICR values (compaction pressure of 125 N cm^{-2}) for coated and bare SS 316L plates before and after polarization at various potentials for 16 hours. The electrolyte was 1 mM H_{2}SO_{4} solution without oxygen at 75 °C.

Figure 6. ICR values as a function of compaction pressure for coated and bare SS 316L plates, before and after linear sweep polarization between potentials -0.26 and 1.04 V_{SHE} with a sweep rate of 2 mV s^{-1}. The electrolyte was a 1 mM H_{2}SO_{4} solution without oxygen at 75 °C.

Figure 7. Current density for coated and bare SS 316L plates when polarized at a potential of 1.0 V_{SHE} for 16 hours. The electrolyte was 1 mM H_{2}SO_{4} solution without oxygen at 75 °C.

Figure 8. Current density for plates polarized at a potential of 1.0 V_{SHE} for one hour. The substrate materials were SS 316L and low alloy structural steel ST52, and these were tested both with and without carbon coatings. The electrolyte was 1 mM H_{2}SO_{4} solution without oxygen at 75 °C.
Figure 1. Schematic of experimental setup used to measure ICR.
Figure 2. Cross sectional SEM images of a) hot-pressed coating b) non-hot-pressed coating
Figure 3. SEM image of the coating surface (top view). Graphite (Gr) and carbon black (CB) particles are visible.
Figure 4. Linear sweep polarization curves starting at -0.26 $V_{\text{SHE}}$ and sweeping at 2 mV s$^{-1}$ up to 1.04 $V_{\text{SHE}}$ for coated and bare SS 316L plates. The electrolyte was 1 mM $\text{H}_2\text{SO}_4$ solution without oxygen at 75 °C.
Figure 5. ICR values (compaction pressure of 125 N cm\textsuperscript{-2}) for coated and bare SS 316L plates before and after polarization at various potentials for 16 hours. The electrolyte was 1 mM H\textsubscript{2}SO\textsubscript{4} solution without oxygen at 75 °C.
Figure 6. ICR values as a function of compaction pressure for coated and bare SS 316L plates, before and after linear sweep polarization between potentials -0.26 and 1.04 V_SHE with a sweep rate of 2 mV s\(^{-1}\). The electrolyte was a 1 mM H\(_2\)SO\(_4\) solution without oxygen at 75 °C.
Figure 7. Current density for coated and bare SS 316L plates when polarized at a potential of 1.0 $V_{SHE}$ for 16 hours. The electrolyte was 1 mM H$_2$SO$_4$ solution without oxygen at 75 °C.
Figure 8. Current density for plates polarized at a potential of 1.0 V$_{\text{SHE}}$ for one hour. The substrate materials were SS 316L and low alloy structural steel ST52, and these were tested both with and without carbon coatings. The electrolyte was 1 mM H$_2$SO$_4$ solution without oxygen at 75 °C.