

A Pd/C-CeO₂ Anode Catalyst for High-Performance Platinum-Free Anion Exchange Membrane Fuel Cells

Hamish A. Miller,* Alessandro Lavacchi, Francesco Vizza,* Marcello Marelli, Francesco Di Benedetto, Francesco D'Acapito, Yair Paska, Miles Page, and Dario R. Dekel*

Abstract: One of the biggest obstacles to the dissemination of fuel cells is their cost, a large part of which is due to platinum (Pt) electrocatalysts. Complete removal of Pt is a difficult if not impossible task for proton exchange membrane fuel cells (PEM-FCs). The anion exchange membrane fuel cell (AEM-FC) has long been proposed as a solution as non-Pt metals may be employed. Despite this, few examples of Pt-free AEM-FCs have been demonstrated with modest power output. The main obstacle preventing the realization of a high power density Pt-free AEM-FC is sluggish hydrogen oxidation (HOR) kinetics of the anode catalyst. Here we describe a Pt-free AEM-FC that employs a mixed carbon-CeO₂ supported palladium (Pd) anode catalyst that exhibits enhanced kinetics for the HOR. AEM-FC tests run on dry H₂ and pure air show peak power densities of more than 500 mWcm⁻².

Recent analyses have shown that among PEM-FC components around 45 % of the cost comes from the platinum (Pt) electrocatalyst.^[1] Therefore, a complete removal of Pt from fuel cells and replacement with metals that are less expensive and more abundant in nature is crucial to make this technology an affordable solution for automotive as well as other large scale applications. As an alternative to PEM-FCs that operate under corrosive acidic conditions the use of

alkaline anion exchange membrane fuel cells (AEM-FC) may reduce costs by avoiding the use of platinum.^[2]

In the AEM-FC cathode, non-noble metals can readily replace Pt.^[3] Varcoe et al. have recently comprehensively reviewed the range of AEMs and ionomers developed for AEM-FCs.^[4] Less attention has been paid to the anode catalyst for the hydrogen oxidation reaction (HOR).^[2e,5] In contrast to PEM-FCs, HOR kinetics are quite slow in alkaline media. Indeed, the HOR activity on noble metals (Pt, Pd and Ir) decreases by a factor of ca. 100 when switching from low to high pH.^[6] Some work has been done on developing non-Pt HOR catalysts^[7] but very few reports of complete AEM-FCs are available. Zhuang and co-workers with NiCr and NiW anode catalysts have demonstrated Pt-free H₂/O₂ AEM-FCs generating around 50 mWcm⁻² peak power.^[5c,8] Recently, with a PdNi anode catalyst 400 mWcm⁻² was obtained by Alesker et al.^[9] The main obstacle is the challenge of overcoming poor HOR kinetics in alkaline media.

In this work, we present a nanoparticle (NP) Pd HOR catalyst with a composite support made of Vulcan XC-72 carbon and CeO₂ (C-CeO₂) which exhibits enhanced HOR kinetics in alkaline media. Ceria (CeO₂) was used, as it is one of the most oxygen deficient compounds, known for rapid its saturation with OH⁻ ions in alkaline media^[10] and spillover of OH⁻ to supported metal nanoparticles.^[10b] We have found in previous studies that a mixed ceria-carbon support enhances the activity of Pd anodes in direct ethanol fuel cells (DEFC) by promoting the transfer of OH⁻ to form active Pd^IOH_{ads} species.^[11]

The mixed support contains 50 wt % CeO₂ and 50 wt % Vulcan XC-72 carbon. Pd (10 wt %) was deposited by chemical deposition and reduction (see Supporting Information (SI) for synthesis details). The fuel cell anode was prepared using either the new composite Pd/C-CeO₂ catalyst or a homemade reference Pd/C catalyst (C = Vulcan XC-72, 10 wt % Pd).^[12] The anode Pd loading was 0.3 mgcm⁻². Silver (Ag) was used as a cathode catalyst with a loading of 3.0 mg_{Ag}cm⁻². Membrane electrode assemblies (MEAs)^[13] with an active area of 5 cm² were tested in AEM-FC single cells (see SI for complete description).^[13b,14]

Figure 1 shows the cell performance at 73 °C with air (< 10 ppm CO₂) at the cathode (1.0 slm, 1.0 barg, dew point 73 °C) and dry H₂ (0.2 slm, 3.0 barg, 25 °C) fed to the anode.

The AEM-FC with the Pd/C anode performed modestly reaching a maximum power density of 0.1 Wcm⁻² and maximum current density of less than 1 Acm⁻². The C-CeO₂ supported Pd catalyst reaches a peak power density of 0.5 Wcm⁻² at a current density of about 1.5 Acm⁻² and a maximum current density of ca. 3 Acm⁻². Significantly

[*] Dr. H. A. Miller, Dr. A. Lavacchi, Dr. F. Vizza
CNR-ICCOM
Via Madonna del Piano 10, 50019 Sesto Fiorentino, Firenze (Italy)
E-mail: hamish.miller@iccom.cnr.it
francesco.vizza@iccom.cnr.it

Dr. M. Marelli
CNR-ISTM
via Camillo Golgi 19, 20133 Milan (Italy)

Dr. F. Di Benedetto
Department of Earth Sciences, Università di Firenze
Via G. La Pira, 4, 50100 Firenze (Italy)

Dr. F. D'Acapito
CNR-IOM-OGG c/o ESRF
71, Avenue des Martyrs, CS, 40220 Grenoble, Cédex 9 (France)

Y. Paska, M. Page
CellEra, Caesarea Business and Industrial Park
Caesarea, 30889 (Israel)

Dr. D. R. Dekel
The Wolfson Department of Chemical Engineering
Technion – Israel Institute of Technology
Haifa, 3200003 (Israel)
E-mail: dario@tx.technion.ac.il

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under <http://dx.doi.org/10.1002/anie.201600647>.

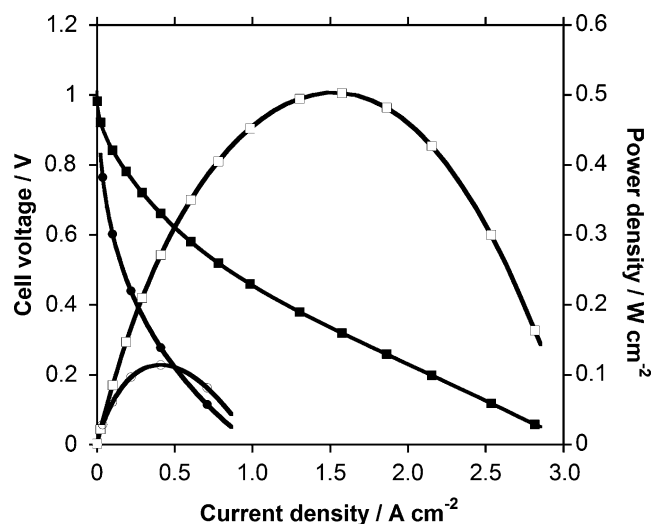


Figure 1. Polarization curves of Pt-free AEM-FCs with Pd/C (○) and Pd/C-CeO₂ (□) anodes. $T_{\text{cell}} = 73^{\circ}\text{C}$. Cathode: air (<10 ppm CO₂, 1 slm); anode: dry H₂ (0.2 slm).

higher fuel cell performance is obtained switching the carbon support for the C-CeO₂ support. The enhancement due to CeO₂ on the HOR activity of Pd was investigated in electrochemical cells. Cyclic voltammograms (CV) recorded with Pd/C and Pd/C-CeO₂ in N₂-sat 0.1 M KOH are shown in Figure 2a. The peaks for hydrogen adsorption and desorption (UPD) can be readily assigned based on literature data.^[11] A negative shift in the H_{UPD} oxidation peak of ca. 90 mV is seen for the C-CeO₂ supported catalyst relative to the C supported catalyst (Figure 2a). This implies that H is bound less strongly on the surface of Pd supported on C-CeO₂. A weakening of the metal-hydrogen (M-H) binding energy generally enhances the HOR in alkaline media.^[15] In fact, the rate-determining step (rds) for HOR at high pH is the oxidative desorption of H_{UPD} .^[15a,b] An increase in the HOR activity of Pd/C-CeO₂ with respect to Pd/C is observed using a rotating disk electrode (RDE) in H₂-sat 0.1 M KOH (Figure 2b). Pd/C exhibits typically sluggish HOR kinetics reaching the diffusion limited current plateau at 0.5 V (RHE).^[15b,16] By contrast, the Pd/C-CeO₂ catalyst reaches the diffusion limited current plateau at ca. 0.25 V.

Tafel analysis for the HOR is shown in Figure 2c.^[17] Electrochemical data are also listed in Table 1, including the electrochemically active surface area (ECSA), exchange current densities (i_0) and the mass activity per gram of Pd ($i_{0,m}$). The HOR exchange current density increases more than 20 fold for the C-CeO₂ supported Pd catalyst relative to Pd/C. Both catalysts have a similar ECSA and Pd NP size distribution (see SI for TEM analysis), so such an increase

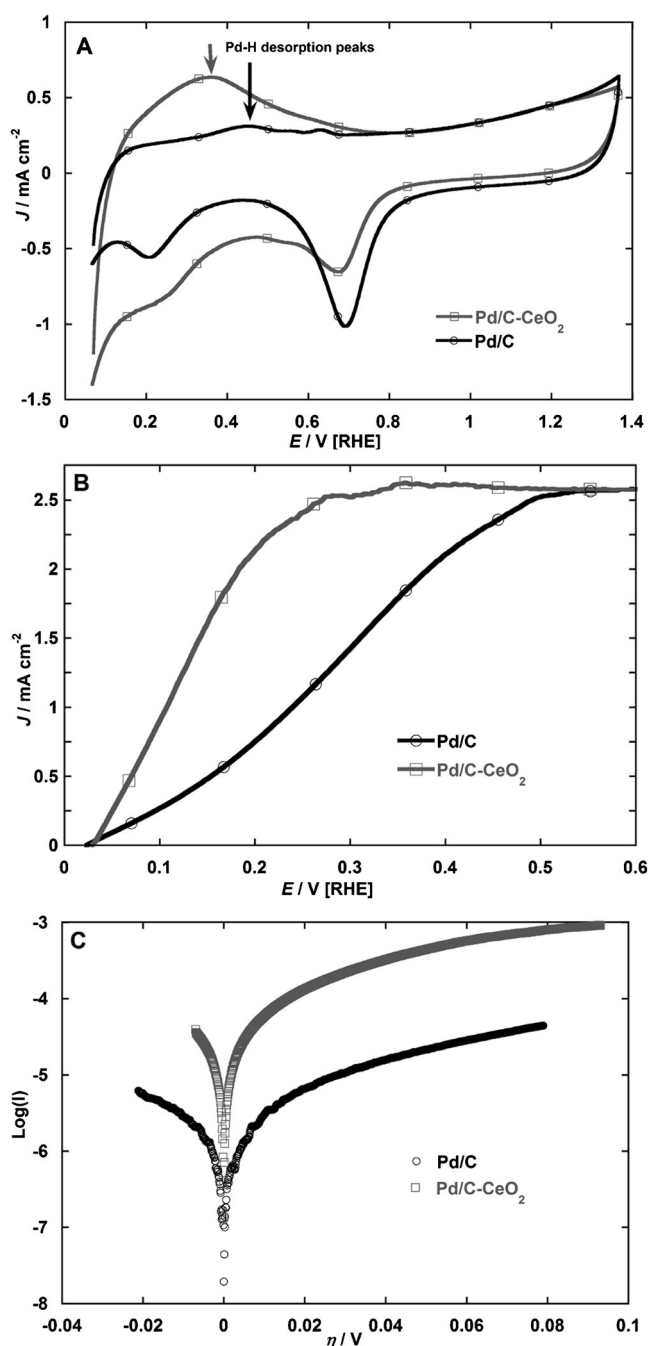


Figure 2. A) Cyclic voltammetry of Pd/C and Pd/C-CeO₂ in static N₂-saturated 0.1 M KOH solution. B) Steady-state polarization curves of HOR in H₂-saturated 0.1 M KOH (1600 rpm). C) Tafel slope analysis obtained in H₂-saturated 0.1 M KOH at 10 mV s⁻¹ and 1600 rpm.

in the activity can be attributed to electronic effects due to Pd-CeO₂ interactions. The Tafel slopes are also similar suggesting the same HOR mechanism (66–68 mV dec⁻¹). Such a range of values indicates that the rds for both catalysts is molecular hydrogen dissociative adsorption (Tafel step).^[15b]

High angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) and high-resolution transmission electron microscopy (HR-TEM) were used to study the catalyst morphology. Z-contrast STEM micrographs

Table 1: Electrochemical data.

	i_0 [mA cm _{Pd} ⁻²]	ECSA [m ² g ⁻¹ Pd]	Tafel slope [mV dec ⁻¹]	$i_{0,m}$ [A g _{Pd} ⁻²]
Pd/C	2.7	45	68	1.1
Pd/C-CeO ₂	54.5	43	66	24

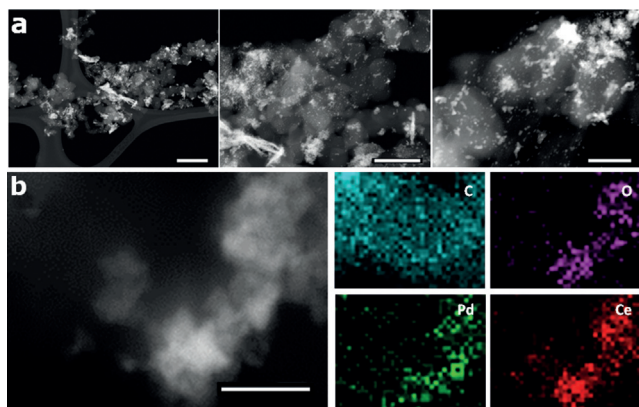


Figure 3. a) STEM micrographs of Pd/C-CeO₂ at different magnifications (scale bars from left to right; 200 nm, 100 nm and 50 nm, respectively). b) STEM image of Pd/C-CeO₂ and related EDX maps for C, O, Pd and Ce, respectively (scale bar is 20 nm).

(Figure 3a) of Pd/C-CeO₂ are shown at various magnifications. The agglomerated CeO₂ structures appear brighter than carbon on the STEM images. Pd NPs are visible only on the carbon part of the sample due to poor resolution between Pd and CeO₂ (mean size of carbon supported NPs 2.0 nm, see SI). Therefore to investigate the Pd distribution over both the carbon and ceria parts of the catalyst we used STEM-EDX (energy-dispersive X-ray) elemental map analysis. A representative area of the catalyst is shown in Figure 3b, pointing to a notable accumulation of Pd on the ceria-rich regions.

Strong Pd-CeO₂ interactions would have a significant effect on the oxidation state of the Pd due to the oxide spillover capacity of ceria that would leave most of the Pd in the oxidized form. To verify this the Pd oxidation state in the Pd/C and Pd/C-CeO₂ catalysts was investigated by X-ray absorption spectroscopy (XAS). Spectra were also collected on PdO and on a foil of metallic Pd as standards.^[18] In Figure 4a a comparison of the XANES (X-ray absorption near edge structure) spectra clearly shows that Pd in Pd/C-CeO₂ is mostly oxidized, while in Pd/C the palladium is prevalently in its metallic state. EXAFS (extended X-ray absorption fine structure) analysis was carried out modeling the data with two components, that is, metallic Pd and PdO. The raw EXAFS data and related Fourier-transforms are shown in Figures 4b and 4c, respectively. The EXAFS analysis shows Pd^{II} accounts for 87 wt % of the total Pd content in Pd/C-CeO₂ (see SI). This is unusual as carbon supported Pd NPs (ca. 2 nm in diameter) are usually at least 50 % metallic.^[19] As expected, only 17 wt % of PdO was found in the Pd/C system.^[19] The XAS data therefore shows for the C-CeO₂ supported catalyst that the Pd exists primarily as oxide also confirming that Pd is largely supported on the ceria regions.^[20] Such a structure not only leads to the weakening of the Pd-H bond but also favors the fast transfer of OH⁻ ions from ceria to Pd during catalysis.

In summary, the presence of CeO₂ deposited onto the carbon support of a nanoparticle Pd catalyst leads to a fivefold increase in the anode performance relative to a Pd/C catalyst. A careful morphological analysis attests to a fine dispersion of the Pd nanoparticles accumulated mostly on the ceria part of

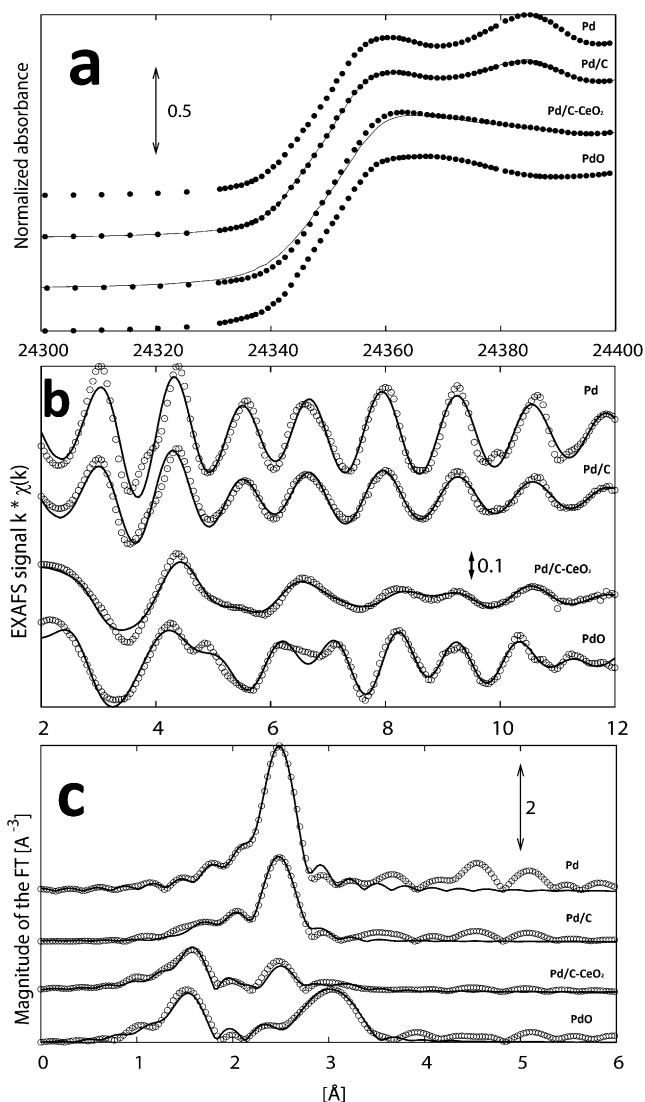


Figure 4. a) XAS at the Pd K α edge of Pd/C-CeO₂ and Pd/C (XANES spectra of Pd-foil and PdO standards are also shown), b) EXAFS data and the related c) Fourier-transforms at the Pd K α edge (transformation range 2.8–13.5 Å⁻¹, k² weight). Dots are experimental data while continuous lines are calculated best-fit data.

the catalyst. Such a structure helps to weaken the Pd-H bonds and assists in supplying OH_{ad} from oxophilic CeO₂ to the Pd-H_{ad} (HOR reaction sites), thus accelerating the overall HOR. A Pt-free AEM-FC using this Pd/C-CeO₂ anode catalyst and a Ag cathode catalyst was tested under dry H₂ and partially filtered ambient air (< 10 ppm CO₂) supplied to the anode and cathode, respectively. This entirely Pt-free AEM-FC produced a peak power density of over 500 mW cm⁻².

Acknowledgements

Ente Cassa di Risparmio di Firenze (project HYDROLAB2 and EnergyLab) and MIUR (Italy) (FIRB 2010 project RBFR10J4H7). M.M. acknowledges the Regione Lombardia project TIMES, Accordo Quadro Regione Lombardia, CNR.

F.D.B. acknowledges A. Giaccherini and G. Montegrossi for help in the acquisition and analysis of the XAS data, and A. Puri for his support at the beamline. XAS data were performed at the BM08 beamline (ESRF, Grenoble, France) during the 08-01-996 experimental beamtime. ESRF is gratefully acknowledged for provision of synchrotron radiation and technical infrastructure. F.D.B. also acknowledges Gabbrielli Technology and the Department of Earth Sciences of the Univ. of Florence (ex 60 % 2013 funds) for funding his research. We thank Carlo Bartoli for having built the hardware for the XAS experiments. D.R.D. thanks Dr. Piotr Zelenay for valuable input. We thank Dr. Stefano Caporali (Univ. of Florence) for the XPS analysis.

Keywords: alkaline membrane · ceria · fuel cells · palladium · platinum free electrodes

How to cite: *Angew. Chem. Int. Ed.* **2016**, 55, 6004–6007
Angew. Chem. **2016**, 128, 6108–6111

- [1] J. S. Spendelow, J. Marcinkoski (2013). DOE Fuel Cell Technologies Office Record 13012: Fuel Cell System Cost - 2013. Accessed November 16, 2015: http://energy.gov/sites/prod/files/2014/03/f11/13012_fuel_cell_system_cost_2013.pdf.
- [2] a) M. Piana, M. Boccia, A. Filpi, E. Flammia, H. A. Miller, M. Orsini, F. Salusti, S. Santiccioli, F. Ciardelli, A. Pucci, *J. Power Sources* **2010**, 195, 5875–5881; b) J. R. Varcoe, R. C. T. Slade, *Fuel Cells* **2005**, 5, 187–200; c) Y. J. Sa, C. Park, H. Y. Jeong, S. H. Park, Z. Lee, K. T. Kim, G. G. Park, S. H. Joo, *Angew. Chem. Int. Ed.* **2014**, 53, 4102–4106; *Angew. Chem.* **2014**, 126, 4186–4190; d) D. Dekel, in *Encyclopedia of Applied Electrochemistry* (Eds.: G. Kreysa, K.-i. Ota, R. Savinell), Springer, New York, **2014**, pp. 33–45; e) D. Dekel in *Encyclopedia of Applied Electrochemistry* (Eds.: G. Kreysa, K.-i. Ota, R. Savinell), Springer, New York, **2014**, pp. 26–33.
- [3] a) Y. Nie, L. Li, Z. D. Wei, *Chem. Soc. Rev.* **2015**, 44, 2168–2201; b) G. Wu, P. Zelenay, *Acc. Chem. Res.* **2013**, 46, 1878–1889.
- [4] J. R. Varcoe, P. Atanassov, D. R. Dekel, A. M. Herring, M. A. Hickner, P. A. Kohl, A. R. Kucernak, W. E. Mustain, K. Nijmeijer, K. Scott, T. W. Xu, L. Zhuang, *Energy Environ. Sci.* **2014**, 7, 3135–3191.
- [5] a) A. Serov, C. Kwak, *Appl. Catal. B* **2009**, 90, 313–320; b) W. C. Sheng, H. A. Gasteiger, Y. Shao-Horn, *J. Electrochem. Soc.* **2010**, 157, B1529–B1536; c) S. F. Lu, J. Pan, A. B. Huang, L. Zhuang, J. T. Lu, *Proc. Natl. Acad. Sci. USA* **2008**, 105, 20611–20614.
- [6] J. Durst, A. Siebel, C. Simon, F. Hasche, J. Herranz, H. A. Gasteiger, *Energy Environ. Sci.* **2014**, 7, 2255–2260.
- [7] W. C. Sheng, A. P. Bivens, M. Myint, Z. B. Zhuang, R. V. Forest, Q. R. Fang, J. G. Chen, Y. S. Yan, *Energy Environ. Sci.* **2014**, 7, 1719–1724.
- [8] Q. P. Hu, G. W. Li, J. Pan, L. S. Tan, J. T. Lu, L. Zhuang, *Int. J. Hydrogen Energy* **2013**, 38, 16264–16268.
- [9] M. Alesker, M. Page, M. Shviro, Y. Paska, G. Gershinsky, D. R. Dekel, D. Zitoun, *J. Power Sources* **2016**, 304, 332–339.
- [10] a) Z. L. A. Feng, F. El Gabaly, X. F. Ye, Z. X. Shen, W. C. Chueh, *Nat. Commun.* **2014**, 5, 4374; b) T. Skála, F. Šutara, M. Škoda, K. C. Prince, V. Matolín, *J. Phys. Condens. Matter* **2009**, 21, 055005.
- [11] V. Bambagioni, C. Bianchini, Y. X. Chen, J. Filippi, P. Fornasiero, M. Innocenti, A. Lavacchi, A. Marchionni, W. Oberhauser, F. Vizza, *ChemSusChem* **2012**, 5, 1266–1273.
- [12] V. Bambagioni, C. Bianchini, J. Filippi, W. Oberhauser, A. Marchionni, F. Vizza, R. Psaro, L. Sordelli, M. L. Foresti, M. Innocenti, *ChemSusChem* **2009**, 2, 99–112.
- [13] a) S. Gottesfeld, D. Dekel, D. S. Simakov (Cellera Inc), US20100216052 A1, **2010**; b) S. Gottesfeld, Z. Gottesfeld, D. Dekel; D. S. , Simakov, (Cellera Inc), US8257872 B2, **2012**.
- [14] a) S. Gottesfeld, D. Dekel, Z. Gottesfeld, D. S. Simakov, (Cellera Inc), US8637196 B2, **2014**; b) D. G. Dekel, S. Gottesfeld, WO2013184269 A3, (Cellera Inc), **2013**; c) S. Gottesfeld, D. Dekel, Z. Gottesfeld, S. D. Simakov, (Cellera Inc), US7943258 B2, **2011**; d) S. Gottesfeld, Z. Gottesfeld, D. Dekel, S. D. Simakov, Japan 2015-038888, **2014**.
- [15] a) Y. Wang, G. W. Wang, G. W. Li, B. Huang, J. Pan, Q. Liu, J. J. Han, L. Xiao, J. T. Lu, L. Zhuang, *Energy Environ. Sci.* **2015**, 8, 177–181; b) S. St. John, R. W. Atkinson, R. R. Unocic, T. A. Zawodzinski, A. B. Papandrew, *J. Phys. Chem. C* **2015**, 119, 13481–13487; c) W. C. Sheng, Z. B. Zhuang, M. R. Gao, J. Zheng, J. G. G. Chen, Y. S. Yan, *Nat. Commun.* **2015**, 6, 5848.
- [16] M. Shao, *J. Power Sources* **2011**, 196, 2433–2444.
- [17] P. J. Rheinlander, J. Herranz, J. Durst, H. A. Gasteiger, *J. Electrochem. Soc.* **2014**, 161, F1448–F1457.
- [18] L. Q. Wang, A. Lavacchi, M. Bellini, F. D'Acapito, F. Di Benedetto, M. Innocenti, H. A. Miller, G. Montegrossi, C. Zaffaroni, F. Vizza, *Electrochim. Acta* **2015**, 177, 100–106.
- [19] W. J. Zhou, M. Li, O. L. Ding, S. H. Chan, L. Zhang, Y. H. Xue, *Int. J. Hydrogen Energy* **2014**, 39, 6433–6442.
- [20] a) W. J. Shen, Y. Matsumura, *J. Mol. Catal. A* **2000**, 153, 165–168; b) Y. Y. Zhou, N. J. Lawrence, T. S. Wu, J. Liu, P. Kent, Y. L. Soo, C. L. Cheung, *ChemCatChem* **2014**, 6, 2937–2946.

Received: January 20, 2016

Revised: February 29, 2016

Published online: April 8, 2016