Sustainably biotemplated palladium catalysts generated on different carbon-based support materials are examined for durability under electrochemical (oxidative) and mechanical-stress conditions. Biotemplated catalysts on carbon paper under both stresses retain 95% (at 0.6 V) of the initial catalytic activity as opposed to 70% for carbon cloth and 60% for graphite. Graphite electrodes retain 95% of initial catalytic activity under a single stress. Using electrodeposited polyaniline (PANI) and polydimethylsiloxane binder increases the current density after the stress tests by 22%, as opposed to a 30% decrease for Nafion. PANI-coated electrodes retain more activity than carbon-paper electrodes under elevated mechanical (94 versus 70%) or increased oxidative (175 versus 62%) stress. Biotemplated catalytic electrodes may be useful alternatives to synthetically produce catalysts for some electrochemical applications.

1. Introduction

Catalytic materials used in many industrial and energy-conversion processes must be durable to maximize their useful lifetimes, especially when expensive precious metal catalysts are utilized.\cite{1} Conventional methods of catalyst formation typically use synthetic stabilizers and reductants to form nanostructures with high surface area and catalytic activity. Synthesized nanostructures are then mixed with a chemical binder to form a catalyst ink that is applied to a support, often alumina\cite{2} or carbon,\cite{3} for various applications.\cite{4} The stability of the bond between the binder and support is important to keep the catalytic material in contact with the electrode support. Additionally, the durability of the ligand material is an important consideration, as ligands account for the bulk of electrode manufacturing costs, largely because they cannot be captured and recycled like the catalytic metal.\cite{1}

Recently, there has been increased interest in developing sustainable, low-cost processes to fabricate nanoparticles and porous nanostructures with high surface areas by using biological materials as supports\cite{5} or biotemplates\cite{6} to replace synthetically formed nanomaterials. An electroactive biofilm of G. sulfurreducens has recently been used as a biotemplate to form a nanoporous catalytic palladium structure that was directly attached to an electrode surface using only materials naturally produced by the biofilm\cite{7} and avoiding the use of synthetic templating materials. The biotemplated palladium structure had a higher catalytic activity than the electrodeposited palladium control electrode or electrodes coated with a palladium/Nafion catalyst ink. Electroactive bacteria offer a sustainable solution for the formation of a highly active nanoporous structure on an electrode, because the biofilm effectively disperses and reduces the catalytic material directly on the electrode surface without the use of any conventional synthetic binders, which increases the sustainability of the process. However, the stability of biotemplated palladium structures has not previously been tested. Although sustainable methods of catalyst formation are desirable, electrode durability must be similar to or better than that of electrodes produced using synthetic methods.

Fuel cells and batteries are the primary applications for catalytically active electrodes. Two of the primary design considerations for electrodes in these systems are thermal\cite{3b,8} and electrochemical\cite{3b,9} stability. Electrode stability of conventional catalysts is often tested by applying a catalyst to an electrode support material before coating with a binder to ensure that the material remains on the surface during testing, or by applying a premixed binder/nanomaterial solution.\cite{10} The most common binders are proton-conducting polymers such as Nafion.\cite{11} More recently, electrically conductive polymers, primarily polyaniline (PANI), have been used as binders because of their ability to conduct electrons and be electropolymerized on an electrode. Pyrolyzed PANI has also been used as a starting material to form catalytic electrodes\cite{12} and corrosion-resistant coatings.\cite{13} Catalytic materials can also be electrodeposited into PANI films on support electrodes or deposited into freshly produced PANI films by soaking the film in a solution containing metal ions. The use of PANI as a conductive intermediate link for other purposes, such as the movement of artificial muscles,\cite{15} highlights its versatility as a binder.

Electrochemical (oxidative) stability is one important factor for biotemplated electrodes, but another critical consideration is mechanical stability. Biotemplated catalyst layers do not require a chemical binder for attachment to the electrode sur-
face, and this may make the catalyst layer more susceptible to degradation by mechanical shear stresses. Mechanical stability is often overlooked in conventional electrochemical systems, because the catalysts are bound to the electrode surface by a synthetic material, the substrates are gases, which have very low viscosity ($\mu \approx 0.02$ cP for air)\textsuperscript{(16)} or the system is used in a stagnant electrolyte.\textsuperscript{(17)} However, other applications use liquid electrolytes that have high viscosities, such as hydrogenation reactions and reductive dechlorination of toxic compounds in water ($\mu \approx 1$ cP).\textsuperscript{(18)} The higher viscosity of a liquid can mean that mechanical shear forces are important to catalyst stability, because the electrolyte imparts an additional stress on the electrode. This aspect of electrode mechanical durability relative to shear stress, however, has not been well studied.

The mechanical and electrochemical durability of biotemplated nanoporous palladium catalysts on carbon supports during hydrogen oxidation was examined herein by using a rotating disk electrode (RDE). Graphitized carbon is a widely used support for growth of electroactive biofilms, because it is electrically conductive and inexpensive.\textsuperscript{(19)} Graphite is also a good material for catalyst deposition due to delocalized pi bonds that can interact with metals to enhance the attachment of catalysts to a surface.\textsuperscript{(20)} However, it is unclear how much mechanical shear stress and electrochemical oxidation these electrodes can withstand. Different electrode support materials (graphite, carbon cloth, and carbon paper) were therefore examined to determine the most durable electrode structure. Several readily available polymer coatings [Nafion, polydimethylsiloxane (PDMS), and PANI] were also investigated as binders to enhance retention of the nanoporous catalytic material to the support material. Electrodes that could best withstand degradation in initial stress tests were further tested under conditions of higher mechanical (85% glycerol as a more viscous electrolyte) and oxidative stresses (1 M $\text{H}_2\text{SO}_4$ electrolyte) to examine durability under harsher conditions.

2. Results and Discussion

2.1. Stability of Biotemplated Palladium Catalyst Layers on Different Carbon Support Materials

The stability of the biotemplated palladium layers depended on the carbon support. Carbon paper exhibited the best durability following exposure to a combination of mechanical shear (1000 rpm, shear rate of 35 s$^{-1}$) and accelerated oxidative stresses (cyclic voltammetry (CV) between −0.1 and 0.65 V at 100 mV s$^{-1}$ for 3000 cycles\textsuperscript{(10b)} in 0.1 M $\text{H}_2\text{SO}_4$). Representative initial and final voltammograms for each type of support showed evidence of performance degradation at potentials above about 0.4 V (Figure 1). Initial and final currents at 0.6 V were used as a basis of comparison here, because this was the minimum potential above which catalytic degradation was first observed. Approximately 95% of the catalytic activity (2.5 ± 0.2 mA cm$^{-2}$ initial, 2.4 ± 0.15 mA cm$^{-2}$ final; at 0.6 V) was retained after the carbon paper support was subjected to a combination of mechanical shear and accelerated oxidative stress (Figure 2A). Biotemplated catalysts were less stable on carbon-cloth supports under the same conditions and retained only about 70% of the initial catalytic activity (4.6 ± 0.4 to 2.9 ± 0.2 mA cm$^{-2}$). Graphite-supported biotemplated electrodes retained about 60% of the initial catalytic activity (1.6 ± 0.01 to 1.0 ± 0.3 mA cm$^{-2}$) after combined stresses. Control electrodes, prepared on a graphite surface by using synthetically produced palladium black nanoparticles held with a Nafion binder, initially produced a lower current density (1.4 ± 0.01 mA cm$^{-2}$) than biotemplated palladium catalysts and lost about 15% of their activity when subjected to the same oxidative and mechanical stresses. Control electrodes prepared by electroplating palladium onto a graphite surface initially produced less current than biotemplated electrodes (1.4 ± 0.04 mA cm$^{-2}$) but retained 78% of the initial catalytic activity (1.1 ± 0.15 mA cm$^{-2}$). Support materials without palladium produced negligible current (see the Supporting Information, Figure S1).

Graphite electrodes did not maintain performance under these combined stresses, but they were adequate supports if only electrochemical or mechanical stress was applied (Figure 2B). There was a minimal decrease in catalytic activity (1.7 ± 0.05 mA cm$^{-2}$ initial, 1.7 ± 0.08 mA cm$^{-2}$ final; at 0.6 V) when only the mechanical shear force was applied. Approximately 94% of the catalytic activity (1.7 ± 0.04 to 1.6 ± 0.04 mA cm$^{-2}$) was maintained during oxidative stability tests without rotation. Plain graphite electrodes were also tested by chronoamperometry at 0.2 or 0.6 V with mechanical stress.

Figure 1. Representative cyclic voltammograms before and after durability testing of biotemplated palladium catalysts on A) carbon paper, B) carbon cloth, and C) graphite.
(1000 rpm) for 12.5 h to assess the catalyst stability at different levels of oxidative stress. Catalytic activity of electrodes decreased by 36% (1.8 to 1.1 mA cm$^{-2}$) at a set potential of 0.6 V, as opposed to a 17% increase in activity (1.8 to 2.0 mA cm$^{-2}$) for electrodes set at 0.2 V. These results confirm that a combination of an oxidizing environment with mechanical shear produced electrode failure. The increase in catalytic activity for the electrode held at 0.2 V was likely due to the conditioning of the palladium catalyst in the hydrogen atmosphere, which could increase the number of active sites. To verify that this conditioning of the electrode occurred, a graphite electrode with a palladium catalyst layer was placed in a hydrogen-sparged electrolyte for 12.5 h and rotated at 1000 rpm. The catalytic activity of the palladium layer increased by 35% (Figure 2 B) after exposure to hydrogen sparging, which suggests that optimization of this biotemplated catalyst-formation process is still needed.

2.2. Electrode Surface Characterization

Biotemplated palladium catalysts formed on carbon-cloth and carbon-paper supports produced higher current densities than those on graphite supports, even though they had the same projected surface area. Carbon paper and cloth are made of carbon fibers, which provide an increased surface area for biofilm growth and formation of the palladium catalyst layer compared to a smooth graphite surface (Figure 3). The catalytic activities of all support materials without palladium were approximately the same (0.07 ± 0.03 mA cm$^{-2}$), indicating no intrinsic effect of the support material on the catalytic activity.

Therefore, the increase in current density was due to an increased available surface area for catalyst attachment. The carbon-paper electrode may have outperformed the other support materials, because of its more rigid structure, which enabled greater resistance to support deformation in combination with the high surface area of the layers of carbon fibers (Figure 3). Carbon-paper electrodes had palladium nanostructures formed primarily along the carbon fibers, but palladium films that interconnected the fibers were also observed. Some of these interconnecting film structures were also observed below the top layer of the support, and this suggests that activity extended beyond the surface plane. More catalytic structures were apparent on the surface of carbon-paper supports after stability testing, but this change in catalyst morphology did not affect the overall performance.

Carbon-cloth electrodes had palladium nanostructures primarily along the carbon fibers. However, films interconnecting different carbon fibers were not observed. One possible reason for the lower durability compared to the carbon-paper electrode is that carbon cloth is nonrigid and therefore more easily deform under mechanical stress. Deformation of the support
could make the palladium catalyst layers susceptible to fracture and detachment, which would decrease the catalytically active area of the electrode.

Graphite blocks offer a rigid support for the catalyst layer, but the smooth, solid surface offers less surface area for biotemplate formation. The flat surface results in a palladium layer that is formed only on the surface of the electrode in one cohesive layer, whereas the paper and cloth could have biotemplated catalyst deposited deeper in the material, which would be more resistant to surface shear. The large areas of bare support that were seen on uncoated graphite electrodes after combined mechanical and oxidative stress suggest that the decrease in catalytic activity was a result of detachment of the material from the surface support (Figure 3).

2.3. Stabilizing Palladium Layers on Graphite with Different Polymers

Three commonly used binders (PANI, PDMS, and Nafion) were tested as coatings to stabilize the biotemplated palladium catalyst layer on the graphite electrodes. Although the addition of synthetic polymers to biotemplated materials decreases the sustainability of the overall process, the improvement in catalyst stability may be a more important factor for applications under harsh conditions of electrochemical or mechanical stress.

PANI was the most effective stabilizer of the three polymers tested (Figure 4). A PANI coating, approximately 15 nm thick \([15] \) (30 electrodeposition cycles), on the palladium layer increased the catalytic activity of the electrode by about 22% \([1.8 \pm 0.02 \text{ mA cm}^{-2} \text{ initial}, 2.2 \pm 0.2 \text{ mA cm}^{-2} \text{ final}; \text{at } 0.6 \text{ V}] \) after exposure to electrochemical and mechanical stress, and this suggests that the PANI layer stabilized the biotemplated layer on the electrode. The increase in catalytic current was due to the conditioning of the palladium catalyst in the hydrogen atmosphere. Catalysts coated with less PANI (1.5 and 5 nm thick layers) did not maintain their initial activity after testing (67 and 75% activity retention), likely because the polymer layer was not thick enough to provide a strong bond between the catalyst and the support. The palladium electrode tested here performed similarly, on the basis of \(\text{mA cm}^{-2} \text{ mgPt}^{-1}\), to a PANI film with palladium nanoparticles reduced inside the film.\(^{[22]}\) However, the electrode was previously synthesized by casting a stabilized nanoparticle solution and aniline mixture onto an electrode by using a chemical reductant before testing. The technique presented here is a simpler method for formation of a palladium catalyst on an electrode, it uses less PANI to bind the catalyst to the surface, and it avoids the use of nanoparticles stabilized with synthetic materials. Biotemplated electrodes could be coated with a variety of electroactive polymers to tailor the electrode to different applications with this method.

PDMS was also tested as a catalyst stabilizer, because it was previously shown to be an effective, low-cost binder material for cathodes in microbial fuel cells.\(^{[23]}\) Catalysts coated with PDMS (10, 5, and 1 wt%) all had an initial activity (1.4±0.07 mA cm\(^{-2}\)) below that of an uncoated electrode (1.7±0.1 mA cm\(^{-2}\)). However, after stability tests the catalysts coated with 10 wt% (1.7±0.1 mA cm\(^{-2}\)) or 5 wt% (1.8±0.1 mA cm\(^{-2}\)) PDMS had activities similar to that of the average uncoated electrode. The catalysts coated with only 1% PDMS lost about 66% of the initial activity, likely because there was not enough polymer to effectively maintain binding of the catalyst layer to the support. The overall current densities were lower with PDMS compared to PANI, likely because PDMS is an insulating polymer.

Nafion was tested as a control, because it is the most commonly used binder for electrode materials\(^{[21]}\) due to its proton-conduction properties, but it is expensive.\(^{[24]}\) However, Nafion was not found to be suitable as a stabilizing polymer for the biotemplated palladium catalyst layer. Catalysts coated with 5 or 1% Nafion had a lower initial catalytic activity (1.4±0.02 mA cm\(^{-2}\)) than the uncoated electrode. The catalytic activity decreased for all Nafion-coated electrodes by about 30% (1.0±0.05 mA cm\(^{-2}\)). Degradation of Nafion-coated electrodes was assumed to be more a result of mechanical than oxidative stress, owing to the good chemical stability of Nafion in acidic environments. The decrease in activity was more pronounced than that observed for electrodes coated with a palladium black and a Nafion suspension, likely because there was less direct contact between the Nafion and the carbon support.

Electrodeposited PANI is advantageous as a stabilizer not only because it can stabilize the catalyst layer on the electrode, but also because it can be electrodeposited directly on the electrode after formation of the catalyst layer, which results in more control over the thickness of the polymer layer.\(^{[22]}\) The other polymers tested had to be applied by a drop-casting method onto the support, which afforded less control over the thickness of the polymer film. Additionally, PANI is a conductive material in acidic solutions, owing to π-π stacking,\(^{[25]}\) which is advantageous for electrochemical applications such as fuel cells. One disadvantage of PANI compared to PDMS is its cost. A PANI layer about 15 nm thick costs about 5.2 $ m\(^{-2}\) (based on 72 $ for 500 g of aniline monomer), which is approximately three times the cost of PDMS (1.5 $ m\(^{-2}\), 50 $ for 500 g).\(^{[23]}\) However, this cost difference is not likely to be prohibitive given the advantages afforded by PANI as a stabilizer, especially since both of these polymers are two orders of magnitude less expensive than Nafion (667 $ m\(^{-2}\), based on 200 $ for 100 mL of 5% Nafion solution).

![Figure 4. Initial and final current densities of palladium catalysts supported on graphite and coated with different stabilizing polymers. All stability tests were conducted with combined electrochemical and mechanical stress in 0.1 M H\(_2\)SO\(_4\). PANI shows the most promise as a stabilizer for coating catalytically active electrodes.](image-url)
The microscopic structure of the catalysts stabilized with PANI and PDMS was similar to that of the uncoated palladium nanostructure formed on the graphite surface[37] (see the Supporting Information, Figure S2). The catalyst layer coated with Nafion could not be observed due to the inability of the electron beam to penetrate the Nafion layer without destroying it.

### 2.4. Enhanced Durability Tests

Biotemplated palladium catalyst layers on carbon-paper supports and on graphite blocks coated with PANI (15 nm) were further tested under increased shear stress and more oxidative conditions (Figure 5). Electrodes were tested under the same physical conditions as above (1000 rpm and 100 mV s\(^{-1}\) cyclic voltammetry for 3000 cycles), except that the electrolyte solution was switched to an 85% glycerol solution to increase the viscosity \([\mu = 110 \text{ cP}]\).[26] This increased the shear stress to 4 Pa compared to 0.1 Pa in 0.1 M H\(_2\)SO\(_4\) (\([\mu = 3 \text{ cP}]\)).[27] Initial and final current densities were obtained in CV tests in the 0.1 M H\(_2\)SO\(_4\) electrolyte to provide conditions consistent with previous tests. The PANI-coated electrode retained 94% of its initial catalytic activity under these conditions (1.7 ± 0.02 mA cm\(^{-2}\) initial, 1.6 ± 0.05 mA cm\(^{-2}\) final; at 0.6 V). The carbon-paper support, however, only retained about 70% of the initial catalytic activity under the increased mechanical shear (2.8 ± 0.02 mA cm\(^{-2}\) to 2.1 ± 0.2 mA cm\(^{-2}\)). Glycerol electrooxidation was minimal, as the glycerol oxidation peak occurs at about 0.8 V.[28] and the maximum potential used here was 0.65 V. These results suggest that, under conditions of high shear stress, stabilization of the catalyst support with PANI or another electroactive polymer is beneficial.

These two electrodes were also subjected to increased oxidative stress by conducting CV in a 1 M H\(_2\)SO\(_4\) electrolyte. The PANI-coated graphite electrode increased in activity by about 75% (1.7 to 3.0 mA cm\(^{-2}\)) after testing. This increase was likely due to complete protonation and reduction of the PANI layer in the highly acidic solution, which gives better electron-transport properties[26] and also prevents catalyst detachment from the electrode surface. PANI is a corrosion-resistant polymer,[13b] and could have protected the electrode from dissolution under the highly oxidative stress in the system. The catalytic activity of the PANI coating also increased the overall catalytic activity of the electrode after treatment in the highly acidic solution. Initially, the PANI-coated electrode produced a current density of 0.1 mA cm\(^{-2}\) in a nitrogen atmosphere. After testing in 1 M H\(_2\)SO\(_4\), the activity increased to 1.68 mA cm\(^{-2}\) in the same nitrogen atmosphere, likely as a result of full protonation and reduction of the PANI layer. The carbon-paper electrodes retained only about 40% of their initial activity (2.3 to 1.0 mA cm\(^{-2}\)) during stability testing in the more corrosive environment. Although the performance of the carbon-paper electrode declined in the enhanced stress tests, findings reported by others suggest that the stability could be improved by increased graphitization and nitrogen doping of the support material.[38]

### 2.5. Mechanical Shear Calculations for Relevant Catalytic Applications

The mechanical shear force in hydrogen fuel cells is negligible, owing to the very low viscosity of gaseous substrates (\([\mu \approx 0.02 \text{ cP for air}]\).[16] However, in other systems that use a liquid electrolyte, such as formic acid fuel cells and water-treatment applications, the shear stress in the system becomes a more important consideration for system performance and longevity. The average shear rate and shear stresses used in the RDE tests herein (35 s\(^{-1}\); 0.1 Pa in 0.1 M H\(_2\)SO\(_4\), and 4 Pa in 85% glycerol)[30] are similar to or higher than those that would be encountered in applications in which biotemplated catalysts could be used. One possible application of biotemplated catalysts is their use on electrodes in direct formic acid fuel cells. If the anode flow pattern is approximated to be a pipe with a diameter of 0.36 cm and a flow rate of 1 mL min\(^{-1}\),[30] the average wall shear rate (18 s\(^{-1}\)) and shear stress (0.03 Pa; \([\mu (\text{formic acid})] = 1.5 \text{ cP}]\) are lower than those that resulted in electrode failure herein, which implies that biotemplated electrodes without a binder should be durable in this system.

Removal of harmful contaminants from water streams is another application that uses catalysts. Flow of contaminated water through a packed-bed reactor is a typical setup for water-treatment systems. Values for particle diameter and reactor cross sections were taken from a previous study that used palladium-coated Al\(_2\)O\(_3\) beads and a hydrogen infuser for reductive dechlorination of chlorinated contaminants.[14] The shear rates through the packed bed were calculated to be approximately ten times higher (360 s\(^{-1}\)) than the shear stress imparted to the biotemplated electrodes by the RDE in 0.1 M H\(_2\)SO\(_4\). However, when the viscosity of water is taken into account (\([\mu (H\(_2\)O) = 1 \text{ cP}]\),[27] the shear stress in the packed bed (0.3 Pa) is similar to the shear stress on the biotemplated electrodes in 0.1 M H\(_2\)SO\(_4\). The shear stress experienced by electrodes tested in 85% glycerol is ten times larger than in either of these applications, implying that biotemplated catalysts may be directly usable in many cases and that a binder would only have to be added under harsh conditions. The results of these calculations show that biotemplated catalysts could likely be used in other applications given their durability to shear conditions in these reactors.
3. Conclusions

The oxidative and mechanical durability of biotemplated nanoporous palladium catalysts was tested with different support materials and polymer coatings. A thin layer of PANI electrodeposited over the palladium catalyst on graphite-block supports greatly increased the durability of the electrode, even when it was subjected to increased electrochemical and mechanical stress. Although the addition of polymer over a sustainably formed catalyst detracts from its environmental sustainability, there may be conditions under which addition of this material is warranted. Carbon paper was the best support material, likely because its rigid but highly porous structure provided accessible recessed layers of carbon fibers protected from surface shear stress. Additionally, the carbon-fiber layers provided increased surface area for biofilm formation and subsequent palladium reduction. Estimates of shear stress in various possible electrode applications suggest that a biotemplated catalyst structure could be sufficiently stable to replace synthetically formed catalysts in these applications. The results demonstrate that biotemplated catalyst electrodes may be good alternatives to electrodes prepared by synthetic methods.

Experimental Section

Reactor Configuration

Two-chamber reactors (duplicates) were connected by side arms (inner diameter of 2.4 cm), sealed with an O ring, and separated by a Nafion 117 membrane (Fuel Cell Store, Boulder, CO, USA) that was held with a screw clamp (35/25, VWR, Radnor, PA, USA). Each chamber had three 20 mm side ports, which were sealed with rubber stoppers and aluminum crimp seals, and a total liquid volume of 120 mL and a headspace volume of 60 mL. The stopper inserted into the middle side port of the working electrode chamber had a 5 mm-diameter hole to allow insertion of a reference electrode.

The working electrode was made by attaching a titanium wire (0.81 mm, McMaster Carr) to different support materials (graphite (McMaster Carr, USA), carbon paper (Spectracarb 0% wet-protected; Clean Fuel Cell Energy LLC, USA), and carbon cloth (0% wet-protected, E-TEK, USA)) cut into 1 cm-diameter pieces through small holes drilled near the top of the electrode. Graphite electrodes were polished with 400 and 1500 grit sandpaper, sonicated briefly to remove loose particles, and then soaked in 1 M HCl overnight. Electrodes were then rinsed three times with deionized water and polished with 400 and 1500 grit sandpaper to remove any remaining loose material. Carbon-paper and carbon-cloth electrodes were placed in a muffle furnace at 450 °C for 45 h to remove any organics on the surface. All electrodes had a resistance of less than 1 Ω between the wire and electrode surface. The electrode was inserted through a butyl-rubber stopper, inserted into the top of the reactor, and sealed with an aluminum crimp seal. A platinum-wire counter electrode was inserted through a stopper in the middle side arm in the counter-electrode chamber. Electrode potentials were measured with Ag/AgCl reference electrodes (100 ± 5 mV vs. the standard hydrogen electrode (SHE); BASI, West Lafayette, IN, USA), and all potentials reported here are versus SHE. The tip (glass frit) of the inserted reference electrode was about 2 cm away from the working-electrode surface. All reactors and media were sterilized before use. The medium was replaced by using sterile, anaerobic techniques.

Culture Conditions and Reactor Operation

Geobacter sulfurreducens PCA was grown from stocks frozen at −80 °C. Cells were cultured in ATCC medium 1957 with 30 mM acetate and incubated at 30 °C. The anode chambers of reactors were inoculated with a 1:10 ratio of mid-log-phase G. sulfurreducens culture to ATCC medium 1957, excluding fumarate. Anode potentials were set to −0.15 V with a potentiostat (Biologic, TN, USA) in a 30 °C temperature-controlled chamber. Anode chambers were stirred at about 200 rpm with a magnetic stir bar to help reduce diffusion limitations of substrate to the biofilm.

The biofilm was grown until current production began to decrease from its maximum (≈6 days). The medium was exchanged for fresh ATCC medium 1957, excluding fumarate, to remove cells in suspension. Na₂PdCl₄ (150 mg L⁻¹ final concentration; Sigma-Aldrich, USA) and sodium acetate (10 mM) were added to the working-electrode chamber with the working electrode set to −0.15 V. Electrodes were disconnected from the potentiostat after 40 min of incubation, removed from the reactor, and stored at 4 °C until further processing (≈30 min). Control electrodes were not exposed to palladium, but exposed to similar conditions.

Electrode Processing

Electrodes were pyrolyzed in a tube furnace (Thermo Scientific, USA) under an argon atmosphere (30 mL min⁻¹ flow rate). The furnace was ramped at 5 °C min⁻¹ to 450 °C, held at that temperature for 45 min, and then allowed to cool to ambient temperature to carbonize cell material. The carbonized cell material was then removed by thermal oxidation in a muffle furnace at 450 °C in air for 2 h to leave a porous palladium catalyst. Some graphite electrodes were coated with a polymer to stabilize the catalyst layer on the surface of the electrode and enhance attachment. PANI, a conductive polymer, was electropolymerized on the electrode by electrochemically cycling (CV) the electrode at 100 mV s⁻¹ between −0.1 and 1.0 V in 1 M sulfuric acid solution with 50 mM aniline monomer.[15] Different amounts of polyaniline were deposited by varying the number of cycles (3, 10, and 30 cycles; 30 cycles ≈15 nm thickness).[15] Electrodeposition of PANI for 30 cycles results in the deposition of 3.7 mg cm⁻² of polymer on the electrode. PDMS was tested as a stabilizer, because of its relative durability and low cost compared to Nafion.[25] A 5% solution of PDMS added approximately 1.4 mg cm⁻² of polymer to the electrode. Solutions containing 1, 5, and 10% PDMS were prepared according to standard protocols in toluene[24] and were dropped onto the surface of the electrode and allowed to cure at ambient temperature for more than 2 days. Nafion was tested as a control, because it is the most commonly used polymer for dispersing nanoparticles and attaching them to electrode surfaces.[19] A solution (10 μL) containing 1 or 5% Nafion in propan-2-ol was dropped from a pipettor onto the surface of the electrode and allowed to dry overnight before testing. Coating the biotemplated catalyst with a 5% solution of Nafion added approximately 0.9 mg cm⁻² of polymer to the electrode.

Electrode Characterization

Catalytic activity of electrodes for H₂ oxidation was evaluated by CV in H₂-saturated 0.1 M H₂SO₄. The electrolyte was prepared by sparging 0.1 M H₂SO₄ for at least 30 min. Initial and final electrochemical performance of all catalysts was tested with an RDE to decrease the effect of diffusion resistance. Tests were run with continuous H₂ or N₂ sparging to differentiate the catalytic currents.
gained by oxidizing H₂ from the background currents. Potentials were cycled between −0.15 and 0.65 V (vs. SHE) at 1 mV s⁻¹ during CV with an electrode-rotation rate of 1000 rpm to evaluate electrode performance. Current densities were normalized to the geometric surface area of the electrode. Data were recorded on a Gamry potentiostat (Gamry, USA). Pt-mesh counter electrodes and Ag/AgCl (3 M NaCl) reference electrodes were used in all tests. Bare electrodes were also characterized electrochemically as controls. All potential values are reported versus SHE. Some support materials tested do not meet requirements for testing on a typical RDE setup. To circumvent this, all materials were tested on an electrode modified with a Teflon screw cap. The electrode was threaded to accommodate this screw cap and a stainless steel plate was fashioned to make contact with the gold current collector of the electrode. A 6 mm hole was drilled in the middle of the cap and the face of the cap tapered to the edge to mimic RDE conditions as closely as possible. A schematic of this setup is shown in the Supporting Information (Figure S3). The resistance between the electrode surface and the body of the electrode was less than 0.5 Ω in all cases. All electrodes were tested with this modified apparatus for the sake of consistency.

**Mechanical and Electrochemical Durability Tests**

The stability of the catalyst layer to electrochemical stress and mechanical stress was evaluated by using an RDE. The initial and final electrochemical performance was evaluated as described above. The electrochemical durability was tested by performing an accelerated electrochemical stability test by potential cycling of the electrode from −0.15 to −0.65 at 100 mV s⁻¹ for 3000 cycles[20] in 0.1 M H₂SO₄. Enhanced electrochemical stability tests were carried out under similar conditions, except that 1 M H₂SO₄ or 85% glycerol was used as the electrolyte. The mechanical durability was tested by applying a shear force by means of the RDE at 1000 rpm for 1 h to accommodate this screw cap and a stainless steel plate was fashioned to mimic RDE conditions after durability testing.

**Microscopic Characterization**

The electrode surface structures before and after durability testing were examined with a field-emission scanning electron microscope (FE-SEM; FEI Quanta 200) equipped with an energy-dispersive X-ray spectrometer (EDS). Elemental spectra of the electrode surfaces were obtained to verify the presence of the electrode coatings after durability testing.

**Acknowledgements**

The authors would like to acknowledge John Cantolina in the Huck Institutes of Life Sciences for his assistance with the SEM. This research was supported by an award KUS-I1-003-13 from the King Abdullah University of Science and Technology (KAUST) and by an award DGE-1255832 to M.D.Y. by the National Science Foundation (NSF) Graduate Student Fellowship Program.

**Keywords**: biotemplates · palladium · supported catalysts · sustainable chemistry · template synthesis