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To cite this article: Anthony P O'Mullane 2020 J. Phys. Energy 2 041001

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Creating active interfaces as a strategy to improve electrochemical water splitting reactions

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Abstract
Electrochemical water splitting has received significant attention recently for the production of green hydrogen as a means to alleviate our need on fossil fuels. There has been immense progress on developing new catalysts that are active for the hydrogen evolution reaction (HER), the oxygen evolution reaction (OER) as well as materials that are bifunctional and are active for both reactions. In this perspective I detail recent developments in tailoring highly active interfacial regions in a variety of catalysts that are suitable for these reactions. In particular the doping of metal oxides and metal-chalcogenides with a secondary metal is discussed and how this influences the activity and stability of the catalyst and how in fact simple systems such as Ni/NiO are also highly active due to the presence of a metal/metal oxide interface. Finally the future direction in characterising electrocatalysts is discussed and the important role that spatially resolved electrochemical data combined with other surface science techniques can be used to study structure-activity relationships at a localised level at such important interfaces.

1. Introduction

Electrochemical water splitting to produce green hydrogen has gained significant traction in the scientific community and is currently in a transition phase to large scale commercial applications [1]. Hydrogen has been identified as a key fuel of the future to rapidly reduce CO₂ emissions in the electricity and transport sectors. Recent developments also show promising results for the electrification of industry using renewable energy sources and hydrogen as a means to decarbonise certain sectors [2]. For example, a significant development is the use of hydrogen and electric arc furnaces for steel making which is an industry with a large carbon footprint [3]. The term ‘hydrogen economy’ was first proposed by Bockris [4] and has recently been adapted to a ‘hydrogen society’ [5, 6]. This is due to the enormous societal, environmental and economic benefits that renewable energy and hydrogen generation, storage and utilisation can deliver via rapid technological developments coupled with scientifically, rather than ideologically, informed political leadership [7].

With this renewed interest in a technology that spans centuries and is routinely demonstrated in schools and universities across the globe there is still much to discover and improve in the area of electrochemical water splitting. In essence the reaction is straightforward but is limited by sluggish kinetics on the oxygen evolution side while the cost of catalysts for the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) is a commercial barrier to the deployment of large scale electrolyser. In recent years there have been significant research efforts in developing non precious metal based electrocatalysts for the HER and the OER based mainly on transition metal oxides/hydroxides for the OER and transition metal chalcogenides, phosphides and MXenes for the HER. I will not summarise the extensive amount of work in these areas here and the reader is pointed to a number of excellent recent reviews [8–21] of non precious metal based electrocatalysts for the HER, OER and overall bifunctional water splitting electrocatalysts where the same catalyst demonstrates activity for both reactions.
In this perspective I will detail recent strategies where noble metal catalysts are still employed but their utilisation is extremely high. In the 1990’s there was an explosion in nanomaterial research which demonstrated the fascinating properties of using metals in a nanostructured form. This was particularly beneficial to fuel cell research where rapid developments in improving Pt utilisation were demonstrated for the oxygen reduction reaction (ORR) as well hydrogen, methanol, ethanol and formic acid oxidation while the use of nanostructured alloys based on Pt also resulted in marked improvements in the efficiency of these reactions [2, 22–25]. In the 1970s there were many reports on dimensionally stable anodes such as RuO2, Co3O4, IrO2, TiO2 that were being investigated for a variety of applications such as the chlor-alkali industry, electrowinning and electrogalvanising [26, 27]. Here it was found that many electrodes of this type were also suitable for electrochemical water splitting, in particular the OER. The recent interest in electrolysis to produce clean hydrogen resolved to replace these expensive metal oxides with Earth abundant materials and hence the concentration on Fe, Co, Ni, Mo and Mn based materials for both the HER and the OER.

Significant progress has been made in terms of lowering the onset potential, the overpotential required to pass 10 mA cm−2 and increasing the current density passed through electrodes that are commercially relevant which now appears to be reaching a plateau in terms of these benchmark performance measures. Recently however, it has been acknowledged by many groups that utilising highly catalytically active precious metals is a viable option to increase activity and importantly stability even further for both the HER and OER. Given the low amount of precious metals used in such studies, the technoeconomic analysis of large scale deployment is still favourable.

This perspective will initially concentrate on two classic nanomaterials, namely gold and platinum which have been incorporated into a variety of Earth abundant OER and HER electrocatalysts that demonstrate excellent performance. This is not limited to the recent emerging area of single atom catalysts but demonstrates the usefulness of the approach when also using clusters and nanoparticles as dopants. The fabrication of multicomponent catalytic systems opens up the area of controlled interfacial engineering between the dopant and support which is the key aspect for improved electrocatalytic performance and is discussed in the relevant sections. I then discuss the use of non precious metals as dopants to achieve similar outcomes and finally concentrate on recent work showing that simple metal-metal oxide interfaces such as Ni/NiO are in fact highly active towards water splitting reactions. This is followed by a discussion on future characterisation strategies to understand these important interfaces.

2. Metal doping for improved electrocatalytic performance

2.1. Incorporation of gold

Gold nanomaterials have been extensively investigated for a wide range of electrocatalytic reactions including the HER but some controversy remains over its activity for the OER. Lyons et al reported that superactivated gold surfaces exhibit a transient OER response subsequent to monolayer oxidation and prior to visible oxygen evolution which is not observed at regular gold surfaces [28]. However Bell et al reported the possibility of Fe surface impurities may be a contributing factor to this OER behaviour by creating active centres for the reaction [29]. This indicates a synergy between Fe and Au that is beneficial for this reaction. Related to this phenomenon a significant number of publications have focussed on the benefit of using gold with a variety of transition metal oxides/hydroxides to promote the OER. This concept of engineering the interface between metallic elements and metal oxides has proven to be highly successful for a variety of systems. Initial studies focused on using gold as a substrate material for materials such as CoOx [30] and Co(OH)2 [31] which showed significantly enhanced activity compared to the same materials supported on other electrode surfaces. For the latter study, Pd, Cu and C support electrodes were studied which showed inferior OER activity compared to the gold supported material. The increase in activity is related to the increased oxidation of cobalt oxide/hydroxide to CoIV species mediated by the gold support which is the active component for the OER. Upon the establishment of this effect a number of papers appeared using gold nanomaterials incorporated into cobalt oxides rather than a large support electrode to minimise the cost of such an electrocatalyst. In all reported cases the effect was the same whereby the presence of gold enhanced the OER activity of cobalt oxide materials. Some examples of this approach are Au@Co3O4 (core@shell) nanocrystals shown in figure 1 which exhibit enhanced performance compared to Co3O4 nanoparticles in terms of onset potential, current density and lower Tafel slope [32].

Li and coworkers synthesised wreath like Au-Co(OH)2 microclusters which were found to be highly active for the OER in neutral media [33], while Zhao et al embedded gold nanoparticles into mesoporous Co3O4 which was active in neutral and alkaline media [34]. Electrocatalytic deposition methods have also been used where Chen and co-workers electrodeposited Au-Co(OH)2 from a cobalt hexacyanoferrate precursor, however the atomic percentage of gold that was used was high at over 50% [35]. An interesting development with Chen’s work however was that the composite was also active for the HER and again a
synergistic interaction between gold and Co(OH)$_2$ was found. This type of approach was also employed by Sayeed et al [36] who also electrodeposited a Au-Co(OH)$_2$ composite from an electrolyte containing cobalt nitrate and KAuBr$_4$. In that instance the concentration of gold was significantly lower at ca. 5 at% which resulted in excellent activity for both the OER and HER in alkaline electrolyte. Significantly this material also demonstrated good electrocatalytic performance for the oxygen reduction reaction where a four electron reduction process to water was observed as well as good sensitivity to the detection of glucose. The development of such a multifunctional catalyst for a variety of reactions illustrates the benefits of using gold as the dopant material. Further extensions of this concept were reported in mixed metal oxide systems such as Au-NiCo$_2$O$_4$ nanomaterials supported on porous graphene which is highly active for the OER where the stability of the catalyst is enhanced by the presence of gold [37]. Sultana and coworkers [38] reported a gold doped layered Co-Ni hydroxide system with a low gold content of 0.25 at% (figure 2) which was active and stable for both the OER and HER under commercially relevant conditions of 6 M NaOH. The key to activity for both reactions was that upon repetitive cycling the material reconstructed which resulted in an accumulation of gold nanoparticles at the surface of the composite which in particular facilitated the HER.

Figure 1. (a) Scheme of the synthetic route to Au@Co$_3$O$_4$ core–shell NCs. (b) TEM image of Au NCs. Inset: histogram of the size distribution. (c) TEM image of Au@Co NCs. Inset: histogram of the size distribution. (d) TEM image of a two-layer array of the Au@Co NCs. Inset: modeled projection of the two-layer NC assembly. (e) HRTEM image of a single Au@Co NC. (f) TEM image of Au@Co$_3$O$_4$ NCs supported on carbon. (g) HRTEM image of a single Au@Co$_3$O$_4$ NC. Reprinted from [32] with permission of Wiley.
2.2. Incorporation of platinum

Pt is undoubtedly an excellent catalyst and has been employed for a variety of important reactions, in particular related to fuel cell technology. Although there are many examples of Pt free catalysts in fuel cells, in particular for the oxygen reduction reaction, there are still ongoing efforts to improve Pt utilisation for use in this technology either by minimising the size of the catalyst or alloying with other elements. In the area of electrochemical water splitting Pt has not been used to aid the OER as there is a very large overpotential associated with this reaction on Pt. In addition, the effect of the substrate on the OER activity for Co oxide as reported by Bell did not show as significant an increase in activity as compared to the benefits of using Au [30]. However, the incorporation of Pt into multicomponent materials for the HER has been investigated by numerous groups, some of which are detailed as follows.

Transition metal chalcogenides have been long identified as being active for the HER, in particular in acidic media but are less active in neutral and alkaline media. However, Jiang et al [39] reported that decorating mesoporous cobalt selenide with Pt single atoms (Pt/np-Co$_{0.85}$Se) resulted in excellent performance for the HER in 1 M phosphate buffer solution (figure 3). In comparison to Pt/C and other transition metal chalcogenides the activity of the catalyst is impressive as evidenced by a low Tafel slope, high turn over frequency, low overpotential to achieve $-10$ mA cm$^{-2}$ and long term stability (figure 3). The enhanced activity was attributed to the inert Co atoms being triggered by single-atom Pt, into more active sites for water dissociation under catalytic conditions. Density functional theory (DFT) calculations revealed that electronic interactions between atomic-level Pt and np-Co$_{0.85}$Se can reduce energy barriers of dissociated water molecules, while also significantly improving the adsorption/desorption behaviour of H on Pt/np-Co$_{0.85}$Se catalyst. Both of these effects results in a synergy that promotes HER performance.

Pt has also been incorporated into metal oxide electrodes for enhanced HER activity under alkaline conditions. Zhao et al reported that Pt decorated on NiO nanoparticles were highly stable and performed better than commercial Pt/C even with a loading as low as 5.1 $\mu$g cm$^{-2}$. The generation of a NiO/PtNi rich interface on the surface of the nanomaterials was the key component to the improved performance as indicated by higher current densities than Pt/C and PtNi nanoparticles. The active site was identified as Ni(OH)$_2$ atomic layers on the Pt (111) facet that facilitates both water dissociation and hydrogen evolution [40]. Multimetallic systems have also been explored for the HER. Li et al [41] demonstrated that de-alloying PtNi nanowires results in a catalyst where the activity of the surface Pt atoms is maximised. DFT calculations revealed that single Ni atoms liganded by two hydroxyl groups electronically promote neighbouring Pt atoms and enhance their electrocatalytic activity towards the HER. The optimum decoration density to maximise performance was Ni:Pt of 1:6. It is interesting to note that hydroxyl groups play a significant role and is similar to the previous study of Zhao [40]. Therefore interfacial engineering catalysts to promote hydroxyl group participation is highly beneficial to this reaction in terms of the water dissociation step. The added benefit of this composition is that it also facilitated the electrocatalytic oxidation of fuel cell relevant molecules such as methanol and ethanol which also outperformed commercial Pt/C. In a more elaborate catalyst design Tiwari et al [41] showed that Pt incorporation into graphitic nanotubes that encapsulate a FeCo alloy and has Cu deposited on the inside of the tube walls results in high Pt utilisation where better HER activity in acidic solution was obtained at 1/80th of the Pt loading of commercial Pt/C. This is equivalent to 1.4 $\mu$gPt cm$^{-2}$ which resulted in a current density of $-10$ mA cm$^{-2}$ at an overpotential of only 18 mV, a TOF of 7.22 s$^{-1}$ (96 times that of Pt/C) and stability to accelerated testing of 10000 cycles. As a minor aside, another recent example exemplifying the benefits of Pt doping is in the area of solid oxide fuel cells whereby the inclusion of Pt resulted in enhanced activity for the hydrogen oxidation reaction with stability at temperatures as high as 600 °C [42].
2.3. Incorporation of other precious metals

Au and Pt are not the only metals to be incorporated into water splitting electrocatalysts to improve performance. As an example of the OER, Lee et al [43] demonstrated that doping layered CoOOH nanosheets with Ag resulted in improved activity. The Ag was initially doped into Co(OH)₂ which facilitated the conversion into the active CoOOH material. DFT calculations indicated that Ag doping enhances the phase stability of CoOOH and exposes Ag dopants which also act as active sites by releasing –OH adsorbates. Taking the HER, Qi and co-workers [44] showed that by decorating a defect rich basal plane of MoS₂ with Pd nanodisks resulted in Pt-like HER activity. The presence of Pd modulates the surface electronic state of MoS₂ while retaining its active sites which results in a low onset potential of 40 mV and low Tafel slope of 41 mV dec⁻¹. Shan et al [45] took a different approach and decorated a RuIr alloy nanocrystal with Co to generate a catalyst that is active for both the OER and HER under acidic conditions. The increase in OER and HER activity is attributed to a dual effect that modifies the concentration of O-based species and Ru sites valence states. The former influences oxygen intermediates adsorption/desorption, while the latter influences the hydrogen binding energy. A cell voltage of only 1.52 V was required to pass 10 mA cm⁻² for overall water splitting. In addition, a series of catalysts was produced, M-RuIr (M = Co, Ni, Fe) which all showed enhanced activity, however the Co-RuIr system gave the best performance due to the increased influence over the presence of O-based species and electronic perturbation to change the hydrogen binding energy. Fan et al [46] also investigated the benefits of Ru by the partial oxidation of RuCo alloys implanted in nitrogen doped carbon (NC) to create a RuO₂/Co₃O₄-RuCo@NC catalyst that exhibited bifunctional behaviour for overall water splitting in acidic media where a cell potential of 1.66 V was required to pass a current density of 10 mA cm⁻². The creation of a Mott–Schottky metal–semiconductor interface was critical as catalysts prepared in the absence of the oxide component were significantly less active.

2.4. Are precious metals needed?

As seen in the previous sections the inclusion of precious metals has a significant impact on electrochemical water splitting reactions. However, given that in most cases a metal-metal oxide or metal-metal chalcogenide interface is the key component for improving activity, the question arises as to whether the metal component needs to be a precious metal? Kenney and co-workers [47] have shown via an electrodeposition and annealing approach that a Ni–Co–Cr metal/metal oxide nanostructured catalyst demonstrates good electrocatalytic performance for the HER in neutral pH where the presence of Cr facilitated improved stability compared to the material without Cr. In addition, Dinh et al [48] also reported the benefits of using Cr in a HER catalyst, comprising of Ni and CrOₓ sites doped onto a Cu surface which also operates efficiently
in neutral media. The Ni and CrO₃ sites have strong binding energies for hydrogen and hydroxyl groups, respectively, which accelerates water dissociation, whereas the underlying Cu has the benefit of weak hydrogen binding energy which promotes hydride coupling and therefore the evolution of hydrogen. This results in a low overpotential of 48 mV at an applied current density of 10 mA cm⁻² in a pH 7 electrolyte. Zhang et al [49] have shown that Ni when doped into MoS₂ nanosheets results in significantly improved performance for the HER under alkaline conditions. The Ni sites reduce the kinetic energy barrier of the initial water-dissociation step and facilitates the desorption of the −OH that are formed which results in an overpotential of 98 mV at −10 mA cm⁻² in 1 M KOH which is not only better than pristine MoS₂ but introduced stability to MoS₂ under alkaline conditions.

Interestingly, recent work has demonstrated that much simpler metal–metal oxide interfaces also show significantly enhanced performance for electrochemical water splitting. Suryanto et al [50] reported a Janus nanoparticle catalyst with a nickel-iron oxide (Ni−γ−Fe₂O₃) interface that was highly active for both the HER and OER under alkaline conditions (figure 4). DFT calculations indicated that the HER was induced by strong electronic coupling between the iron oxide and nickel at the interface. This induces a slight oxidation of Ni at the interface which results in a binding energy close to 0 eV which is ideal for the HER. When this is coupled with the metallic and highly conducting properties of Ni, electron transfer to the active sites is facile and lowers the barrier to the Volmer step of the reaction. H₂ evolution was then promoted by the unique Ni–O–Fe configuration at the interface. Another advantage of such an Fe–Ni based system is that it is also highly active for the OER which has been reported previously by many groups [51–55]. For overall water splitting a cell potential of only 1.47 V was required to achieve 10 mA cm⁻². In addition the polarity of the cell could be switched without any decrease in performance which indicates that the catalyst produced has inherent bifunctional activity for both reactions and will have implications for commercial electrolysers and direct integration with intermittent energy sources. Zhang et al [56] reported atomically thin FeCoNi ternary (oxy)hydroxide nanosheets (FeCoNi-ATNs) which also showed similar bifunctional behaviour where they demonstrated a fully reversible water electrolyser cell which exhibited robust reversibility between the two half reactions under high current density of 100 mA cm⁻¹. Therefore, this recent body of work indicates that highly efficient HER and OER electrocatalysts can indeed be produced without the inclusion of precious metals. However, the long term stability of these new types of catalysts that include and exclude precious metals is yet to be determined at timescales beyond a few days of continuous operation. In this area, significantly longer term testing needs to be undertaken and there is significant scope to develop appropriate accelerated ageing tests for water electrolysis that are routinely used in the fuel cell community.
To simplify catalyst design even further Peng et al. [57] reported both a Ni/RuO$_2$ and Ni/NiO catalyst that are highly active for the HER under alkaline conditions. Here they describe interfacial charge transfer between the metal and metal oxide which creates a ‘chimney effect’ at the metal/metal oxide interface. This special chemical environment at the interface inhibits H$_2$O$^*$ and OH$^*$ adsorption and results in selective H$^*$ adsorption which is at a binding energy that facilitates easy H$_2$ removal from the catalyst as indicated by DFT calculations. Therefore the interfacial Ni atoms are the active sites which exhibit high selectivity to H$^*$ adsorption compared to the non-interfacial Ni atoms. The change in the electronic nature of the interfacial Ni atoms then facilitates the most appropriate binding strength for H$^*$ which results in highly efficient hydrogen evolution which was denoted as a ‘chimney effect’ (figure 5) where the HER is localised at the interface (figure 5(b)) compared to regular hydrogen evolution at non-interfacial regions (figure 5(b)).

Wang et al. [58] also demonstrated that NiO$_x$ supported on bamboo like carbon nanotubes was active for the HER in alkaline electrolyte. The Ni$^0$ at the interface of Ni/NiO$_x$ was also found to be critical to the HER performance while the gradual in-situ generation of Ni$^0$ during the HER resulted in continuously improved performance with cycling. It was found that the Ni$^0$ content increased from 36.2% to 55.4% after the HER.

Huan et al. reported a high surface area porous and dendritic Cu/Cu$_2$O/CuO material that was modified by a further thin layer of electrodeposited CuO nanoparticles. The catalyst was active for the OER but suffered from large overpotentials compared to other transition metal oxide systems, however the metal-metal oxide system was required to maintain the conductivity of the sample and therefore prolonged activity for the OER [59].

3. Outlook

From the examples presented here, which is certainly not an exhaustive list, there is a clear indication that the formation of metal-oxidised metal interfaces whether they be metal-metal oxide or metal-metal chalcogenide interfaces are the origin of increased activity for both the HER and OER under a wide variety of pH conditions. In numerous studies experimental observation has been backed up with theoretical calculations showing the benefits of creating a unique interface that facilitates optimum binding of reactants, intermediates or products via electronic effects. The inclusion of noble metal particles such as Au and Pt is highly effective and is beneficial for the stability of the system but recent work on non precious bimetallic metal-metal oxide systems and indeed very simple interfaces such as that seen for Ni/NiO indicate the effect is highly influential on electrocatalytic activity. The fabrication of truly bifunctional systems that are active for both the HER and OER and can switch between both reactions without a decrease in performance is particularly promising [50, 56] which will simplify the electrolyser fabrication process and allow for the direct integration of electrolyser with intermittent renewable energy sources which suffer from reverse current flow upon rapid start up and shutdown conditions [60–62]. This is highly damaging for current
commercial electrolysers which are required to operate at a certain load to avoid this issue. Therefore direct integration with wind or solar energy sources is not possible and grid connection is required which would then put a question mark on whether the hydrogen produced is truly green?

In determining the role of the interface care must be taken to perform extensive characterisation of the catalyst after the HER and in particular the OER. For the latter it has been widely reported that large structural, crystallinity and compositional changes can occur at OER catalysts after the catalytic reaction. This has been noted in particular at metal chalcogenide and phosphide systems that are generally oxidised into the oxide or oxyhydroxide active form \[13, 63, 64\] and therefore any metal doped system should also be subjected to careful post catalysis analysis to ensure that the metallic component still exists or may have been reduced during the reaction. Even for the HER this is critical, as noted for the Ni/NiO system the percentage of Ni\(^0\) was found to increase during the course of the HER and a gradual improvement in performance was observed \[58\]. This is particularly important for support of theoretical calculations which are generally based on the composition of the pristine catalyst.

An additional point to consider which has not been addressed in great detail in the literature is the possibility of heterogeneous changes in a catalyst during the reaction. Most measurements that are undertaken to probe the catalyst after the reaction are localised measurements such as x-ray photoelectron spectroscopy (XPS), x-ray diffraction (XRD), transmission electron microscopy (TEM), x-ray absorption near edge spectroscopy (EXAFS), Raman which have a relatively small sampling area as well as electrochemical characterisation which is performed on the entire catalyst. The question arises as to whether any changes or lack of changes is homogeneous across the sample? A recent study \[65\] on electrochemically deposited Ni(OH)\(_2\) which was investigated for the OER revealed that changes in the catalyst after the reaction were quite heterogeneous. Atomic force microscopy revealed clustering of the sample after the reaction and EXAFS mapping (figure 6) revealed compositional changes across the sample with regions rich in NiO as well as areas that remained as Ni(OH)\(_2\). This was also confirmed by performing XPS measurements at various points on the sample which correlated with the EXAFS data. This could have potential implications for a wide variety of electrocatalytic systems where often homogeneous changes are implied.

From an electrochemical perspective the development of the new scanning electrochemical cell microscopy (SECCM) technique could also aid in assessing heterogeneity effects during electrocatalytic reactions. Unwin et al \[66\] have already demonstrated unequivocally that while the basal plane of bulk MoS\(_2\) (2 H crystal phase) possesses significant activity, the HER is greatly facilitated at the edge plane and at surface defects such as steps, edges or crevices (figure 7). The significant change in electrocatalytic activity across various defects and steps can be clearly seen in figure 7(a) while the basal plane shows consistent activity across the sampled area. This was followed up by Takahashi et al \[67\] who measured the HER activity difference at the edge and terrace of MoS\(_2\) as well as the heterojunction of MoS\(_2\) and WS\(_2\). They also directly visualized the relationship of HER activity and number of MoS\(_2\) nanosheet layers and revealed the heterogeneous aging state of MoS\(_2\) nanosheets.

A further development to this approach is when the spatially resolved electrochemical data is coupled with other surface science techniques to explore structure-activity relationships. Unwin \[68\] demonstrated this by combining electrochemical data with co-located structural information from scanning electron microscopy, electron backscatter diffraction, and energy-dispersive x-ray spectroscopy in a correlative electrochemical multimicroscopy approach where they investigated the HER activity on low carbon steel under acidic conditions where the activity of the low-index planes were shown to increase slightly in the order of \((100) > (111) > (101)\). It was also found that grain boundary terminations and MnS inclusions exhibit greatly enhanced HER activity compared to the crystallographic planes which has implications also for the field of corrosion. However, this demonstration of a multimicroscopy and electrochemical approach has significant potential for characterising the types of electrocatalysts detailed in this perspective and is likely to be a key approach in truly understanding water splitting reactions at metal-metal oxide and metal-metal chalcogenide interfaces.

4. Conclusion

To summarise this perspective highlights the important role that metal-metal oxide and metal-metal chalcogenide interfaces play in electrochemical water splitting reactions. The inclusion of precious metals to create these interfaces shows excellent promise, however recent developments have shown that equally effective electrocatalysts can be produced using more cost effective materials when these interfaces can be engineered and controlled. DFT calculations are beginning to provide new insights into the critical nature of establishing these interfaces as well as the emergence of new spatially resolved experimental techniques to probe catalysts both post reaction and under \textit{in situ} conditions. The direct integration of electrolysers with intermittent energy sources is another exciting development where, again, behaviour at these interfacial
Figure 6. Ni(OH)₂ films electrodeposited on Cu/C-formvar TEM grids (LHS) before and (RHS) after the OER. Elemental Ni is shown in (a and b) for each case, with the minimum and maximum displayed areal density values shown in µg cm⁻². K-edge Ni XANES maps of the same areas are shown in (c) and (d), where the encoded colour corresponds to the proportion NiO/ΣNi where ΣNi is equal to NiO + Ni(OH)₂. The colour scale for (a)–(d) is shown in (c). XANES spectra taken from different pixels as indicated are shown in (e) and (f) together with the standard spectra for NiO (dotted line) and Ni(OH)₂ (dashed line). Spectra from areas of high Ni(OH)₂ are shown in blue in (e) and (f) while high NiO spectra are shown in orange (f) [65]. Reproduced by permission of The Royal Society of Chemistry.

Figure 7. (a) 26 × 26 µm spatially resolved current map (equipotential image) obtained at −0.85 V vs. RHE. Surface current line profile (surface current at −0.85 V vs. RHE versus x-position) taken from the dashed red line indicated in (a). (c) 18 × 18 µm AFM topographical scan taken of the scan area in (a). (d) AFM line profile of the area indicated by the dashed red line in (c). Each of the surface defects (steps) are labelled (1) to (6) [66]. Reproduced by permission of The Royal Society of Chemistry.
regions is key to OER and HER activity and the ability to switch between both reactions without a decrease in performance. However, for the majority of newly developed catalysts, longer term testing will need to be undertaken. It is now critical that accelerated ageing tests, similar to those protocols developed in the fuel cell community, are carried out on electrode materials to truly probe their suitability for commercial deployment. I am optimistic that the recent rapid development of this research area can result in the manufacture of electrolysera at a scale that will fulfill the urgent need for realising a sustainable hydrogen society to combat global greenhouse gas emissions.

Acknowledgments

AOM acknowledges support from the Australian Research Council (DP180102869) and the Australian Renewable Energy Agency (MG030).

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