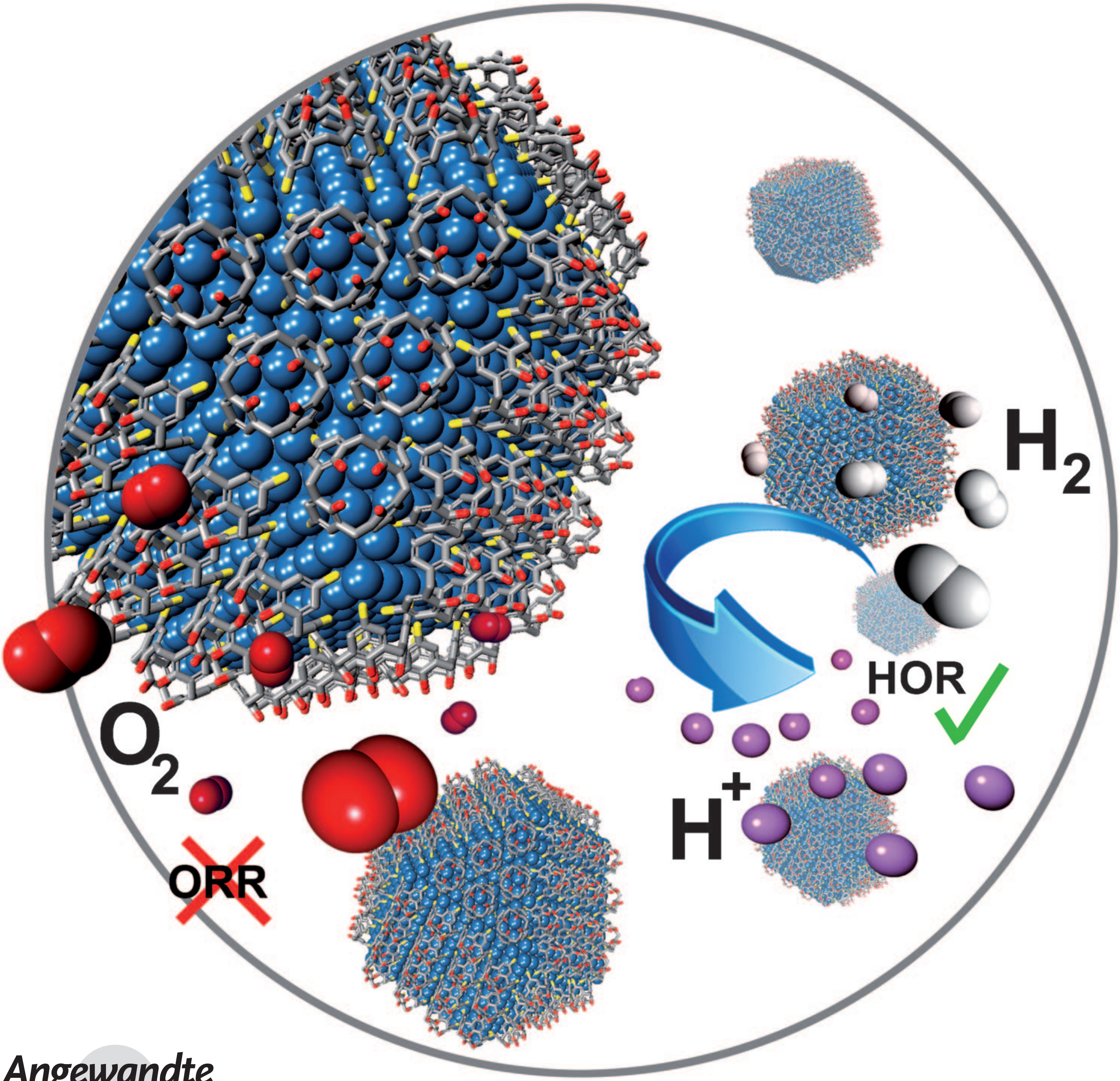
Heterogeneous Catalysis

DOI: 10.1002/anie.201100744

Tailoring the Selectivity and Stability of Chemically Modified Platinum Nanocatalysts To Design Highly Durable Anodes for PEM Fuel Cells**

*Bostjan Genorio, Ram Subbaraman, Dusan Strmcnik, Dusan Tripkovic, Vojislav R. Stamenkovic, and Nenad M. Markovic**



An ever-changing energy landscape and the global drive toward greener energy technologies have made fuel cells a focal point of numerous research initiatives. In their current form, proton-exchange-membrane fuel cells (PEMFCs) have been shown to perform well under operating conditions for both automotive and stationary applications. In order for PEMFCs to reach commercial implementation, issues such as durability under both normal and startup and shutdown conditions have to be tackled effectively. Reactivity, selectivity, and stability are the quintessential properties that need to be tailored to develop catalysts that can tackle the durability issues arising during startup and shutdown.[1] One approach to accomplish this task is to design an anode catalyst that can efficiently suppress the undesired oxygen reduction reaction (ORR; imparting selectivity) and preserve the platinum-like hydrogen oxidation reaction (HOR) activity (imparting reactivity), while remaining stable under operating conditions (imparting stability). Such an approach not only reduces the overpotential on the cathode side owing to negligible ORR currents on the anode but also prevents formation of detrimental products such as hydrogen peroxide, which can be formed under "normal" anode startup and shutdown conditions. We have shown that chemically modified electrodes (CME) consisting of self-assembled monolayers (SAMs) of calix[4]arene molecules on extended platinum single-crystal surfaces can selectively block the ORR without affecting the HOR activities and kinetics.[2] Usually, the lessons learned from such extended surfaces have helped in the understanding of nanocatalysts that mimic the reactivity and catalytic behavior of the extended surfaces.[3] Seldom, however, can the behavior of extended surfaces be completely translated down to the nanocatalysts.

Herein, we show that the platinum modified with calix[4]arene (calix) is, in fact, one of these rare examples in which the modified nanocatalyst system behaves in line with the corresponding extended-surface system. First, we demonstrate high selectivity of the HOR on calix-modified Pt(1099){10(111) × (100)}and Pt(110){2(111) × (100)} step surfaces. Then, we developed a methodology to form highly selective and stable SAMs of calix molecules on commercial nanocatalysts (3M nanostructured thin film (NSTF)[4] and Tanaka 5 nm Pt/C (TKK) catalysts). We find that if the synthesis is precisely controlled, the selectivity of nanoparticles for the ORR in the presence of hydrogen under conditions relevant to PEMFC operations is almost 100 %.

We start with the electrochemical characteristics of calix[4]arene-decorated Pt(110) and Pt(1099). As summarized in Figure 1, both stepped surfaces show characteristic cyclic voltammograms; the under-potentially deposited (H_{upd}) hydrogen (0–0.4 V) is followed first by a double-layer region and then at $E > 0.6$ V by reversible (OH_{ad}) and irreversible oxide formation.[5] On the calix-covered surfaces, however, both the H_{upd} and OH_{ad} regions are significantly suppressed. In line with Ref. [2], on the highly covered surfaces the number of "free" Pt sites (determined from the H_{upd} charge) is extremely low (ca. 2–3 %). However, on the same surface the HOR is similar to calix-free Pt, thus confirming that the turnover frequency (TOF) of the hydrogen reaction is extremely high[6] and that the Pt–H_2 energetics are not affected by the adsorbed calix molecules.

More importantly, we find that at $E > 0.6$ V, while the ORR is almost completely inhibited (these modifications are not accompanied by undesired peroxide production),[2] the HOR is under pure diffusion control. This unique selectivity is attributed to very strong ensemble effects in which the number of bare Pt sites available for adsorption of O_2 is much smaller than that for the adsorption of H_2 and the subsequent HOR.[2] We conclude therefore that the selectivity achieved using calix-modified electrodes is not affected by the presence of steps. This result is very important because it provides evidence that such behavior can be successfully translated to the most commonly used forms of nanocatalysts, which are known to contain a vast majority of such sites (steps and short-range terraces).

Having established the behavior of well-defined surfaces, we move on to the most relevant electrocatalyst systems: nanocatalysts. To encompass a wide range of electrocatalyst designs and properties, we provide an analysis for the two most commonly used commercial electrocatalysts. The TKK catalyst and the 3M NSTF catalyst were both studied (Figure 2). The TKK catalyst represents supported nanocatalysts, where platinum nanoparticles 2–10 nm in diameter are supported on amorphous carbon black. NSTF catalysts, comprised of a unique catalyst structure which is free of carbon support, are usually applied directly to the membrane to provide a compact membrane electrode assembly structure (Figure 2). Aqueous electrochemical experiments conducted using the RDE/RRDE (RDE = rotating disk electrode, RRDE = rotating ring disk electrode) methods for these nanocatalysts are well-established[7] and have been shown to correlate very well with operating fuel-cell systems.

We present herein results obtained from the RDE study that should be relevant for operating fuel-cell systems. Various modifications of the calix molecules were studied, including the thiolated derivatives of calix[6]arenes and calix[8]arenes (see the Supporting Information for the synthesis), but only the derivatives of the calix[4]arene family

---

[*] Dr. B. Genorio, Dr. D. Strmcnik, Dr. D. Tripkovic,
Dr. V. R. Stamenkovic, Dr. N. M. Markovic
Materials Science Division, Argonne National Laboratory
Argonne, IL 60439 (USA)
E-mail: nmmarkovic@anl.gov

Dr. B. Genorio
Faculty of Chemistry and Chemical Technology
University of Ljubljana (Slovenia)

Dr. R. Subbaraman
Nuclear Engineering Division
Argonne National Laboratory (USA)

[**] This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Materials Sciences, US Department of Energy under Contract No. DE-AC03-76SF00098 and the Center of Excellence Low Carbon Technologies Slovenia (CO NOT), Center of Excellence Advanced Materials and Technologies for the Future Slovenia (CO NAMASTE). R.S. is grateful for financial support from an Argonne postdoctoral fellowship. PEM = Proton-exchange membrane.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201100744.

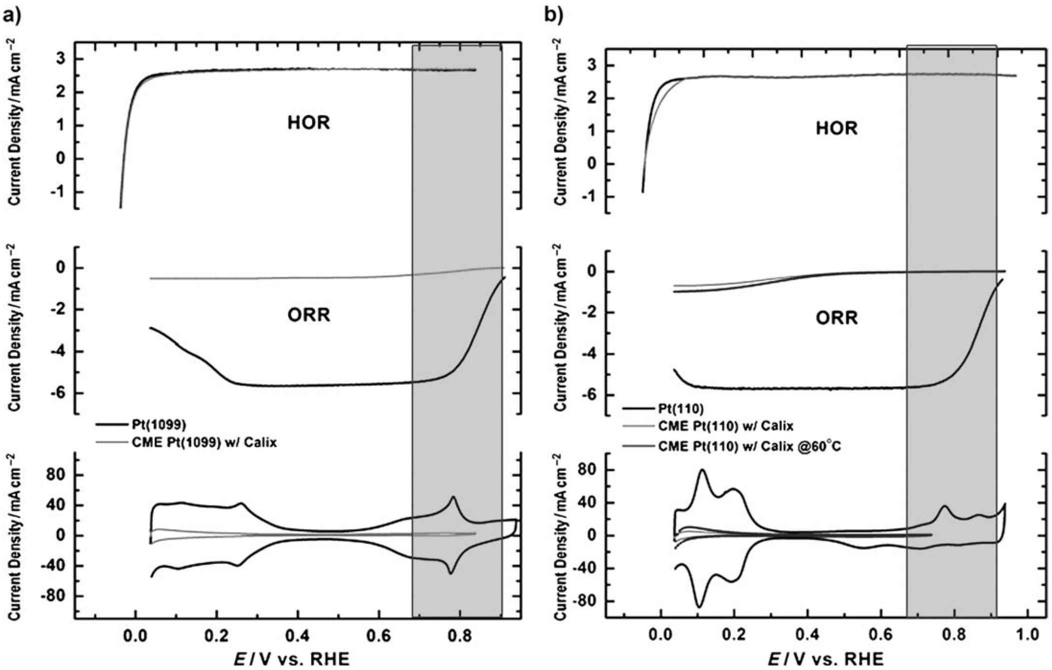


Figure 1. Electrochemical characteristics of calix-modified stepped surfaces: a) Pt(1099), b) Pt(110). Potentials of interest during startup and shutdown are shown in the shaded region.[1,2]

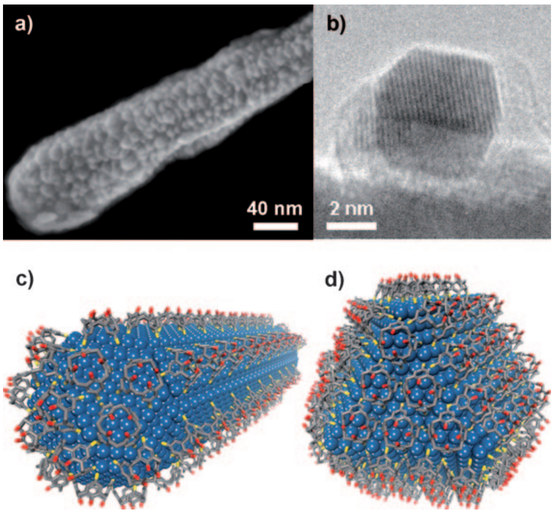


Figure 2. a) SEM image of an unmodified Pt nanowhisker. b) TEM morphology of typical TKK nanocatalysts. Calix molecules are not visible by electron microscopy. Based on our previous STM study,[2] we present a schematic representation of calix-modified nanocatalysts: c) Model morphology of calix[4]arene (yellow-gray-red)-modified Pt NSTF nanowhisker (blue). d) Model for TKK nanocatalyst chemically modified with calix[4]arene.

proved to be effective in achieving the selectivity, so only the results pertaining to the latter are presented. As can be seen in Figure 3, the calix[4]arene molecules are found to suppress the H_{upd} region (0.05–0.4 V) for both NSTF and TKK catalysts. The relative coverages for similar methods of preparation are slightly different, but the net results appear to be the same: an exceptional selectivity for the HOR versus ORR. As for stepped surfaces discussed above, the diffusion-limiting currents for the HOR are observed at potentials above 0.1 V and the activities below 0.1 V are, within the experimental limits, almost identical.

Furthermore, the ORR polarization curves show limited or insignificant currents in the potential region of interest for the anode-side catalyst. As was shown in the earlier study with Pt(111),[2] the peroxide yield on all extended and nanoparticle Pt–calix systems is negligible above 0.6 V, and the overall ORR behavior of these surfaces mimic ORR on uncovered or partially covered patches.[6] All of these observations suggest that SAMs of calix molecule can be used to tailor the selectivity of the nanocatalyst toward ORR while preserving the HOR activity, the goal for an ideal anode catalyst. It is also important that the established selectivity was possible only because the required number of active sites for maximal rates of the HOR is, in fact, extremely small but is sufficient to provide enough sites for the diffusion-limiting currents.[2]

In addition to selectivity of CME, both thermal and electrochemical stability of these electrodes are important properties that need to be addressed to evaluate the anode catalyst's applicability to PEMFC. In order to study the stability of calix-modified electrodes, we tested a Pt–calix system in an oxygen-rich environment at 0.8 V for approximately 14 h in solution at 60°C. These conditions are expected to be harsher than those experienced by the electrode in a real fuel-cell system. The exposure of the anode catalyst to high potentials ($E < 0.8$ V for anode) in an air (oxygen)-rich atmosphere during startup and shutdown is expected to last between tens of seconds and a few minutes a day. The temperatures are expected to be similar to those used in our test conditions.

Figure 4 shows the current–time relationship for the CME held at 0.8 V in an oxygen-rich atmosphere. The ORR current

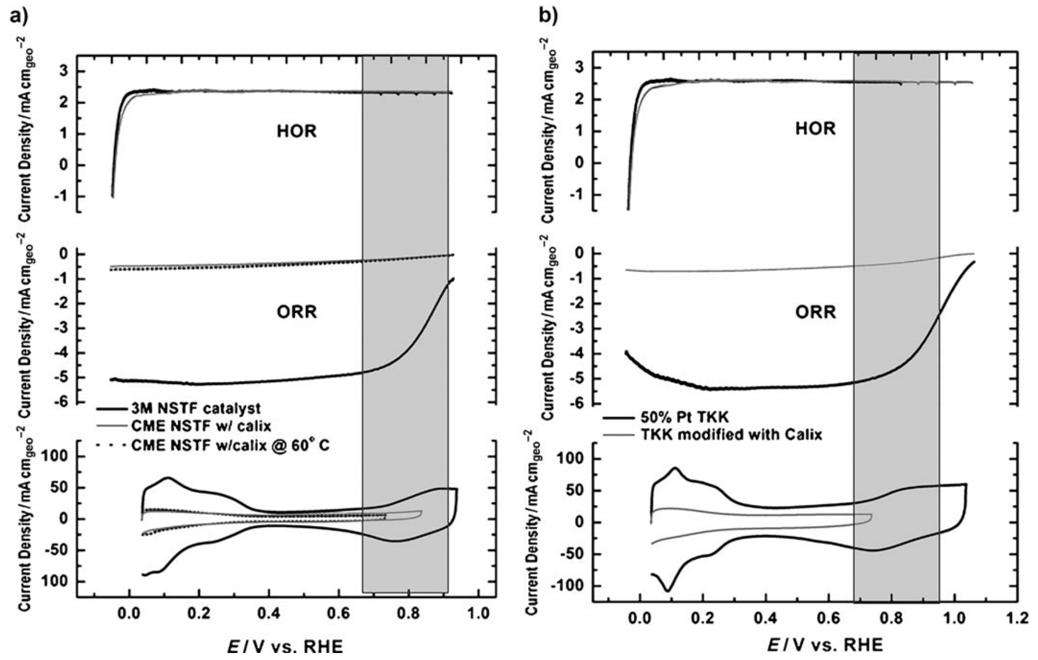


Figure 3. Electrochemical characteristics of calix-modified Pt nanocatalysts: a) NSTF, b) TKK (50% Pt loading). Catalyst loadings were approximately 14–16 μg cm^{-2}; lower loadings were also used to mimic anode catalyst performance, yielding similar qualitative results. All current densities are given with respect to the disk geometric area.

actually shows a small decay, thus suggesting that there is no loss of the calix molecules from the surface owing to oxidation. (Removal of the molecules by oxidation or desorption would increase the reduction current.) A similar experiment was also performed for the nanocatalysts (TKK) modified with calix[4]arene molecules, which show qualitatively similar results. This finding suggests that the calix[4]-arene-modified electrodes are stable under these operating conditions. Moreover, during the long-term experiments, the HOR (results not shown) is not affected at all.

In conclusion, our CMEs prepared by modifying Pt with calix[4]arene molecules are highly stable and can effectively tune the selectivity of anode catalysts for ORR without altering the maximum activity of the HOR. This behavior is highly transformational, extending from long-range-ordered stepped single-crystal surfaces to nanocatalysts. The CME approach is not restricted to a Pt–calix system, and we envision it to provide many applications in analytical, synthetic, and materials chemistry as well as in chemical energy conversion and storage.

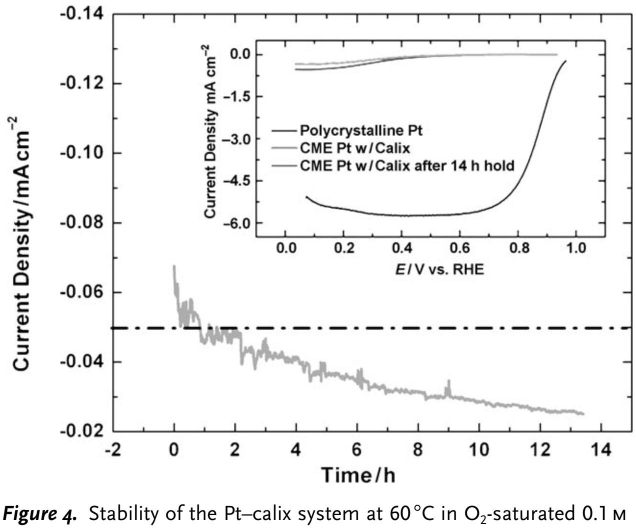


Figure 4. Stability of the Pt–calix system at 60 °C in O_2-saturated 0.1 M $HClO_4$ at 0.8 V. Inset: ORR curves for unmodified surface and Pt–calix surface both before and after the stability test. Note: the HOR remains unchanged for the duration of the experiment.

Experimental Section

Synthesis of the thiolated derivative of calix[4]arene: Adsorption of organic groups on noble-metal surfaces has been well-established for various groups (-S, -CN, -A, where A denotes the anchoring group).[8] The driving force for ordering of such large molecules is presumable governed by a synergy between the strong chemical bond between the anchoring groups and Pt surface atoms and the local steric interaction between adsorbed molecules. The calix[4]arene molecules' anchoring groups are usually of the form S(R) where (R) is used to cap the thiol group on the quadrupole anchoring groups. A detailed description of the synthesis procedure as well as molecular designs considered are presented in the Supporting Information.

Preparation of Pt(1099), Pt(110), and Pt(polycrystalline) surfaces and self-assembly: Pt electrodes were prepared by inductive heating for 10 min at approximately 1100 K in an argon–hydrogen flow (3% hydrogen). The annealed specimen was cooled slowly to room temperature in this flow stream and immediately covered by a droplet of water. The electrode was then immersed in a THF solution of calix[4]arene for 24 h, allowing the formation of a calix[4]arene SAM. The concentration of calix[4]arene in THF was 600 μM to obtain samples with very high coverages of calix on Pt surface. Coverages were estimated from the H_{upd} measurements. The effect of coverage on ORR and HOR was previously presented.[3] The coverages can be modified by either varying the concentrations of the calix/THF solution or the exposure time to the high-concentration solution. After SAM preparation, the crystals were washed thoroughly with deionized water before assembly and immersion in the electrochemical cell.

Preparation of NSTF and TKK catalyst electrodes and their self-assembly: The catalysts were mixed with water at a concentration of 1 mg mL^{-1}. This dispersion was then ultrasonically mixed for one hour, after which a stable suspension was obtained. A glassy carbon disk (6 mm diameter) was then mechanically polished. Known volumes of the suspensions were then added using a micropipette onto the glassy carbon disk electrode. The electrode was dried at 60 °C in an inert atmosphere. The suspension was applied so that it coated the surface of the electrode very uniformly. Once dry, these electrodes were washed with water to verify the good adhesion of particles to the glassy carbon substrate. Subsequently, the electrodes were immersed in 1000 μm solution of calix in THF. We chose to use a high concentration of calix owing to the larger surface area of Pt compared to the disk electrodes. The systems were equilibrated for 24 h. Another method involved assembly of the disk electrode in a hanging meniscus arrangement with subsequent immersion of the electrode in the calix solution with rotation (600 rpm) for 4 h. Both of these methods yielded similar coverages. After equilibration, the samples were washed thoroughly with water before being immersed in the electrochemical cell. For a discussion on the relative coverages obtained for the same conditions for TKK and NSTF, please refer to the Supporting Information.

RDE method, electrolytes, and electrochemical setup: After extensive rinsing, the electrode was embedded into the rotating-disk electrode (RDE) and transferred into a standard three-compartment electrochemical cell containing 0.1 m $HClO_4$ (Sigma–Aldrich). In each experiment, the electrode was immersed at 0.07 V in solution saturated with Ar. After obtaining a stable voltammogram between 0.07 and 0.7 V the polarization curve for the ORR was recorded on the disk on the disk electrode. Subsequently, oxygen was purged out of the solution and replaced with hydrogen, and HOR polarization curves were measured. Finally, the voltammetric response was again recorded in argon-purged solution to confirm that calix coverages had not changed significantly.

All gases were 5N5 quality purchased from Airgas Inc. The sweep rate for all measurements was 50 mV s^{-1}; for the ORR measurements, the electrode was rotated at 1600 rpm. Electrode potentials are given versus the reversible hydrogen electrode (RHE).

Received: January 29, 2011

Keywords: calixarenes · electrochemistry · heterogeneous catalysis · oxygen reduction reaction · platinum

[1] R. Borup, J. Meyers, B. Pivovar, Y. S. Kim, R. Mukundan, N. Garland, D. Myers, M. Wilson, F. Garzon, D. Wood, P. Zelenay, K. More, K. Stroh, T. Zawodzinski, J. Boncella, J. E. McGrath, M. Inaba, K. Miyatake, M. Hori, K. Ota, Z. Ogumi, S. Miyata, A. Nishikata, Z. Siroma, Y. Uchimoto, K. Yasuda, K. I. Kimijima, N. Iwashita, *Chem. Rev.* **2007**, *107*, 3904 – 3951; C. A. Reiser, L. Bregoli, T. W. Patterson, J. S. Yi, J. D. L. Yang, M. L. Perry, T. D. Jarvi, *Electrochem. Solid-State Lett.* **2005**, *8*, A273 – A276; J. P. Meyers, R. M. Darling, *J. Electrochem. Soc.* **2006**, *153*, A1432 – A1442; R. A. Sidik, *J. Solid State Electrochem.* **2009**, *13*, 1123 – 1126.

[2] B. Genorio, D. Strmcnik, R. Subbaraman, D. Tripkovic, G. Karapetrov, V. R. Stamenkovic, S. Pejovnik, N. M. Markovic, *Nat. Mater.* **2010**, *9*, 998 – 1003.

[3] H. A. Gasteiger, N. M. Markovic, *Science* **2009**, *324*, 48 – 49; V. R. Stamenkovic, B. S. Mun, M. Arenz, K. J. J. Mayrhofer, C. A. Lucas, G. F. Wang, P. N. Ross, N. M. Markovic, *Nat. Mater.* **2007**, *6*, 241 – 247.

[4] M. K. Debe, A. K. Schmoeckel, G. D. Vernstrorn, R. Atanasoski, *J. Power Sources* **2006**, *161*, 1002 – 1011.

[5] N. M. Markovic, P. N. Ross, Jr., *Surf. Sci. Rep.* **2002**, *45*, 117 – 229.

[6] D. S. Strmcnik, P. Rebec, M. Gaberscek, D. Tripkovic, V. Stamenkovic, C. Lucas, N. M. Markovic, *J. Phys. Chem. C* **2007**, *111*, 18672 – 18678.

[7] K. J. J. Mayrhofer, D. Strmcnik, B. B. Blizanac, V. Stamenkovic, M. Arenz, N. M. Markovic, *Electrochim. Acta* **2008**, *53*, 3181 – 3188.

[8] J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo, G. M. Whitesides, *Chem. Rev.* **2005**, *105*, 1103 – 1169.