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"Sacrificial protection in action!": ultra-high stability of palladesite mineral towards the oxygen reduction reaction[†]

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It is of the utmost importance to design an oxygen reduction electrocatalyst with high durability and good activity for large scale utilization in industry. Although several materials have been developed at the laboratory scale with extremely good activity, the durability of most of these materials is not sufficient enough to scale them up. Inspired by the high stability of naturally occurring minerals, we have synthesized palladesite (Pd₁₇Se₁₅) via a one pot colloidal method. This material exhibits exceptionally high stability towards the oxygen reduction reaction (ORR) for at least 50 000 cycles, which is several times higher than that of many of the best reported materials. Due to the low surface energy of Se (0.10 J m^{-2}) compared to that of Pd (1.43 J m⁻²), Pd active sites get protected by a Se overlayer. X-ray diffraction (XRD) and extended X-ray absorption fine structure (EXAFS) analyses confirmed that the material we have synthesized has the same crystal structure and atomic arrangement as the palladesite mineral. This nanomaterial holds great potential as the cathode material in PEMFCs in terms of facile one-pot synthesis, high conductivity without any support and enhanced ORR durability. DFT calculation reveals that the lower adsorption energy of the intermediate -OH and the enhancement of the adsorption energy of O₂ and -OOH as Se gets oxidatively leached forming a Pd-enriched surface enhance its stability towards the ORR. The Se leaching has been experimentally confirmed by in situ XAFS and ICP analysis.

Growing energy demands have encouraged intense research on alternative energy conversion and storage systems with high efficiency, low cost and high stability. Despite tremendous efforts, developing an ORR catalyst with combined high activity and high durability remains a great challenge. To date, only materials based on Pt have shown sufficient activity and stability for reliable proton exchange membrane fuel cell (PEMFC) operation.¹⁻⁴ Additionally, Ir- or Ru-based metals and their chalcogenides are also being studied as ORR electrocatalysts.^{5,6} The use of Pt, Ir and Ru, however, poses problems due to their high cost and limited resources; thus, mass production of such electrode-based PEMFCs might be restricted. Extensive research efforts have been devoted towards reducing the amount of expensive metals required in electrocatalysts with activity on a par with that of the state-of-the-art materials and enhanced stability.

As a potential replacement for Pt based electrocatalysts for the ORR, palladium (Pd) has received considerable attention because of its similar chemical and physical properties to Pt, including crystal structure (face-centered cubic), atomic size and electronic configuration.7 In addition, Pd is less expensive and more abundant than Pt. Intermetallics, bimetallics and alloys such as PdFe,8 PtPd,9 Pd₃Sn,10 PdCo11 and PdNi12 have higher stability in harsh electrolytic conditions compared to pristine Pd. Similarly, nitrides such as Fe-Ni-Mo nitrides are found to show good ORR activity.13 However, during prolonged cycling processes, transition metals undergo dealloying which may lead to the loss of active sites. Several strategies have been exploited to enhance the stability of ORR catalysts. Wang et. al. have reported the enhancement in the stability of Pt with the introduction of Pd upto 10 000 cycles.14 Schuth et al. have reported the encapsulation of Pt nanoparticles inside the pores of graphitized carbon to reduce catalyst degradation.¹⁵ There have been several reports on protecting catalysts with various coating layers, including a carbon shell¹⁶ and graphitic hollow spheres.15,17 However, in these studies external protective agents were exploited to enhance the stability.

Naturally occurring oxygen activation catalysts, such as cytochrome oxidase c and tyrosine-244, provide a fundamental basis for overcoming these durability issues. They have an electron donating center that prevents the formation and release of unfavourable partially reduced oxygen by-products and intermediates and bulky protein chains maintains the stability of the active sites for a longer time.^{18,19} This has formed the foundation of our present work, which takes into account

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both of these properties. A Se rich catalyst surface serves as an electron rich center and also protects the active palladium sites from degradation.^{20,21} As previously reported, the presence of Se modifies the relative positions of the valence and conduction bands bringing them closer to the theoretical water oxidation-reduction levels.²²

There are several chalcogenide-based catalysts, such as $Rh_xS_{\nu}^{6}$, RuSe,²³ Ru-Mo-Se,²⁴ Ru-Fe-Se,²⁵ CoSe₂,²⁶ Co₃S₄,²⁷ FeSe₂,²⁸ NiSe²⁹ and Mo_{4.2}Ru_{1.8}Se₈ (ref. 30), that have been reported as efficient materials for the ORR; however they are not known to be stable materials. Since Pd is second best to Pt, this work reviewed several palladium based selenides like PdSe,31 Pd₁₇Se₁₅,³² Pd₇Se₄, Pd_{2.5}Se, Pd₃Se,³³ Pd₄Se,³⁴ Pd_{4.5}Se, Pd₇Se, Pd₈Se and PdSe₂.³⁵ Among them, the Pd₁₇Se₁₅ phase first discovered at the Itabira deposits in Brazil³⁶ exhibits high stability under harsh acidic (1 M H₂SO₄) and basic (6 M KOH) conditions.³² This phase is highly conducting as seen from the reported literature.³⁴ To date, Pd₁₇Se₁₅ has been synthesized using thermal decomposition of complex precursors involving multi-step reactions.37-40 Herein, we report a facile one-pot synthesis of Pd₁₇Se₁₅ using NaBH₄ as the reducing agent and tetraethylene glycol (TEG) as the solvent for the first time.

The synthesized compound was characterized by XRD, in which prominent peaks (Fig. 1a) were observed at 27.78° , 44.2° ,



Fig. 1 (a) Comparison of the experimental PXRD pattern with the simulated pattern of Pd₁₇Se₁₅, (b) TEM image showing the aggregated nature of the particles, and core level XPS spectra of (c) Pd $3d_{5/2}$ and Pd $3d_{3/2}$ and (d) Se 3d in $Pd_{17}Se_{15}$ nanoparticles. EXAFS measurements were performed to elucidate the electronic structure and local environment in Pd₁₇Se₁₅ NPs.⁴¹ The small shift of the absorption edge towards high photon energy compared to Pd foil is evident from the normalized Pd k-edge X-ray absorption near edge structure (XANES) spectrum (Fig. 2a). This reveals the charge transfer from Pd to Se and the formation of the positive oxidation state of the active Pd site. The Fourier transform of the Pd k-edge EXAFS oscillations in R space of Pd₁₇Se₁₅ catalysts is shown in Fig. 2b. EXAFS fitting confirms the formation of pure Pd₁₇Se₁₅. The structural parameters obtained by EXAFS analysis are shown in Table S2.[†] The peak at 2.5 Å in *R*-space corresponds to the first coordination sphere around Pd and was fitted using Pd-Se1 and Pd-Se3 single scattering paths.

and 48.36° corresponding to the (311), (511, 333) and (440) planes of Pd₁₇Se₁₅, respectively, and can be indexed to a cubic system with a *Pm*3*m* space group. TEM images show that the nanoparticles are in the size range of less than 50 nm and are interlinked with each other (Fig. 1b and S1a and b†). The *d*-spacings (between two lattice fringes) observed in the HRTEM image were calculated to be 0.47 nm and 0.33 nm, respectively, corresponding to the (210) and (311) crystallographic planes (Fig. S1c†). The SAED pattern (Fig. S1d†) exhibits the polycrystalline nature of the Pd₁₇Se₁₅ nanoparticles. The XPS analysis (Fig. 1c) result exhibits the characteristic peaks of Pd 3d_{5/2} and Pd 3d_{3/2} located at 336.3 eV and 341.5 eV, respectively, which correspond to the partial positive oxidation state due to a positive shift of the peaks w.r.t the previously reported values of 335.1 eV and 340.5 eV, respectively.

On the other hand, the Se $3d_{5/2}$ peak is located at 54.7 eV (Fig. 1d), which is a negative shift from the previously reported value of 56.7 eV and indicates the partial negative oxidation state of Se. Integrating the area under the peak and dividing it by the relative sensitivity factor (RSF) reveals that the surface has a Pd : Se ratio of 1 : 2 indicating a Se rich surface. FESEM images of the particles show the highly aggregated nature of Pd₁₇Se₁₅ nanoparticles (Fig. S2[†]). From EDX elemental analysis, the atomic percentages of Pd and Se are found to be 44.63 \pm 1.6% and 55.37 \pm 1.2%, respectively. The presence of excess selenium may be because of the fact that Se has a lower surface energy of 0.10 J m^{-2} compared to that of Pd with a surface energy of 1.43 J m $^{-2}$. Thus, Se forms an overlayer on the catalyst surface. The composition was further confirmed by ICP measurements, where the atomic percentages of Pd and Se are found to be 46.80 \pm 0.1% and 53.20 \pm 0.1%, respectively (Table S1[†]).

The electrochemical activity of the compound was tested by running cyclic voltammetry (CV) of a catalyst modified glassy carbon rotating disk electrode (GC-RDE), in both O₂-saturated and N₂-saturated 0.1 M KOH solutions (Fig. S3a⁺). The activity of Pd₁₇Se₁₅ towards the ORR is evident from the enhancement of current in O_2 saturated electrolyte (-0.25 to -0.4 V vs. RHE). RDE measurements were carried out at different rotation rates in 0.1 M KOH. The polarization curves for the ORR at different rotation rates are shown in Fig. S3b[†] in which the current densities are normalized with respect to the geometrical surface area (0.0706 cm²). At 1600 rpm, the catalyst showed an ORR onset potential of about 0.87 V versus RHE. The ORR current density at 1600 rpm was about 5.8 mA cm $^{-2}$ at 0.7 V versus RHE. Fig. S3c[†] shows the corresponding Koutecky-Levich (K-L) plot obtained from plotting the inverse current densities (j^{-1}) as a function of the inverse square root of the rotation rate ($\omega^{-1/2}$) at different potentials. The number of electrons calculated from the slope of the K-L plots is close to four on an average, which indicates the complete reduction of oxygen to water.

To have a better understanding of the electrochemical activity in comparison to that of the state-of-the-art catalysts, rotating-ring disk electrode (RRDE) measurements were performed for the catalyst and compared to those of the commercial Pd/C (20 wt%) and Pt/C (20 wt%). The $Pd_{17}Se_{15}$ catalyst exhibited better activity in terms of onset and half-wave



Fig. 2 (a) The normalized Pd k-edge XANES spectra of Pd₁₇Se₁₅ and Pd foil. (b) Fourier transform magnitudes of the Pd k-edge EXAFS oscillations in Pd₁₇Se₁₅. The inset shows the corresponding EXAFS oscillations.

potential compared to the commercial Pd/C (Fig. S4†). As shown in Fig. S5a,† an electron transfer number of \sim 3.68 was maintained over a wide potential range for Pd₁₇Se₁₅ in comparison to that for Pd/C (ranging from 2.88 to 3.78) and Pt/C (\sim 3.92). H₂O₂ produced during the reduction reaction was much higher for Pd/C compared to our catalyst. Though Pd₁₇Se₁₅ lags behind the commercial Pt/C in terms of activity, it can be improved through strategic modification of the electronic structure through alloying/substitution with a secondary metal as done in our recent work.^{42,43}

An accelerated degradation test (ADT) for 50 000 cycles was performed to assess the durability of the catalyst. Cyclic potential sweeps were performed between 0.4 V and 0.9 V at a high scan rate of 0.1 V s⁻¹ and a rotation speed of 800 rpm in O₂ saturated 0.1 M KOH. A graphite counter electrode was used to perform the stability test to avoid Pt dissolution. Comparison of the catalyst before and after cycling reveals a positive shift of 11 mV as shown in Fig. 3a. To the best of our knowledge, only Pt/PdAu showed such a high stability, but it is comprised of expensive Pt and Au metals.⁴⁴ The durabilities of some of the ORR catalysts prevalent in the literature are listed in Table S3.[†]



Fig. 3 (a) Polarization curves of $Pd_{17}Se_{15}$ before and after cycling, (b) CV curves as functions of cycle number showing the removal of Se from the surface due to prolonged cycling, (c) ORR polarization curves showing the negative shift due to exposed Pd sites and (d) Tafel slopes confirming that a similar mechanism is being followed before and after cycling.

The enhancement in the activity of our catalyst after cycling is due to the evolution of a prominent Pd surface for $Pd_{17}Se_{15}$, which was confirmed from the CV curve recorded at periodic intervals in Fig. 3b.

The peak at 0 to 0.2 V vs. RHE corresponds to the hydrogen adsorption/desorption region. The Se overlayer on the catalyst surface prevents hydrogen adsorption during the initial cycles. But during prolonged cycling, the Se coating on the surface leaches out forming selenite/selenate (SeO₃²⁻/SeO₄²⁻) ions at higher oxidation potential,⁴⁵ exposing the Pd active sites. This facilitates the adsorption/desorption of hydrogen.23,46 Se removal from the catalyst has been confirmed from the reduction of the oxidative current at a higher potential in the range of 0.9-1.1 V which corresponds to Se oxidation. The peak around 0.5-0.8 V corresponds to the Pd-O reduction region. The formation of two types of Pd active sites $[Pd(0) \text{ and } Pd(\pi)]$ is confirmed from the two humps in the Pd-O reduction region. At periodic cycle intervals, a decrease in the Se oxidation peak indicates the decrease in the amount of Se in the system. This happens due to the higher solubility of selenium oxides in KOH electrolyte compared to that of elemental Se. As soon as Se forms oxides on the surface of the catalyst, it starts getting degraded and the concentration of Se in the electrolyte increases which was confirmed by ICP-OES measurements. The amount of Se in the electrolyte was found to be around 0.582 ppm at the end of 50 000 cycles. A cumulative Se release plot obtained during the ADT is shown in Fig. S6.† The polarization curve in Fig. 3c clearly shows a positive shift due to the formation of the pristine Pd surface, which has a better onset potential compared to the parent compound Pd₁₇Se₁₅. The formation of the Pd surface is further confirmed from the PXRD pattern of the compound after the stability test (Fig. S7[†]). The coexistence of both the phases is observed in the PXRD pattern. A comparison of the mass-transport corrected Tafel slope of the catalyst before and after 50 000 cycles shows a negligible change in the value from 65 mV dec^{-1} to 67.5 mV dec^{-1} (Fig. 3d) indicating that the catalyst follows the same mechanism even after prolonged cycling. This Tafel slope value indicates that the ORR catalyzed by the chalcogenide is controlled by the first charge-transfer step, similar to that of a Pt catalyst.

Analysis of the EIS data reveals the appearance of two large overlapping semi-circles (Fig. 4a). The data are fitted with a Randles equivalent circuit consisting of a series resistance (electrolyte or solution resistance, R_s) and two parallel R/C terms with two different potential dependent time constants. The deformation of the impedance semi-circle indicates the formation of a rough surface and hence the capacitance terms in the R/C circuit are replaced with a constant phase element (CPE). The solution resistance (R_s) and total polarization resistance (R_p) can be directly obtained from the impedance spectra, where the high-frequency intercept of the impedance spectra on the X(Z') axis represents the R_s and the distance between the highest and lowest frequency intercepts of the impedance spectra with the X(Z') axis corresponds to the R_p . For a quantitative comparison of the activity and durability of the catalyst, the fitting parameters are listed in Table S4.† The highfrequency (HF) arc is related to the transport of oxygen



Fig. 4 (a) EIS profile of the catalyst before and after 50 000 cycles. The inset shows the corresponding Randles equivalent circuit; (b) SEM image of the catalyst $Pd_{17}Se_{15}$ after 50 000 cycles. The elemental composition of the sample is provided as an inset, and it shows a significant decrease in the percentage of selenium.

intermediates within the electrode/electrolyte interface, the medium-frequency (MF) arc is associated with atomic oxygen diffusion within the electrode followed by charge transfer and the low-frequency (LF) arc is related to molecular oxygen dissociation and adsorption phenomena.47,48 Since the MF arc increases from 669 ohm to 775.9 ohm, it probably indicates the resistance associated with the diffusion of atomic oxygen within the electrode. This may happen due to the saturation of the porous site with H₂O which hinders oxygen diffusion within the electrode.48 However, the HF arc decreases from 398.8 ohm to 201.5 ohm, which corresponds to molecular oxygen dissociation and adsorption phenomena. Due to the exposed Pd active sites, O2 adsorption is favored, which corroborates well with our DFT calculation (the binding energy of O_2 on the Pd (-1.03 eV) surface is more favorable than that on the $Pd_{17}Se_{15}$ (-0.65 eV) surface).

The presence of Se at the surface plays an important role. Oxygen removal from Pd active sites becomes much easier than that without additives. Even the FESEM image and EDAX data shown in Fig. 4b confirm the removal of Se. The TEM and FESEM images of the catalyst after the stability test are presented in Fig. S8 and S9,† respectively. The sacrificial protection mechanism is explained in eqn (1) and (2) and the schematic representation is given in Scheme 1.

$$Pd_{17}Se_{15} \leftrightarrow Pd_{17}Se_{15-x} + xSe$$
(1)

$$x$$
Se + 2 x KOH $\leftrightarrow \frac{x}{3}$ K₂SeO₃ + $\frac{2x}{3}$ K₂Se + x H₂O (2)



Scheme 1 Proposed sacrificial protection mechanism of stability and degradation in Pd₁₇Se₁₅ during the ORR.

In situ XAFS measurement, presented in Fig. 5, was performed to understand the mechanism which causes the enhanced stability of the material during the ORR. As seen from the EXAFS fitting parameters in Table S5,† the number of Pd atoms around Se, CN_{Se-Pd}, remains almost the same during the electrochemical process. However, a sharp change is seen in the number of metallic selenium atoms, CN_{Se-Se}, in the coordination environment. CN_{Se-Se} decreases from 6.72 to 2.71 during the reaction. This supports our proposed mechanism that selenium on the surface forms selenite/selenate ions and gets dissolved in the alkaline electrolyte. Thus, the amount of selenium on the surface decreases. The dissolution of Se is further supported by the comparison of unnormalized Se-k edge data obtained during the dissolution process. The edge jump, which can be directly correlated with the amount of selenium, decreases during the electrochemical ORR. Hence, the dissolution of selenium from the catalyst has been proved experimentally.

DFT calculations were performed to compare the adsorption energies of intermediates on the Pd₁₇Se₁₅ surface as well as on Pd isolated sites, which are formed due to Se leaching out of the system. Thus, the comparison reflects the adsorption energy before and after the stability test. Since the ORR is a multistep reaction with several possible pathways, it involves the formation of intermediate species such as atomic hydrogen (H), atomic oxygen (O), hydroxyl (OH), peroxyl (OOH) and hydrogen peroxide (H₂O₂).⁴⁹ Each of these intermediates is geometry optimized prior to their use in various elementary steps of the ORR on the surface (Fig. S10[†]). For a good ORR catalyst, the adsorption energies of -OOH and O₂ should be high enough for the reaction to take place and that of -OH should be low enough for easy removal.⁵⁰ A low adsorption energy for -OH ensures cleaning up of the catalyst surface for fresh O2 adsorption.



Fig. 5 Main panels in (a-c) show Fourier transform magnitudes of the Se *k*-edge EXAFS oscillations in (a) initial, (b) dipped in solution, and (c) after ADT samples. The insets in (a-c) show the corresponding EXAFS oscillations. (d) Comparison of unnormalized Se *k*-edge XANES spectra during the electrochemical process.

Table 1 Adsorption energies (in eV) for –H, –O, –OH, O2, –OOH, H_2O_2 and H_2O on the catalyst (100) surface

-0.77	-1.49
-3.56	-3.06
-0.65	-1.03
-0.32	-0.50
-1.97	-2.36
-2.32	-2.89
-0.49	-2.54
	-0.77 -3.56 -0.65 -0.32 -1.97 -2.32 -0.49

As seen from Table 1, Pd₁₇Se₁₅ has a lower adsorption energy for the intermediate -OH giving the catalyst its enhanced stability. However, the lower adsorption energies of O2 and -OOH compared to those observed in Pd decrease its activity towards the ORR. The higher adsorption energies of O_2 and OOH on the Pd surface explain the better onset of the catalyst after the stability test. It is worth noting that H₂O₂ has a lower adsorption energy on the Pd₁₇Se₁₅ surface compared to that on the Pd surface which guarantees a low level of H₂O₂ poisoning on the catalyst surface and higher stability of the Pd₁₇Se₁₅ surface. The lower adsorption energy of the catalyst towards oxyspecies can be attributed to the interatomic charge transfer which is represented in Fig. 6 using Hirshfeld charge analysis. Se atoms become negatively charged due to ionic Se-Pd bonding with Se accepting a significant amount of charge from Pd, which has been proved via XANES analysis (Fig. 2a). According to Stolbov, since O and OH also become negatively charged upon adsorption, Se and these intermediates repel each other electrostatically.⁵¹ This repulsion increases the total energy of the system and thus reduces the binding energies of oxy-species.

In conclusion, the palladesite mineral in a cubic $Pm\bar{3}m$ space group has been successfully synthesized at the laboratory scale using a facile one-pot colloidal synthesis route. This work addresses the durability issues of cathode materials which pose



Fig. 6 Hirshfeld charge analysis showing approximate positive charge on Pd and negative charge on Se and O. The label on each atom indicates the charge on the corresponding atom. Blue, yellow, red and white atoms correspond to Pd, Se, O and H, respectively.

major roadblocks to commercialization and practical applications of PEMFCs by using a very simple chalcogenide system which works through a "sacrificial protection mechanism". It has been carefully observed that there is a structural reorganization of the entire system where Se not only acts as an electron donor but also sacrificially protects the active Pd sites during prolonged cycling under harsh conditions. Multiple experimental characterization techniques, along with DFT calculations, have been successfully employed to understand the mechanism at the molecular level, and confirm that lower adsorption energies for H_2O_2 and –OH species provide exceptionally high durability and enhanced activity to the catalyst.

Conflicts of interest

There are no conflicts to declare.

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References

- 1 Y. Liu and W. E. Mustain, J. Am. Chem. Soc., 2013, 135, 530– 533.
- 2 K. Sasaki, H. Naohara, Y. M. Choi, Y. Cai, W. F. Chen, P. Liu and R. R. Adzic, *Nat. Commun.*, 2012, **3**, 1115.
- 3 L. L. Zhang, M. Wei, S. Q. Wang, Z. Li, L. X. Ding and H. H. Wang, *Chem. Sci.*, 2015, **6**, 3211–3216.
- 4 V. R. Stamenkovic, B. Fowler, B. S. Mun, G. Wang, P. N. Ross, C. A. Lucas and N. M. Marković, *Science*, 2007, **315**, 493–497.
- 5 G. Liu and H. Zhang, J. Phys. Chem. C, 2008, 112, 2058-2065.
- 6 D. C. Papageorgopoulos, F. Liu and O. Conrad, *Electrochim. Acta*, 2007, **52**, 4982–4986.
- 7 H. Liu, C. Koenigsmann, R. R. Adzic and S. S. Wong, *ACS Catal.*, 2014, 4, 2544–2555.
- 8 M. Neergat, V. Gunasekar and R. Rahul, *J. Electroanal. Chem.*, 2011, **658**, 25–32.
- 9 H. Q. Li, G. Q. Sun, N. Li, S. G. Sun, D. S. Su and Q. Xin, J. Phys. Chem. C, 2007, 111, 5605–5617.
- 10 C. Y. Lu, W. S. Guan, T. K. A. Hoang, Y. L. Li, T. N. L. Doan and H. B. Zhao, *Int. J. Electrochem. Sci.*, 2015, **10**, 5077–5085.
- 11 W. Wang, D. Zheng, C. Du, Z. Zou, X. Zhang, B. Xia, H. Yang and D. L. Akins, *J. Power Sources*, 2007, **167**, 243–249.
- 12 L. Chen, H. Guo, T. Fujita, A. Hirata, W. Zhang, A. Inoue and M. Chen, *Adv. Funct. Mater.*, 2011, **21**, 4364–4370.
- 13 C. Zhu, Z. Yin, W. Lai, Y. Sun, L. Liu, X. Zhang, Y. Chen and S.-L. Chou, *Adv. Energy Mater.*, 2018, 1802327.

- 14 S. Bai, C. Wang, W. Jiang, N. Du, J. Li, J. Du, R. Long, Z. Li and Y. Xiong, *Nano Res.*, 2015, **8**, 2789–2799.
- 15 C. Galeano, J. C. Meier, V. Peinecke, H. Bongard, I. Katsounaros, A. A. Topalov, A. H. Lu, K. J. J. Mayrhofer and F. Schuth, J. Am. Chem. Soc., 2012, 134, 20457–20465.
- 16 L. Guo, W.-J. Jiang, Y. Zhang, J.-S. Hu, Z.-D. Wei and L.-J. Wan, ACS Catal., 2015, 5, 2903–2909.
- 17 C. Baldizzone, S. Mezzavilla, H. W. P. Carvalho, J. C. Meier, A. K. Schuppert, M. Heggen, C. Galeano, J.-D. Grunwaldt, F. Schüth and K. J. J. Mayrhofer, *Angew. Chem., Int. Ed.*, 2014, 53, 14250–14254.
- 18 S. Mukherjee, A. Mukherjee, A. Bhagi-Damodaran, M. Mukherjee, Y. Lu and A. Dey, *Nat. Commun.*, 2015, **6**, 8467.
- 19 M. R. A. Blomberg, Biochemistry, 2016, 55, 489-500.
- 20 M. Bron, P. Bogdanoff, S. Fiechter, I. Dorbandt, M. Hilgendorff, H. Schulenburg and H. Tributsch, *J. Electroanal. Chem.*, 2001, 500, 510–517.
- 21 D. Cao, A. Wieckowski, J. Inukai and N. Alonso-Vante, J. Electrochem. Soc., 2006, 153, A869–A874.
- 22 J. Masud and M. Nath, ACS Energy Lett., 2016, 1, 27-31.
- 23 D. Cao, A. Wieckowski, J. Inukai and N. Alonso-Vante, J. Electrochem. Soc., 2006, 153, A869–A874.
- 24 T. J. Schmidt, U. A. Paulus, H. A. Gasteiger, N. Alonso-Vante and R. J. Behm, *J. Electrochem. Soc.*, 2000, **147**, 2620–2624.
- 25 C. Delacôte, A. Lewera, M. Pisarek, P. J. Kulesza, P. Zelenay and N. Alonso-Vante, *Electrochim. Acta*, 2010, **55**, 7575–7580.
- 26 Y. J. Feng, T. He and N. Alonso-Vante, *Electrochim. Acta*, 2009, **54**, 5252–5256.
- 27 Y. Feng, T. He and N. Alonso-Vante, *Chem. Mater.*, 2008, **20**, 26–28.
- 28 Q. L. Zheng, X. Cheng and H. Y. Li, *Catalysts*, 2015, **5**, 1079–1091.
- 29 A. T. Swesi, J. Masud and M. Nath, *Energy Environ. Sci.*, 2016, 9, 1771–1782.
- 30 N. A. Vante, W. Jaegermann, H. Tributsch, W. Hoenle and K. Yvon, J. Am. Chem. Soc., 1987, 109, 3251–3257.
- 31 I. Ijjaali and J. A. Ibers, Z. Kristallogr. New Cryst. Struct., 2001, 216, 485–486.
- 32 S. Kukunuri, S. N. Karthick and S. Sampath, *J. Mater. Chem. A*, 2015, **3**, 17144–17153.

- 33 M. S. Hannu-Kuure, K. Palda'n, R. Oilunkaniemi, R. S. Laitinen and M. Ahlgren, J. Organomet. Chem., 2003, 687, 538–544.
- 34 S. Kukunuri, P. M. Austeria and S. Sampath, *Chem. Commun.*, 2016, **52**, 206–209.
- 35 T. Olsen, E. Rost and F. Gronvold, *Acta Chem. Scand., Ser. A*, 1979, 33, 251–256.
- 36 A. R. Cabral, B. Lehmann, R. Kwitko, H. F. Galbiatti and M. C. Pereira, *Mineral. Mag.*, 2002, 66, 327–336.
- 37 S. Dey, V. K. Jain and B. Varghese, J. Organomet. Chem., 2001, 623, 48–55.
- 38 M. K. Pal, V. K. Jain, N. P. Kushwah, A. Wadawale, S. A. Glazun, Z. A. Starikova and V. I. Bregadze, J. Organomet. Chem., 2010, 695, 2629–2634.
- 39 L. B. Kumbhare, V. K. Jain, P. P. Phadnis and M. Nethaji, J. Organomet. Chem., 2007, 692, 1546–1556.
- 40 L. B. Kumbhare, V. K. Jain and B. Varghese, *Inorg. Chim. Acta*, 2006, **359**, 409–416.
- 41 S. V. Myers, A. I. Frenkel and R. M. Crooks, *Chem. Mater.*, 2009, **21**, 4824–4829.
- 42 S. C. Sarma, V. Mishra, K. A. Ann Mary, S. Roy and S. C. Peter, ACS Energy Lett., 2018, 3, 3008–3014.
- 43 S. C. Sarma, U. Subbarao, Y. Khulbe, R. Jana and S. C. Peter, *J. Mater. Chem. A*, 2017, **5**, 23369–23381.
- 44 K. Sasaki, H. Naohara, Y. Choi, Y. Cai, W.-F. Chen, P. Liu and R. R. Adzic, *Nat. Commun.*, 2012, **3**, 1115.
- 45 D. G. Brookins, in *Eh-pH Diagrams for Geochemistry*, Springer Berlin Heidelberg, Berlin, Heidelberg, 1988, pp. 18–19.
- 46 S. S. Mahapatra and J. Datta, *Int. J. Electrochem.*, 2011, **2011**, 16.
- 47 M. J. Escudero, A. Aguadero, J. A. Alonso and L. Daza, *J. Electroanal. Chem.*, 2007, **611**, 107–116.
- 48 X. Zhang, W. Wu, Z. Zhao, B. Tu, D. Ou, D. Cui and M. Cheng, *Catal. Sci. Technol.*, 2016, 6, 4945–4952.
- 49 S. Kattel, Z. Duan and G. Wang, J. Phys. Chem. C, 2013, 117, 7107–7113.
- 50 M. P. Hyman and J. W. Medlin, *J. Phys. Chem. C*, 2007, **111**, 17052–17060.
- 51 S. Stolbov, J. Phys. Chem. C, 2012, 116, 7173-7179.