Nanoporous oxide coatings on stainless steel to enable water splitting and reduce the hydrogen evolution overpotential

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A B S T R A C T
Nanoporous oxides (SiO2, TiO2, ZrO2, and AlOOH) synthesized from sol–gel chemistry techniques were used as coatings for stainless steel electrodes in water electrolysis systems. These oxide coatings have been shown to provide corrosion protection of the stainless steel electrodes at potentials positive enough to evolve oxygen on the positive electrode. In addition, all four oxide coated electrodes showed a 100–200 mV lower overpotential for hydrogen evolution than an uncoated stainless steel electrode. This was attributed to the ability of the oxide coatings to adsorb hydrogen on the surface of the electrode. To verify gas production from these electrodes, a custom alkaline electrolyzer was built and tested with a constant applied current. The flow rate of gas was measured for five different electrode connection configurations, utilizing both monopolar and bipolar electrodes. The efficiency of the system was calculated to be between 66 and 75% as defined as the ratio of the higher heating value of hydrogen to the energy applied to the system. The oxide coated stainless steel electrodes were used without any additional catalysts, including the precious metals.

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1. Introduction

It is widely accepted that energy production from renewable energy sources will have to increase to mitigate the rising costs and limited availability of fossil fuels. In fact, the concept of “peak oil” has been gaining acceptance and some reports indicate that the global production of oil will peak in the early decades of the 21st century [1]. Both solar and wind power provide two very viable sources of renewable energy, however the variability of the power output for both solar and wind is higher than traditional fossil fuel plants [2,3]. It has been suggested that instead of using linear ramp rate generators which utilize natural gas to dampen grid fluctuations, energy storage devices (such as batteries, electrochemical capacitors, and fuel cells) would be more efficient in matching short-period fluctuations that occur with solar and wind power [2]. While each energy storage technology has its advantages and disadvantages, the concept of using renewable energy to produce hydrogen via water electrolysis to later be used by fuel cells is gaining recognition due to its minimal environmental impact [4,5]. Water electrolysis can generate high purity hydrogen and oxygen and, if coupled with other renewable energy systems, is environmentally friendly. Also, it does not require large, centralized plants and the cost of hydrogen production scales well from smaller to larger systems [6]. However, in order to make this process more
efficient and cost effective, further improvements in low cost electrode materials having low overpotentials are desirable goals.

The widely accepted mechanism for hydrogen evolution on most catalysts is a step involving the formation of adsorbed atomic hydrogen (Equation (1)) followed by either chemical desorption (Equation (2)) or electrochemical desorption (Equation (3)) [7].

\[
\text{H}^+ + \text{e}^- \rightarrow \text{H}_{\text{ads}} \tag{1}
\]

\[
2\text{H}_{\text{ads}} \rightarrow \text{H}_2 \tag{2}
\]

\[
\text{H}^+ + \text{e}^- + \text{H}_{\text{ads}} \rightarrow \text{H}_2 \tag{3}
\]

This adsorption of hydrogen on the electrode plays a critical role in the overpotential for hydrogen evolution and it has been shown that metals with high hydrogen overpotential adsorb hydrogen very weakly [8]. In addition to hydrogen adsorption, the overpotential of hydrogen is also influenced by other properties of the system such as the electrode properties (i.e. surface roughness), type and concentration of electrolyte, as well as the operating temperature [7].

There have been many studies investigating materials that lower the overpotential of both the hydrogen and oxygen evolution reactions. In particular, Ni, Mo, or Co alloys are all good candidates for lowering the overpotential of hydrogen production via water electrolysis [9–16]. In addition, various types of carbons and carbon nanotubes have been studied [6,17–20]. Since the surface morphology of the electrode material is also important, many have investigated improving the hydrogen production by utilizing electrodes with nanostructures or increased surface porosity [17,18].

Our study takes a slightly different approach toward creating low-cost electrodes for water electrolysis. Iron or stainless steel electrodes are typically not well suited for water electrolysis. At positive potentials (where oxygen evolution occurs), iron corrodes into Fe₂O₃, Fe³⁺, or other iron species depending on the potential and pH as shown in typical Eh-pH diagrams [19,20]. However, iron or stainless steel is suitable for the hydrogen part of electrolysis due to the fact that at high negative potentials iron will be protected from corrosion. In order to employ stainless steel as an electrode for water electrolysis, we first build on the fact that our group has shown that metals with high hydrogen overpotential are able to reduce the overpotential of hydrogen evolution. In particular, Ni, Mo, or Co alloys are all excellent candidates for lowering the overpotential of both the hydrogen and oxygen evolution reactions. While some oxides have previously been investigated for the electrochemical and photoelectrochemical production of hydrogen and oxygen [26–29], we will focus on coatings consisting of SiO₂, AlOOH, TiO₂ and ZrO₂ synthesized by sol–gel chemistry techniques. In addition, these oxide coated stainless steel electrodes were used without any additional electrocatalysts, including precious metals, to determine their innate ability for water splitting.

2. Materials and methods

SiO₂, AlOOH, TiO₂ and ZrO₂ nanoparticles were synthesized in suspension using previously reported known sol–gel chemistry techniques [30–32]. The SiO₂ sol–gel was produced by mixing tetraethylorthosilicate (TEOS) with concentrated ammonium hydroxide and Milli-Q water in a volume ratio of 4.5:1:30 respectively. The suspension was stirred on a magnetic stirrer for at least 1 h or until the suspension became clear.

The AlOOH sol was created by mixing aluminum tri-sec-butoxide (ATSB), 2-butanol, Milli-Q water, and 1.6 M HNO₃ in a volume ratio of 1:1:8:2. First, the mixture of water, ATSB, and 2-butanol was mixed for at least 2 h at 85 °C. Next, the HNO₃ was added and the suspension was stirred for another 6 h. Finally, the suspension was allowed to reflux for at least 12 h and then filtered through a 0.45 μm filter.

The TiO₂ sol was created by mixing titanium isopropoxide, Milli-Q water, and concentrated HNO₃ in a volumetric ratio of 11.5:140:1. The suspension was stirred on a magnetic stirrer for at least 72 h or until the suspension became clear. The resulting sol–gel was dialyzed through a 3500 MWCO membrane until the pH of the suspension reached c.a. 2.5.

The ZrO₂ sol was created by mixing zirconium propoxide, Milli-Q water, and concentrated HNO₃ in a 3.7:50:1 volumetric ratio. The suspension was similarly stirred on a magnetic stirrer for at least 24 h or until the suspension became clear. The resulting sol–gel was dialyzed through a 3500 MWCO membrane until the pH of the suspension reached c.a. 2.5. Suspensions were verified by witnessing the refraction of a handheld laser off the particles through the suspension.

Commercial 316 stainless steel was used for all electrode materials. Each of the four nanoparticles were deposited on the stainless steel support electrodes by a dip-coating technique whereby the electrodes were withdrawn from a stable suspension of the oxide nanoparticles at a controlled velocity of 24 cm/min. Before coating, the stainless steel electrodes were heated to 400 °C for 3 h in order to increase the wettability of the stainless steel. To improve nanoparticle coverage, the stainless steel electrodes were dipped into the nanoparticle suspension twice with approximately 30 min of air-drying between coats. After coating, the electrodes were sintered at 400 °C for 3 h in air. For all tests, electrical contact was made to the electrode on an uncoated portion located outside of the electrolyte as to have a minimal effect on the electrical resistance. Tests were also performed with one and three coats and there was not any significant difference in performance versus number of coats, so only results with two coats are reported here.

Cyclic voltammetry on individual electrodes (6.5 cm² coupons) was performed with a SolarRayo ETS-2003 potentiostat using a three-electrode technique with a Pt cage counter electrode and a saturated calomel reference electrode in solutions of 1 M Na₂SO₄ where pH adjustments were made.
using either H₂SO₄ or NaOH. Corrosion studies were performed on a Princeton Applied Research VMP2 potentiostat in 0.6 M NaCl where the pH was adjusted using HCl or NaOH.

In addition to the individual electrode tests, a large cell was also constructed to measure the gas production and determine the efficiency of an electrolyzer built with these electrodes. The electrodes used for the large cell study were coated with ZrO₂ nanoporous coating as described above. Uncoated electrodes were not used in this configuration due to problems with the corrosion of the uncoated electrodes. The electrolyzer was built using eleven 15.25 cm x 15.25 cm electrodes each with electrolyte flow channels cut into the top and bottom of the electrode. This configuration of 11 electrodes was employed in both bipolar and monopolar configurations. Sealing was performed by placing rubber gaskets (~0.5 mm thick) between each electrode and bolting the electrolyzer together with plastic end plates. A gas outlet was drilled into one of the plastic end plates and this gas outlet was fed into a gas flow meter to determine the amount of gas being generated by the electrolyzer. Electrolysis was performed by applying a constant current of 2 A (the maximum output of our instrumentation) in a two-electrode configuration using a SolRayo ETS-2003 potentiostat.

### 3. Results and discussion

In order for stainless steel electrodes to be effective for water splitting, we first must apply a protective coating to inhibit the corrosion at positive potentials. This is done by applying an approximately 1 μm thick oxide coating onto the stainless steel. Fig. 1 shows SEM micrographs at two resolutions of TiO₂ and ZrO₂ coated stainless steel.

As stated above, stainless steel is typically not suitable for water splitting because iron will oxidize at less positive potentials than is required for oxygen evolution. Previously, our group has demonstrated that one can protect stainless steel with ceramic coatings, and this protection can occur at potentials that are positive enough to make oxygen evolution on the stainless steel electrode possible [21,22]. While a complete manuscript on the details of the corrosion protection of stainless steel is in progress, a summary of this previously disclosed data is shown in Fig. 2 for emphasis [21]. Fig. 2 shows linear sweep voltammograms of uncoated stainless steel along with ones coated with a TiO₂, ZrO₂ and a 1:1 mixture of TiO₂/SiO₂ in 0.6 M NaCl at pH 8. Even though the corrosion mechanism is different in the presence of Cl⁻ than it is without Cl⁻, NaCl was used for the corrosion studies to accelerate corrosion because Cl⁻ ions promote corrosion on stainless steel. At pH 8 the thermodynamic potential for oxygen evolution is 0.52 V vs. SCE. As shown in Fig. 2, the untreated stainless steel shows an anodic (oxidation) current well below the thermodynamic potential for oxygen evolution. This demonstrates that this anodic current is due to the oxidation of stainless steel and not oxygen evolution. In contrast, the oxide coated samples do not show a strong oxidation current until either ~0.2 V or ~0.5 V more positive than the thermodynamic potential for oxygen evolution. However, since oxygen evolution is a four-electron transfer inner-sphere reaction, there is usually a significant overpotential for this reaction when electrocatalysts are not used. Even though it is evident that these coatings are able to protect the stainless steel from corrosion due to the more positive onset potential, it is difficult to determine if the anodic current is due to oxygen evolution, iron oxidation, or a combination of both. However, since the ZrO₂ coating does not show a strong anodic current until ~0.5 V more positive than the

![Fig. 1 – SEM micrographs at two resolutions of ZrO₂ (A & B) and TiO₂ (C &D) coated stainless steel electrodes. ZrO₂ and TiO₂ were first synthesized by sol-gel chemistry techniques and coated onto stainless steel electrodes by a dip-coating technique which was followed by sintering at 400 °C.](image-url)
thermodynamic oxygen evolution potential, it is possible that this oxidation current is due to oxygen evolution. It should be noted however, that since these experiments were performed in the presence of \( \text{Cl}^-/\text{C}_0 \) in order to accelerate corrosion, the anodic current could be from \( \text{Cl}^- \) oxidation and not water oxidation. However, even in this event, this would suggest that the \( \text{ZrO}_2 \) coating is able to protect the stainless steel at potentials where water oxidation is at least possible. From these results, the \( \text{ZrO}_2 \) coating is the best candidate to enable oxygen evolution on stainless steel without corrosion.

Next, we wanted to examine if these oxide coatings have any effect on the hydrogen evolution reaction on stainless steel. To examine this effect, cyclic voltammetry was conducted on an uncoated stainless steel electrode and electrodes coated with \( \text{SiO}_2 \), \( \text{TiO}_2 \), \( \text{ZrO}_2 \), and \( \text{AlOOH} \) under neutral conditions, pH 7, (Fig. 3A&B) and under basic conditions, pH 12 (Fig. 3C and D), with a maximum current of 200 mA (c.a. 30 mA/cm²). Qualitatively speaking, the potential at which the hydrogen evolution reaction begins is at the inflection point where the slope begins to increase. Interestingly, Fig. 3 shows that for each of the four coated electrodes the hydrogen evolution reaction begins at a lower (less negative) potential than the uncoated electrode. Under both pH conditions the oxide coatings are able to reduce the overpotential of hydrogen evolution by around 100–200 mV.

By examining the cyclic voltammograms at potentials just before the evolution of hydrogen one can note an interesting property of these oxide coatings. For both neutral (Fig. 3B) and basic pH conditions (Fig. 3D), we see that oxide coatings show evidence of the formation and oxidation of an absorbed...
hydrogen layer, whereas the uncoated stainless steel does not. Platinum is well known for showing the formation and oxidation of absorbed hydrogen, and a CV on a platinum foil electrode under neutral pH conditions is also shown in Fig. 3B. As stated above, absorbed hydrogen is an important factor in the mechanism for the production of hydrogen, and the fact that these oxide coatings show peaks for absorbed hydrogen may be the reason that they can evolve hydrogen at lower potentials than uncoated stainless steel.

In addition to the observation of absorbed hydrogen, we also see that the oxide coated stainless steel electrodes exhibit a higher double-layer capacitance than those of the uncoated stainless steel as noted by the higher current at low potentials (around 0 V vs. SCE). Our group has already determined that these oxide coatings can increase the capacitance of carbon electrodes, so this increase in capacitance is not a surprising result [24, 25]. It is known that higher surface area materials can promote hydrogen evolution [18], thus this increase in capacitance could also contribute to the lower overpotential and increased production of hydrogen. In addition, the porosity of the oxide coating could promote bubble nucleation and release from the electrode surface. Having bubbles release from the electrode surface is also beneficial for electrolyzers because bubbles on the surface increase the system resistance, reducing contact between the electrolyte and the electrode, and thereby blocking electron transfer [7].

In order to verify that hydrogen and oxygen can indeed be generated from oxide coated stainless steel electrodes, a large 11-electrode electrolyzer was constructed as described in the experimental section using ZrO₂ coated electrodes with the pH 12 electrolyte (without Cl⁻ ions present). The gas output of the electrolyzer was connected to a gas flow meter to directly measure the gas output and calculate hydrogen efficiency. A diagram of the electrolyzer as well as a diagram of the experimental arrangement are shown in Fig. 4. The electrodes in the electrolyzer were connected in five different configurations using both monopolar and bipolar electrodes. A bipolar electrode when used in an electrolyzer is an electrode in which one side acts as a cathode and the other side acts as an anode, and is connected in series with no direct electrical contact made to the electrode [33]. It is known that bipolar electrodes can be used in electrolyzer systems and they typically reduce the internal ohmic losses to improve efficiency of the electrolyzer [33]. Since both hydrogen and oxygen are produced on the same electrode in the bipolar configuration, all electrodes in the electrolyzer must be coated to prevent corrosion.

The large cell experiments were performed under constant current conditions at an applied current of 2 A. A summary of the results are shown in Table 1. For the different electrical configurations the positive and negative terminal of the power source was split and connected to multiple electrodes alternating between positive and negative and evenly spaced. For example, for configuration A the positive terminal of the power source was connected to electrodes 1, 6, and 11, and the negative terminal of the power source was connected to electrodes 3 and 8 as shown in Fig. 4B. A description of all of the electrical connections tested is shown in Table 1.

Fig. 5 shows the total gas flow rate as a function of time for each of the five electrode configurations listed in Table 1. A couple of observations can be made about Fig. 5. First, the gas flow rate remains fairly constant as a function of time for each of the five configurations. Second, as the number of bipolar electrodes increases (i.e. the number of electrical connections decrease) the gas flow rate also increases as demonstrated by the highest gas flow rate occurring for configurations C&D. In addition, based on the similar measured flow rates for configurations B&C and A&E, the number of positive monopolar or negative monopolar electrodes has less influence on the flow rate than the total number of monopolar and bipolar electrodes.
Table 1 – Summary of data for five different electrical configurations of the 11-electrode electrolyzer utilizing ZrO2 coated stainless steel electrodes.

<table>
<thead>
<tr>
<th>Configuration A</th>
<th>Configuration B</th>
<th>Configuration C</th>
<th>Configuration D</th>
<th>Configuration E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Positive connections (electrode numbers)</td>
<td>3 (1,6,11)</td>
<td>4 (1,4,7,11)</td>
<td>2 (1,11)</td>
<td>1 (5)</td>
</tr>
<tr>
<td>Negative connections (electrode numbers)</td>
<td>2 (3,8)</td>
<td>3 (5,8)</td>
<td>1 (5)</td>
<td>2 (1,11)</td>
</tr>
<tr>
<td>Average H2 flow rate (cm3/min)</td>
<td>67.9</td>
<td>41.6</td>
<td>121.0</td>
<td>120.8</td>
</tr>
<tr>
<td>Average power (W)</td>
<td>20.1</td>
<td>11.8</td>
<td>39.1</td>
<td>37.3</td>
</tr>
<tr>
<td>Supplied energy/g H2 produced (kJ/g)</td>
<td>197.1</td>
<td>189.3</td>
<td>215.6</td>
<td>206.1</td>
</tr>
<tr>
<td>Efficiency (%)</td>
<td>72%</td>
<td>75%</td>
<td>66%</td>
<td>69%</td>
</tr>
</tbody>
</table>

Using the gas flow rate data, we are able to calculate an efficiency of our electrolyzer system as shown in Table 1. The average hydrogen flow rate was estimated to be 2/3 the total gas flow rate using the assumption of a 2:1 hydrogen to oxygen ratio. The average power supplied to the system was calculated by multiplying the average voltage measured during the experiment by the constant applied current. The supplied energy (for water electrolysis) per g of hydrogen produced was calculated by dividing the average supplied power by the product of the average hydrogen flow rate and the density of hydrogen gas as shown in Equation (4).

\[ E_{\text{on}} = \frac{P_{\text{in}}}{\rho_{\text{H2}} \cdot \frac{1}{m_{\text{H2}}} \cdot \frac{1}{1000} \cdot \text{J/g/L}} \] (4)

Finally, to calculate the efficiency we determined the ratio of the energy of combustion of the hydrogen generated to the supplied electrical energy to produce that hydrogen. As opposed to using the standard enthalpy of formation of water vapor from its elemental constituents to calculate the energy of combustion of hydrogen, we used the higher heating value (HHV) as a more accurate calculation of the combustion of hydrogen for calculation of the efficiency of water splitting. The HHV is determined by bringing all the products of combustion back to the original pre-combustion temperature and, in particular, condensing any vapor produced. This assumes a common temperature of the compounds before and after combustion, in which case the water produced by combustion is liquid. In other words, HHV assumes all water products are in the liquid state at the end of combustion. To calculate the efficiency, we used the standard value of 141.8 kJ g\(^{-1}\) as the HHV for hydrogen combustion.

Using this method, we calculated the efficiencies of hydrogen production via water electrolysis to be between 66 and 75% depending on the electrical configuration for our oxide coated stainless steel electrodes. Even though the electrical configurations with the largest number of bipolar electrodes produced the highest gas flow rate under constant current conditions, they actually had the lowest efficiencies because the bipolar electrode configurations required the most power. The National Renewable Energy Laboratory has reported efficiencies (also calculated by the ratio of the HHV of hydrogen to the applied energy to the system) between 63 and 73% for commercial bipolar electrolyzer systems [34]. Thus, the efficiency for our oxide coated stainless steel electrolyzer is very comparable to other commercial systems. Again, it should be noted that these efficiency values are for the ZrO2 coated stainless steel electrodes without the use of any additional electrocatalysts, including precious metals. Also, these efficiencies were determined without gas separation and it is feasible that some of the applied current may reduce some of the produced oxygen or oxidize some of the produced hydrogen. Higher efficiencies may be obtainable in a system that separates the produced gas by eliminating the oxygen reduction reaction and hydrogen oxidation reaction, however this was not tested here due to the difficulty of gas separation in a multi-electrode bipolar configuration.

In addition, we did not observe any discoloration of the electrolyte (from the presence of iron oxide for example) or corrosion of the electrodes during the experiments. If corrosion of the stainless steel was the dominate process over the production of hydrogen and oxygen, we would expect to see very low efficiency values because most of the supplied energy would go into the parasitic corrosion reaction and not water splitting. However, since our measured efficiency is very comparable to the reported values for commercial electrolyzer systems, we believe that these coatings are able to protect the stainless steel electrodes from corrosion during water electrolysis.

Fig. 5 – Gas flow rate as a function of time for the 11-electrode electrolyzer in the pH 12 electrolyte utilizing ZrO2 coated stainless steel electrodes for five different electrode configurations. All configurations were run under constant current at 2 A. Details of the electrode configurations are shown in Table 1.

4. Conclusion

Here we have shown that by adding oxide coatings to the stainless steel electrodes one can make them suitable for use in water electrolysis. The oxide coating can protect against
corrosion and allow for oxygen evolution on the positive electrode. In addition, the oxide coating can lower the overpotential for hydrogen evolution on the negative electrode. The reduction in the overpotential has been attributed to the oxide coating allowing for the formation of adsorbed hydrogen which is a known feature of many hydrogen evolution electrocatalysts, and we have determined that the oxide coating can reduce the overpotential by approximately 100–200 mV. In addition, we have used these oxide coated stainless steel electrodes in an electrolyzer to verify gas production from the system and calculate the efficiency of these systems. An efficiency of this system was calculated to be 66–75%, which is very comparable to current commercial electrolyzer systems. Here, we were able to demonstrate the ability of oxide coated stainless steel electrodes to electrochemically split water without the use of any additional electrocatalysts, including precious metals.

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