Synthesis of CeO$_x$-Decorated Pd/C Catalysts by Controlled Surface Reactions for Hydrogen Oxidation in Anion Exchange Membrane Fuel Cells

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Due to the sluggish kinetics of the hydrogen oxidation reaction (HOR) in alkaline electrolytes, the development of more efficient HOR catalysts is essential for the next generation of anion-exchange membrane fuel cells (AEMFCs). In this work, CeO$_x$ is selectively deposited onto carbon-supported Pd nanoparticles by controlled surface reactions, aiming to enhance the homogenous distribution of CeO$_x$ and its preferential attachment to Pd nanoparticles, to achieve highly active CeO$_x$-Pd/C catalysts. The catalysts are characterized by inductively coupled plasma–atomic emission spectroscopy, X-ray diffraction, high-resolution transmission electron microscopy, scanning transmission electron microscopy (STEM), electron energy loss spectroscopy, and X-ray photoelectron spectroscopy to confirm the bulk composition, phases present, morphology, elemental mapping, local oxidation, and surface chemical states, respectively. The intimate contact between Pd and CeO$_x$ is shown through high-resolution STEM maps. The oxophilic nature of CeO$_x$ and its effect on Pd are probed by CO stripping. The interfacial contact area between CeO$_x$ and Pd nanoparticles is calculated for the first time and correlated to the electrochemical performance of the CeO$_x$-Pd/C catalysts. Highest recorded HOR specific exchange current ($51.5 \text{ mA mg}^{-1}\text{Pd}$) and H$_2$–O$_2$ AEMFC performance (peak power density of 1,169 mW cm$^{-2}$ mg Pd$^{-1}$) are obtained with a CeO$_x$-Pd/C catalyst with Ce$_{0.38}$/Pd bulk atomic ratio.

1. Introduction

Significant progress has been achieved recently in the field of anion exchange membrane fuel cells (AEMFCs).[1–3] In spite of the remarkable development of this technology, the deployment of AEMFCs is still hindered by the chemical degradation of the anion exchange membrane (AEM) and ionomers,[4–11] carbonation issues,[12–15] and by the sluggish kinetics of the hydrogen oxidation reaction (HOR).[2,16,17] It has been shown that the HOR kinetics in alkaline media is two to three orders of magnitude lower than that in acidic media,[18,19] even for the most active catalysts such as Pt,[17,19–22] Rh,[23] and Ir.[23] There are increasing efforts in the development of HOR electrocatalysts based on more abundant elements,[24–31] as well as Pd.[32,33] In order to increase the HOR kinetics of Pd, previous studies focused their efforts in the development of Pd-CeO$_x$ composites, as the most promising Pt-free catalyst for HOR.[34–39] The
use of ceria (CeO$_2$) is justified because i) it is an oxygen-deficient compound with a fast OH$^-$ saturation[34,40] and ii) it has a high oxophilic character.[43]

The metal-metal oxide interaction on Pd-CeO$_2$ systems has been thoroughly investigated for several chemical reactions, such as CO oxidation, CH$_4$ oxidation, and NO reduction.[42–46] These studies focused on the formation of Pd$_x$Ce$_{1-x}$O$_2$ local solid solutions, which provide tight contact and specificity on Pd-ceria based systems in catalysis. These have been thoroughly investigated by using extended X-ray absorption fine structure (EXAFS), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and density functional theory (DFT) calculations.[42–46] Pd-CeO$_2$ systems have not only been studied in electrochemical but have also been widely used in environmental catalysis.[47–53] For example, Tan et al. investigated the support morphology-dependent catalytic activity of Pd/CeO$_2$ to eliminate indoor formaldehyde pollution.[47]

Several methods have been employed to prepare Pd/C-CeO$_2$ catalysts as an efficient HOR catalyst. Using a conventional chemical wet method, Miller et al. replaced 50% of the carbon catalyst support with CeO$_2$, followed by the deposition of Pd nanoparticles. The thus obtained Pd/C-CeO$_2$ catalyst exhibited a 20-fold improvement in the HOR activity compared to that of Pd/C in rotating disk electrode (RDE) measurements.[34] After careful analysis of the morphology of the catalyst, the authors claimed that the Pd particles are accumulated in the proximity of CeO$_2$, which helps in supplying OH$^-$ from CeO$_2$ to Pd-H$_2$. The superior HOR activity of Pd/C-CeO$_2$ is hence attributed to the OH$^-$ spillover from CeO$_2$ to Pd, which enhances the rate-limiting Volmer reaction alongside with weakening of the Pd-H bonding, and thus, the hydrogen binding energy (HBE) estimated from the contact between the nanoparticles, affecting, in turn, the OH$^-$ spillover from CeO$_2$ to the Pd nanoparticles. The CeO$_x$ content in the composites is varied using sequential CSR cycles and was used to demonstrate the crucial role of the amount of CeO$_x$ in the promotion of the HOR kinetics of the CeO$_x$-Pd/C catalysts. A comprehensive set of experimental techniques is used to follow the structural, morphological, and compositional changes occurring in the catalysts along with the CeO$_x$ content variation, as well as to observe the evolution of the local and surface chemical state and the modification of the electrochemical properties of the CeO$_2$-Pd/C catalysts. Finally, a CeO$_x$-Pd/C catalyst prepared by the CSR method, selected with the highest activity towards HOR, is successfully tested in operando H$_2$-O$_2$ AEMFCs, showing its potential as HOR catalyst for this technology.

### 2. Results and Discussion

The bulk and surface compositions of the CeO$_x$-Pd/C catalysts were determined by ICP-AES and XPS, respectively, and are given in Table 1. As can be seen, CeO$_x$-Pd/C catalysts with a

| Catalyst | ICP-AES Pd bulk [wt%] | ICP-AES Ce bulk [wt%] | Calculated Ce/Pd [at. ratio]* | ICP-AES Measured bulk Ce/Pd [at. ratio] | XPS Measured surface Ce/Pd [at. ratio] |
|----------|-----------------------|------------------------|------------------------------|----------------------------------------|---------------------------------------|
| Pd/C     | 9.08                  | 0.00                   | 0.00                         | 0.00                                   | 0.00                                  |
| 0.24 CeO$_x$-Pd/C | 7.67                  | 2.47                   | 0.26                         | 0.24                                   | 0.66                                  |
| 0.38 CeO$_x$-Pd/C | 7.87                  | 3.99                   | 0.39                         | 0.38                                   | 0.66                                  |
| 0.59 CeO$_x$-Pd/C | 7.82                  | 6.06                   | 0.85                         | 0.59                                   | 1.56                                  |

* Based on Pd and Ce theoretical loadings (Section S1, Supporting Information).
wide Ce/Pd atomic ratio range (0–0.65) have been successfully prepared by the CSR method. The Ce/Pd bulk atomic ratios measured after CSR cycles are similar to the calculated ratios based on the target composition (see the Supporting Information for more details), with a slight deviation for the catalyst with the highest loading. This suggests the saturation of the surface by CeO$_2$ after several CSR cycles. If there is no available surface for the Ce precursor to bond, the precursor might get physically absorbed on the surface and easily decompose during the reduction step. The surface Ce/Pd atomic ratios are higher than those on the bulk, which is in agreement with the surface affinity of the CSR approach, in which the ceria nanoislands are formed at the surface of the metal nanoparticles. [59–61] Based on the bulk composition obtained from ICP-AES measurements, the samples were labeled as $n$ CeO$_2$-Pd/C, where $n$ indicates the measured Ce/Pd bulk atomic ratio (0.24 CeO$_2$-Pd/C, 0.38 CeO$_2$-Pd/C, and 0.59 CeO$_2$-Pd/C).

The XRD patterns of monometallic Pd/C and CSR-synthesized CeO$_2$-Pd/C catalysts are shown in Figure 1. Phases of Pd, CeO$_2$, and carbon are observed. The details of the reflections from each phase are given in the Supporting Information. With the addition of CeO$_2$, the intensity of the (111), (200), and (311) facets of CeO$_2$ (at 28.6$^\circ$, 33.1$^\circ$, and 56.3$^\circ$, respectively) increases gradually. No shift is observed in the position of the XRD peaks for Pd after the incorporation of CeO$_2$, indicating that alloying is not taking place between Pd and CeO$_2$. Thus, any changes in the properties of the catalyst could be ascribed solely to the decoration of the Pd surface by CeO$_2$, rather than the bulk electronic effect. The details of the crystallite size calculation of CeO$_2$ are given in the Supporting Information. Unlike the Pd/C-CeO$_2$ composites reported earlier, [34] the CSR method results in the formation of low crystalline ceria nanoparticles, with crystallite size between 1.7–3.2 nm (see Table S1 in the Supporting Information), showing low-intensity XRD reflections with significant broadening.

Pd3d (Figure S1a–c, Supporting Information) and Ce3d (Figure S2a–c, Supporting Information) XPS spectra were recorded to get information about the chemical environment of Pd, CeO$_2$, and their surface atomic composition. The Pd3d XPS spectrum of Pd/C is shown in Figure S3 in the Supporting Information. The Pd3d spectrum splits into two peaks corresponding to 3d$_{3/2}$ and 3d$_{5/2}$ due to the spin-orbit coupling. Each pair is fitted into three different Pd species of metallic Pd(0), Pd(II) and Pd(IV). The peak pair at lower binding energy is assigned to Pd(0) and those with higher binding energies to Pd(II) and Pd(IV), respectively. The metallic Pd(0) peak position is comparable to that reported in the literature. [36, 62] The summary of the XPS results in the formation of low crystalline ceria nanoparticles, with crystallite size between 1.7–3.2 nm (see Table S1 in the Supporting Information), showing low-intensity XRD reflections with significant broadening.

Table 2. Surface compositions and peak positions of Pd(0), Pd(II), and Pd (IV) species of Pd/C and CSR-synthesized CeO$_2$-Pd/C catalysts.

| Catalyst | Pd species | Percentage | Pd 3d$_{3/2}$ position [eV] | Pd 3d$_{5/2}$ position [eV] | Pd3d FWHM [eV] |
|----------|------------|------------|----------------------------|----------------------------|----------------|
| Pd/C     | Pd(0)      | 61.43      | 335.18                     | 340.44                     | 0.97           | 0.97           |
|          | Pd(II)     | 20.05      | 336.10                     | 341.36                     | 0.97           | 0.97           |
|          | Pd(IV)     | 18.52      | 337.65                     | 342.91                     | 2.20           | 2.20           |
| 0.24 CeO$_2$-Pd/C | Pd(0)      | 57.57      | 335.07                     | 340.33                     | 0.86           | 0.86           |
|          | Pd(II)     | 21.65      | 335.94                     | 341.20                     | 0.86           | 0.86           |
|          | Pd(IV)     | 20.78      | 337.40                     | 342.66                     | 2.20           | 2.20           |
| 0.38 CeO$_2$-Pd/C | Pd(0)      | 49.39      | 335.17                     | 340.43                     | 0.87           | 0.87           |
|          | Pd(II)     | 13.72      | 336.01                     | 341.27                     | 0.87           | 0.87           |
|          | Pd(IV)     | 36.89      | 337.40                     | 342.66                     | 2.20           | 2.20           |
| 0.59 CeO$_2$-Pd/C | Pd(0)      | 47.27      | 334.87                     | 340.13                     | 0.87           | 0.87           |
|          | Pd(II)     | 32.48      | 335.52                     | 340.78                     | 1.10           | 1.10           |
|          | Pd(IV)     | 20.25      | 337.16                     | 342.42                     | 2.20           | 2.20           |
present in 0.38 CeO\textsubscript{x}-Pd/C results from partial charge transfer from metallic Pd to CeO\textsubscript{x}. This observation is in line with previously reported results\cite{36}, where the higher ratio of Pd(0)/Pd(II) arises from poor Pd and CeO\textsubscript{x} homogeneity, as CeO\textsubscript{x} contributes to lower reducibility of Pd. The lower percentage of metallic Pd in Pd/C, compared to 70% and 65% reported by Yu et al.\cite{36} and Singh et al.\cite{62}, respectively, can be correlated with the smaller particle size. Typically, smaller particles are more oxidized than large particles as they have a larger fraction exposed to the environment.

Ce3d photoelectron spectra were also recorded to get information about the surface oxidation state of Ce (Figure S2a–c, Supporting Information). Deconvolution results suggest that the concentration of Ce(IV) species increases with the addition of CeO\textsubscript{x}. The Ce(III)/Ce(IV) ratio was calculated from the Ce 3d\textsubscript{5/2} signals, being 0.26, 0.23, and 0.21 for 0.24 CeO\textsubscript{x}-Pd/C, 0.38 CeO\textsubscript{x}-Pd/C, and 0.59 CeO\textsubscript{x}-Pd/C, respectively (Table 3).

According to Deshpande et al., there is a clear correlation between the concentration of Ce\textsuperscript{3+} sites and the CeO\textsubscript{x} particle size, being the large particles richer in Ce\textsuperscript{4+}.\cite{64} Therefore, our results indicate the formation of larger islands upon the addition of CeO\textsubscript{x}. The amount of Ce(III) decreases when increasing the Ce/Pd ratio. In the case of 0.59 CeO\textsubscript{x}-Pd/C, the high Ce/Pd surface atomic ratio (1.56 by XPS) contributes to a reduced proportion of Pd entering the CeO\textsubscript{x} lattice.\cite{65} This would explain the decreased concentration of Pd(IV) species in 0.59 CeO\textsubscript{x}-Pd/C.

High-resolution transmission electron microscopy (HRTEM) images (Figure 2a–d) and the corresponding scanning transmission electron microscopy/energy-dispersive X-ray spectroscopy (STEM/EDS) maps (Figure 2e–h) of Pd/C and CSR-synthesized CeO\textsubscript{x}-Pd/C catalysts are shown in Figure 2. As can be seen, Pd nanoparticles are uniformly distributed on the carbon support. Some minor agglomeration can also be seen, likely due to the sintering of the nanoparticles during the thermal treatments. Particle sizes of \( \approx 3-4 \) nm were obtained for Pd/C and CSR-synthesized CeO\textsubscript{x}-Pd/C catalysts (Figure S4, Supporting Information), which are comparable to other Pd-CeO\textsubscript{2} catalysts synthesized using different methods in the literature (2–5 nm).\cite{34,36}

The uniform distribution of CeO\textsubscript{x} on Pd was also observed for 0.38 CeO\textsubscript{x}-Pd/C by STEM/EDS maps and it is in line with a lower Pd(0)/Pd(IV) ratio obtained from XPS (Figure 2e–h).

The STEM/EDS maps (Figure 2e–h), high-angle annular dark-field (HAADF)-STEM image (Figure 3a) and ultra-high-resolution electron energy loss spectroscopy (EELS) maps (Figure 3b–e) of 0.38 CeO\textsubscript{x}-Pd/C catalysts show that CeO\textsubscript{x} is in intimate contact with Pd. The intensity ratio of I\textsubscript{M5}/I\textsubscript{M4} of CeO\textsubscript{2} suggests that most CeO\textsubscript{x} is in the form of CeO\textsubscript{2} (Figure 3f). However, the presence of Ce\textsuperscript{3+} cannot be ruled out, specially near the surface of the particles.\cite{49} From the single nanoparticle EELS map of 0.38 CeO\textsubscript{x}-Pd/C, it is seen that CeO\textsubscript{x} is forming a shell around the Pd core. The interfacial contact area seems to be much higher than other previously reported Pd-CeO\textsubscript{2} catalysts synthesized by other methods,\cite{34–36} suggesting that the CSR method resulted in a higher selective deposition of CeO\textsubscript{x} on Pd. The interface between Pd and CeO\textsubscript{x} is further evidenced by high-resolution HAADF-STEM images shown in Figure 4. It is worthwhile mentioning that analyzing the particle size distribution of CeO\textsubscript{x} is challenging because it does not form well-defined nanoparticles, and its contrast is similar to that of Pd, as can be seen in the HAADF-STEM micrographs (Figure 4) and the EELS color mapping (Figure 3).
Moreover, we were able to calculate the interplanar spacing from the CeO$_2$ reflections as shown in Figure 4. The additional (110) reflection is observed for the 0.38 CeO$_{x}$/Pd/C catalysts (Figure 4b). The different lattice spacing of Pd and CeO$_2$ phases of the n CeO$_{x}$/Pd/C catalysts (Tables S2, S3, and S4, Supporting Information), together with the HRTEM images and corresponding diffraction patterns shown in Figures S5, S6, and S7 in the Supporting Information, allowed us to further investigate the interface.

In an attempt to quantify this interface, the intimate interfacial contact area between Pd and CeO$_{x}$ was calculated using ten different STEM maps for each sample. The CeO$_2$-Pd contact area of the different synthesized catalyst was segmented and calculated using Image J software. Detailed calculations and representative STEM maps are included in the Supporting Information (see Tables S5, S6, S7 and Figures S8, S9, S10 in the Supporting Information). The calculated interfacial contact areas between Pd and CeO$_{x}$ of 184.8, 259.7, and 250.3 nm$^2$ were obtained for 0.24 CeO$_{x}$/Pd/C, 0.38 CeO$_{x}$/Pd/C, and 0.59 CeO$_{x}$/Pd/C, respectively; which represents an average percentage interfacial contact area of 17.8%, 20.8%, and 18.9%, respectively. The interfacial contact area increases with the addition of CeO$_x$, reaching a maximum at 0.38 CeO$_{x}$/Pd/C, and decreases upon further addition of CeO$_x$. This is consistent with the formation of larger islands upon the addition of CeO$_x$, as shown before, observed for 0.59 CeO$_{x}$/Pd/C. This can be explained by the complete coverage of the Pd surface and the increased deposition of CeO$_x$ onto the support. As previously stated, in order to achieve the best catalytic performance, it is believed that a high interfacial contact between Pd and CeO$_x$ is required, as it enhances the OH$^-$ spillover from CeO$_x$ to Pd. This is further confirmed by electrochemical measurements as shown below.

The electrochemical behavior of CeO$_{x}$/Pd/C catalysts in 0.1 m KOH electrolyte is shown in Figure 5. As can be seen in Figure 5a, the CVs of the synthesized catalysts exhibited typical features of Pd, with a well-defined hydrogen adsorption/desorption region within 0.05–0.45 V,[34–36] oxide formation at potentials above 0.80 V,[34] and oxide reduction region within 0.60–0.70 V.[34,38,39] The H-desorption (H$_{des}$) peak in the potential window of 0.05–0.45 V gradually increases up to Ce/Pd bulk atomic ratio of 0.38 and decreases after that. Interestingly, the H$_{des}$ peak at 0.33 V in the case of Pd/C is less pronounced in comparison to that in CeO$_x$/Pd/C catalysts. In addition, there is a border H$_{des}$ peak observed at >0.60 V with Pd/C (see Figure S11a in the Supporting Information). The sharp H$_{des}$ peak of 0.38 CeO$_{x}$/Pd/C starts at slightly lower potential (0.32 V) in comparison to Pd/C (0.33 V). This sharp H$_{des}$ peak

![Figure 3](https://www.afm-journal.de)

**Figure 3.** a) High-resolution HAADF-STEM image and the b–e) corresponding EELS mapping of 0.38 CeO$_{x}$/Pd/C. The overlay map (b) and green, blue, and red colors in maps (c–e) correspond to Ce, O, and Pd, respectively. f) EELS spectra of CeO$_x$ recorded at point 1 shown in (a).

![Figure 4](https://www.afm-journal.de)

**Figure 4.** HAADF-STEM images of a) 0.24 CeO$_{x}$/Pd/C, b) 0.38 CeO$_{x}$/Pd/C, and c) 0.59 CeO$_{x}$/Pd/C. Inset show interplanar spacing from reflections (200), (110), and (222) corresponding to CeO$_2$. 

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The overlaid CO-stripping voltammograms of CSR-synthesized CeO$_x$-Pd/C catalysts are shown in Figure 5b. A sharp CO stripping peak is observed for all the catalysts at $\approx 0.83$–$0.85$ V, which is characteristic of precious metals.$^{[20,23]}$ The highest CO-stripping peak potential of 0.857 V is observed for Pd/C and gradually decreases with an increase in the Ce/Pd ratio in the catalyst. The maximum shift of 0.025 V to lower potentials is calculated with the 0.38 CeO$_x$-Pd/C, in line with the highest interfacial area calculated between CeO$_x$ and Pd. Besides, we see the broad CO-stripping peak at the lower potential of $\approx 0.3$–$0.7$ V on CSR-derived catalysts which suggest the presence of OH$_{ad}$ at lower potential.$^{[20]}$ This broad peak is more pronounced with 0.38 CeO$_x$-Pd/C, which is in line with the highest calculated interfacial contact area and thus the efficient OH$^-$ spillover from CeO$_x$ to Pd. The shift in the CO stripping peak potential to a lower value is attributed to the presence of OH$_{ad}$ at lower potentials, which promotes the Volmer step and thus facilitates the HOR, in line with OH$^-$ transfer from CeO$_x$ to Pd.$^{[20]}$ In order to compare the surface HOR activity, accurate electrochemically active surface area (ECSA) determination of these CSR-synthesized catalysts is necessary. Due to the difficulty in separating the hydrogen adsorption and absorption phenomena with Pd,$^{[66,67]}$ the ECSA estimated from the H$_{upd}$ charge may not lead to reliable results. Therefore, the ECSA was determined from both PdO reduction and CO stripping charges. ECSA values estimated from both methods are comparable and follow a similar trend (Table 4). ECSA decreases with an increase in the Ce/Pd ratio of the CeO$_x$-Pd/C catalysts. This decrease is attributed to the surface Pd coverage by CeO$_x$.

The HOR LSVs of the CeO$_x$-Pd/C catalysts are shown in Figure 6. The HOR current starts at 0.0 V and reached to limiting current value of $\approx 2.75$ mA cm$^{-2}$. The HOR limiting current observed at 0.2 V with both 0.24 CeO$_x$-Pd/C and 0.38 CeO$_x$-Pd/C catalysts reflects the influence of the mass-transport limitation. Importantly, the HOR current onset potential starts at

Table 4. CO stripping peak potentials and electrochemical surface area of Pd/C and CSR-synthesized CeO$_x$-Pd/C catalysts estimated from both CO stripping and PdO reduction charge.

| Catalyst         | $E_{\text{peakCO}}$ [V] | ECSACO [m$^2$ g$^{-1}$Pd] | ECSAPdO [m$^2$ g$^{-1}$Pd] |
|------------------|------------------------|---------------------------|---------------------------|
| Pd/C             | 0.857                  | 54.8                      | 46.9                      |
| 0.24 CeO$_x$-Pd/C| 0.846                  | 55.5                      | 49.7                      |
| 0.38 CeO$_x$-Pd/C| 0.832                  | 52.4                      | 46.3                      |
| 0.59 CeO$_x$-Pd/C| 0.841                  | 36.5                      | 26.2                      |
The HOR specific exchange current ($i_{o,m}$) of the catalysts reported here are compared to previously reported Pd/C-CeO$_2$ catalysts in Figure 7. The catalyst with optimum Ce/Pd bulk atomic ratio of 0.38 exhibited an $i_{o,m}$ of 51.5 mA mg$^{-1}$ Pd. This 0.38 CeO$_x$-Pd/C catalyst exhibit the highest $i_{o,m}$ from all previously reported Pd-CeO$_2$ catalysts (see the summary of all values in Table S8 in the Supporting Information), showing that CSR is a promising method to achieve high contact between CeO$_x$ and Pd, and in turn, a high electrochemical activity towards HOR. It is worth noting that the CeO$_x$ loading in 0.38 CeO$_x$-Pd/C is only 4 wt% (278 wt% considering only CeO$_x$-Pd), which further demonstrates that the CSR method results in highly active catalysts with a minimum amount of CeO$_x$ added. The interfacial contact area as a function of the Ce/Pd bulk atomic ratio is shown in Figure 8. The calculated $i_{o,m}$ is correlated with the highest interfacial area and Ce/Pd ratio as shown in the high-resolution STEM micrographs. As the coverage of CeO$_x$ increases, the interfacial area increases and thus, the HOR activity up to Ce/Pd of 0.38, followed by an activity decrease with a further rise in Ce/Pd ratio to 0.59. The decrease in activity is mainly attributed to the deposition of CeO$_x$ onto carbon rather than Pd and the formation of large CeO$_x$ nanoislands, as confirmed by XPS and STEM analyses.

Table 5. Kinetic HOR parameters of the Pd/C and CSR-synthesized CeO$_x$-Pd/C catalysts in 0.1 M KOH solution.

| Catalyst      | $i_{o,m}$ [mA mg$^{-1}$ Pd] | $i_{j_{o,m}}$ [mA cm$^{-2}$ Pd] | Tafel slope [mV decade$^{-1}$] |
|---------------|-----------------------------|---------------------------------|-------------------------------|
| Pd/C          | 20.84                       | 0.045                           | 218.0                         |
| 0.24 CeO$_x$-Pd/C | 45.08                      | 0.092                           | 131.5                         |
| 0.38 CeO$_x$-Pd/C | 51.54                      | 0.118                           | 129.3                         |
| 0.59 CeO$_x$-Pd/C | 20.11                       | 0.077                           | 144.1                         |

$^a$The Tafel slopes were calculated in the overpotential range of 100–250 mV.

Due to its high specific exchange current, the 0.38 Pd-CeO$_x$/C catalyst was selected to be tested in a fuel cell. The H$_2$–O$_2$ AEMFC performance of the 0.38 Pd-CeO$_x$/C catalyst (and its comparison with Pd/C catalyst) is shown in Figure 9a,b. The
AEMFC experiments were repeated twice to ensure reproducibility. A peak power density of 1169 mW cm\(^{-2}\) mg\(\text{Pd}\)\(^{-1}\) is achieved with the 0.38 CeO\(_x\)-Pd/C catalyst, 1.8 times higher than that achieved with the Pd/C (663 mW cm\(^{-2}\) mg\(\text{Pd}\)\(^{-1}\)). This is consistent with the higher \(i_{\text{on}}\) of 0.38 CeO\(_x\)-Pd/C as compared to Pd/C (Table 4). This performance is also higher as compared to other similar catalysts, as shown in a comparison of the AEMFC performance of previously reported Pd-based catalysts (see Table S9 in the Supporting Information).\[^{32,34,35,68,69}\]

Moreover, the IR-corrected single-cell AEMFC peak power density increased significantly, reaching to record high 1565 mW cm\(^{-2}\) mg\(\text{Pd}\)\(^{-1}\) at 333 K, which shows a promising impact in the future research and potential practical applications (Figure S13, Supporting Information). The stability test of the cell based on 0.38 CeO\(_x\)-Pd/C catalyst is shown in Figure 9c. The AEMFC was tested at 200 mA cm\(^{-2}\) constant current density load for 24 h, showing a stable voltage output, suggesting that the 0.38 CeO\(_x\)-Pd/C catalyst has good stability under the harsh AEMFC environment.

### 3. Conclusion

CeO\(_x\)-Pd/C catalysts with various Ce/Pd ratios were synthesized by selective deposition of CeO\(_x\) onto carbon-supported Pd/C nanoparticles by controlled surface reactions (CSR). The higher surface Ce/Pd atomic ratio when compared to the bulk Ce/Pd, demonstrated the surface affinity of the CSR method. EELS and high-resolution STEM images revealed the core-shell structure of the CeO\(_x\)-Pd nanoparticles and Ce\(^{4+}\) mainly present in CeO\(_x\), respectively. We have clearly shown that CeO\(_x\) nanoparticles are in intimate contact with Pd, as seen from the high-resolution STEM images recorded on single particles. A very high interfacial contact area between CeO\(_x\) and Pd nanoparticles was achieved, and for the first time, it was also calculated. Most interestingly, this interfacial contact area was found to be directly correlated to the HOR activity of the CeO\(_x\)-Pd/C catalysts. The CSR method used in this work yielded the catalyst with the highest HOR specific activity ever measured for Pd-CeO\(_x\) catalysts—high value of 51.5 mA mg\(^{-1}\)\(\text{Pd}\) was measured for the 0.38 CeO\(_x\)-Pd/C. This was explained by the improved distribution of CeO\(_x\) onto Pd, the higher concentration of Pd(IV) sites, as well as the higher interfacial contact area between CeO\(_x\) and Pd nanoparticles. Moreover, the 0.38 CeO\(_x\)-Pd/C catalyst showed a very high performance while tested in a fuel cell. The H\(_2\)-O\(_2\) AEMFC made with this catalyst exhibited a peak power density of 1169 mW cm\(^{-2}\) mg\(\text{Pd}\)\(^{-1}\) at 333 K, significantly higher than other cells with similar HOR catalysts.

### 4. Experimental Section

**Materials:** For the catalyst synthesis, palladium (II) acetate (Acros Organics, 99.9%), dichloromethane (Acros Organics, 99.6%, ACS reagent, stabilized with amylene), tris(cyclopentadienyl)cerium(III) (STREM Chemicals, Inc. 99.9%), anhydrous tetrahydrofuran (Sigma-Aldrich, ≥99.9%, inhibitor-free), and Vulcan XC-72 carbon (Cabot) were used. For the electrolyte and catalysts ink preparation, potassium hydroxide flakes (85.0–100.5% w/w AR grade, Bio-Lab, Israel), isopropyl alcohol (99.8 assay from the Gadot group, Israel), and Nafion® ionomer...
perfluorinated resin (10 wt% in water from Sigma-Aldrich) were used. For the fuel cell electrode fabrication and testing, Toray Paper (060 – TCP-H-060 with 5 wt% PTFE wetproofing from Fuel Cell Store), Vulcan XC-72 carbon (Cabot), and 40% platinum on carbon black (HiSPEC 4000 from Alfa Aesar) were used. Argon, oxygen, nitrogen and hydrogen gases of purity 99.999% were purchased from Maxima, Israel. Carbon monoxide gas of purity 99.999% (Gas Technologies, Israel) was used for the CO stripping experiments. High purity (18.2 Ω) double-distilled water was used. All the chemicals were used without any further purification.

**Catalyst Synthesis:** A series of CeO$_2$-Pd/C catalysts were synthesized by selective deposition of CeO$_2$ onto carbon-supported Pd nanoparticles by controlled surface reactions (CSR) ([37-40, 79]). For the first, a 10 wt% Pd/C catalyst was prepared by wet impregnation by adding a solution of 0.84 g of palladium (II) acetate in 100 mL of dichloromethane to 3.6 g of Vulcan XC-72 carbon. The mixture was stirred in an open vessel at 323 K to evaporate the solvent. Once dry, the catalyst was reduced in a Schlenk tube at 343 K (heating ramp of 0.8 K min$^{-1}$) for 2 h under H$_2$ flow. After the reduction, the Schlenk tube was sealed and transferred to a glove box under an ultrapure argon atmosphere to prevent oxidation. Then, tris(cyclopentadienyl)cerium(III) was used as a precursor for the addition of CeO$_2$, using sequential CSR cycles. For each CSR cycle, 0.2 g of tris(cyclopentadienyl)cerium(III) was dissolved into 90 mL of anhydrous tetrahydrofuran under argon atmosphere in the glove box, then 15 mL of the CeO$_2$ precursor solution was added to 1 g of the reduced Pd/C catalyst. The Schlenk tube was then sealed and stirred for 3 h, after which the solution becomes clear, indicating the total uptake of the precursor. Then, the solvent was evaporated using Schlenk techniques and the tube was filled with argon and sealed to carry out a second thermal treatment. The catalyst was then heated at 573 K (heating ramp of 1.6 K min$^{-1}$) for 2 h under H$_2$ flow. This second thermal treatment removes the ligands of the CeO$_2$ precursor in order to obtain an effective interaction between Pd and CeO$_2$, while maintaining Pd reduced for subsequent deposition cycles. After the last cycle was applied, the catalysts were reduced in H$_2$ flow at 573 K (heating ramp of 1.6 K min$^{-1}$) for 2 h and used without prior passivation. Every CSR cycle provides a theoretical atomic ratio of Ce/Pd of 0.13 (see Supporting Information for calculation details). A series of CeO$_2$-Pd/C catalysts with different number of CSR cycles were prepared aiming to obtain different (theoretical) Ce/Pd atomic ratios: 0.26, 0.39, and 0.65. For the electrochemical measurements, the catalysts were grounded with a mortar and pestle to obtain uniform powders.

**Catalyst Characterization:** The composition of the synthesized catalysts was determined via Inductively Coupled Plasma–Atomic Emission Spectrometry (ICP-AES). Samples (~30 mg) were fused with sodium peroxide over a Bunsen burner, then dissolved in water. The resultant solutions were then acidified and analyzed using an ICP-OES Optima 5300 spectrometer.[79, 78] X-ray diffraction (XRD) data were collected using a Rigaku Smartlab diffractometer with$^\lambda$scan mode ($\lambda = 0.15406$ nm). The X-ray diffractograms were recorded at medium resolution parallel beam geometry at a tube current of 150 mA and a tube voltage of 45 kV, in $\theta/2\theta$ scan mode with a scan rate of 2° min$^{-1}$ in 0.01° steps, in a range of diffraction angles from 20° to 90°. Phases were identified via matching results with the International Centre for Diffraction Data (ICDD) PDF4+ (2018) database. Electron microscopy images and analyses were conducted in a Thermo Scientific™ TalosF200 × 200 kV D6329 X-Twin Transmission Electron Microscope (TEM), using both Bright Field and High Angle Annular Dark Field (HAADF) Scanning Transmission Electron Microscopy (STEM) modes. The samples were first dispersed in 50 v/v% of isopropyl alcohol and distilled water, then ultrasonicated using a 2510R-DTH Branson$^3$ Ultrasonic Cleaner for 15–30 min (130 W, 40 kHz) and deposited on a holey carbon-coated Cu grid for TEM characterization, followed by drying for 30 min under an ultraviolet lamp. Energy Dispersive Spectroscopy (EDS) with a ChemiSTEM$^4$ technology system contained within the TEM was used for elemental analysis of the catalyst samples, using hyper-mapping collected by an ESPIRIT Microanalysis Software. The mapping was performed using a screen current of 2.5 nA, beam dwells time of 1000 µs per pixel for one mapping cycle. For high-resolution STEM imaging, the samples were studied with Titan Themis 60-300. The TEM images were performed at 300 keV and with its DCorr+ probe corrector that corrects condenser spherical aberration higher than 25 mrad, enabling a spatial resolution down to 0.08 nm with 25 mrad convergence angle for its atomic resolved HAADF-STEM imaging. For high-resolution Electron Energy-loss Spectroscopy (EELS) measurements, the data were collected through Gatan GIF Quantum 963 spectrometer system attached to Themis operating at 300 kV in STEM mode with EELS collection angle of 50 mrad. A 0.5 eV channel dispersion was used to map elemental distribution in a wide energy range and 0.05 eV per channel dispersion was selected for the highest energy resolution (1.1 eV). An X-ray photoelectron spectroscopy (XPS) equipment with a monochromated Al source (1486.6 eV, Kratos Axis) was used to record the XPS spectra. The XPS resolution was about 0.6 eV when the pass energy of 20 eV was used. The energy scale was calibrated with Ag 3d$_{5/2}$ that was assigned at 368.21 eV. No charge neutralizer was used as all the samples were conductive.

**Electrochemical Characterization:** Electrochemical measurements of the synthesized catalysts were performed in a conventional three-electrode rotating disc electrode (RDE) set-up using a WaveDriver potentiostat in an electrolyte solution (1.6 M KOH) from Pine Instruments (water-jacketed, five compartment glass cell). All the RDE measurements were performed at 298 ± 0.2 K. The catalyst-coated glassy carbon disc was used as a working electrode, a standard Pt counter electrode was immersed inside a fritted glass tube to avoid any Pt dissolution, and Hg/HgO (4.24 M KOH) was used as a reference electrode (both from Pine Instruments). The potential of the reference electrode was calibrated against the reversible hydrogen electrode (RHE) (880 mV).

The catalyst ink was prepared by mixing 10 mg of catalyst, 2.5 mL of de-ionized water, 5.5 mL of isopropyl alcohol, and 9.52 µL of Nafion ionomer (10 wt% solution in water). The mixture was sonicated at 100% intensity (580 W) in a Grant XUBA3 ultrasonic bath filled with water and ice to keep the temperature below 278 K for 30 min to form a uniform catalyst ink. The homogeneous ink was drop-coated on a glassy carbon disc working electrode to obtain a nominal loading of 13 mg cm$^{-2}$, and dried in an ambient atmosphere for 1 h. Prior to hydrogen oxidation measurements, the electrode was cycled in 0.1 M KOH solution at the sweep rate of 100 mV s$^{-1}$ from 0.0 to 1.2 V versus RHE for 50 cycles, to get a reproducible voltammogram. Then a cyclic voltammogram (CV) was recorded from 0.05 to 1.35 V at the sweep rate of 20 mV s$^{-1}$ for the estimation of electrochemical surface area (ECSA) from PdO reduction using Equation (1).[30, 31] The upper potential of CV was selected in such a way that the surface area estimation corresponds to the monolayer oxide coverage on the Pd surface.[34] For the ECSA estimation using CO-stripping voltammograms, the electrolyte solution was saturated with CO for 10 min, followed by CO adsorption at 0.025 V for 10 min. Then the solution was saturated with argon at 0.025 V for 30 min to remove the CO from the electrolyte while maintaining the same potential load. The CO stripping voltammograms were then recorded from 0.0 to 1.2 V at the sweep rate of 20 mV s$^{-1}$. The ECSA from the CO stripping charge was then estimated using Equation (2):

\[
\text{ECSA}_{\text{PdO}} = \frac{\text{PdO reduction charge}}{\text{scan rate} \times \text{specific charge} \times \text{catalyst loading}} \quad (1)
\]

\[
\text{ECSA}_{\text{CO}} = \frac{\text{CO stripping charge}}{\text{scan rate} \times \text{specific charge} \times \text{catalyst loading}} \quad (2)
\]

where, ECSA is in cm$^2$ g$^{-1}$, PdO reduction charge in C cm$^{-2}$, CO scan rate in V s$^{-1}$, catalyst loading is in g cm$^{-2}$, the measured Pd content from ICP-AES is used, and CO stripping charge in C cm$^{-2}$ γ. A specific charge of 420 × 10$^{-6}$ C cm$^{-2}$ was used for ECSA determination using PdO reduction[80, 81] and CO stripping charges.[82]

HOR linear sweep voltammograms (LSVs) were recorded with rotation rates from 2000 to 900 rpm in H$_2$-saturated 0.1 M KOH solution at a scan rate of 2 mV s$^{-1}$. The kinetic current density is usually estimated from the Randles-Sevcik equation as follows:[83, 84]
\[ i = \frac{1}{R} + \frac{1}{i_d} \]  

(3)

where \( i \) is the measured current, \( i_k \) is the kinetic current, and \( i_d \) is the diffusion limiting current.

\[ i_k = i_s \times \frac{F n}{R T} \]  

(4)

where \( F \) is the Faraday constant (96485 C mol\(^{-1}\)), \( T \) is the temperature (298 K), and \( R \) is the universal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)). All the electrochemical measurements were repeated twice to ensure reproducibility.

**Anion Exchange Membrane Fuel Cells:** Gas diffusion electrodes (GDEs) were prepared for both anode and cathode for the fabrication of anion exchange membrane fuel cells. Both the anode and cathode electrodes consisted of three layers: a gas diffusion layer (GDL) (Toray Paper), a microporous layer (MPL) of carbon black (Vulcan XC-72), and a catalyst layer. The details of the anode and cathode ink preparations were given in the Supporting Information. Each electrode was prepared by spray coating the MPLs directly onto the GDLs, then adding the respective cathode and anode catalyst inks on top of the MPLs. Two 5 cm\(^2\) active area fuel cells electrodes were made using 40 wt% Pt/C as the cathode catalyst (0.7 mg Pt cm\(^{-2}\)) and either CSR-synthesized CeO\(_2\)-Pd/C (0.55 mg Pd cm\(^{-2}\)) or Pd/C (0.64 mg Pd cm\(^{-2}\)) catalysts as anodes. A 16 cm\(^2\) piece of poly(ethylene-co-tetrafluoroethylene)-benzyltrimethylammonium chloride (ETFE-BTMMA) radiation grafted anion exchange membrane was sandwiched between the anode and cathode electrodes to make two membrane electrode assemblies (see the Supporting Information for more details). The AEMFCs were tested at the same conditions in an 850E Scribner Associates fuel cell test station. Polarization curves were recorded at 333 K under \( \text{O}_2 \) flow at the cathode (1000 mL min\(^{-1}\), dew point 328 K) and \( \text{H}_2 \) flow at the anode (1000 mL min\(^{-1}\), dew point 325 K).

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

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