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## Review Article

## New insights into working nanostructured electrocatalysts through operando spectroscopy and microscopy

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One of the biggest challenges in electrocatalysis is unravelling the structural and chemical changes that can occur in complex nanostructured catalyst materials under reaction conditions. Such knowledge is vital for understanding dynamic changes in catalyst reactivity and mechanisms behind catalyst stability or degradation. Due to significant technological developments in recent years, investigations of working electrolyte/electrode interfaces have become increasingly feasible. This review highlights recent results in the use of *operando* spectroscopy and microscopy tools to unravel the behavior of electrocatalysts under reaction conditions. In particular, insight into the dynamic nature of electrocatalysts and the evolution of their structure and chemical properties under electrochemical reaction conditions will be presented.

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## Introduction

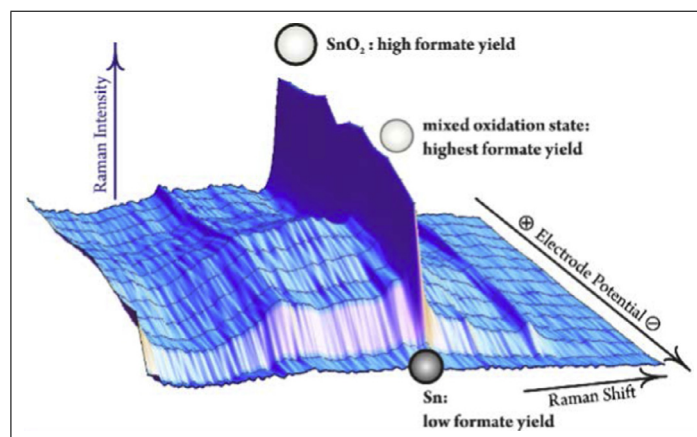
In the search for new catalysts to enable the next-generation of energy technologies and the synthesis of alternative fuels, researchers are actively pursuing advances in catalyst design leading to nanostructures with tunable activity and selectivity. However, additional progress in catalyst characterization is also needed to uncover whether these rationally designed nanocatalysts maintain their structural and chemical properties in the course of a reaction. Changes in nanocatalysts during a reaction may occur on different time scales, i.e. fast changes on the

same scale as reaction kinetics [1], or long-term changes which are related to the catalyst stability and degradation [2\*]. Additionally, changes may occur on different length scales, for example evolution of the catalyst nanostructure [3] or meso- and microscale changes to catalyst dispersion or support [4]. To meet these characterization challenges, the use of time- and spatially-resolved *operando* techniques to complement *ex situ* characterization methods are becoming increasingly important. *Operando* characterization refers to measuring a catalyst under operating conditions, with the catalyst in its working state, while at the same time characterizing the activity and selectivity of the reaction [5]. Particularly for electrochemical reactions, *operando* characterization can be challenging due to the complex nanostructured surface of the catalyst and support, the presence of an electrolyte, solvated and adsorbed species, applied potential, and the evolution of gas or liquid products at the catalyst surface. Nevertheless, the use of such techniques could help achieve unprecedented insights into the fundamental mechanisms behind reactivity of electrocatalysts in realistic and complex environments. In this review, we describe the recent advances in applying *operando* spectroscopy and microscopy methods to nanostructured electrocatalysts, and we highlight some of the unique mechanistic insights into electrocatalyst reactivity that can be gained using these techniques.

**Operando spectroscopic characterization of electrocatalysts  
Infrared (IR) spectroscopy**

It is important for electrocatalytic reactions to investigate which chemical species exist on the electrode surface and their oxidation state. This can be done by tracking the formation/extinction of IR peaks corresponding to the adsorbed reactants, the intermediates and the products. For example, Zandi et al. [6\*\*] discovered the key H<sub>2</sub>O-oxidation intermediate, Fe<sup>IV</sup>=O, on a hematite electrode through attenuated total reflectance infrared spectroscopy (ATR-IR), which allowed them to propose a reaction mechanism for H<sub>2</sub>O oxidation on this electrode. In addition, the coupling of IR spectroscopy with other *operando* electrochemical techniques, for instance, *operando* Fourier transform infrared spectroscopy (FTIR) combined with electrochemical impedance spectroscopy (EIS) can explain how active participants such as H<sub>2</sub>O and D<sub>2</sub>O chemisorb on YSZ, ZrO<sub>2</sub>, and Y<sub>2</sub>O<sub>3</sub> solid oxide fuel cell (SOFC) electrodes as a function of the pressure and

Figure 1



Potential dependence of the Raman spectra of SnO<sub>2</sub> electrocatalysts during CO<sub>2</sub> electroreduction. Reprinted with permission of ref. [10<sup>•</sup>].

temperature. This technique provided valuable insight into the mechanism behind gas adsorption in heterogeneous catalytic reactions by confirming that chemisorbed OH groups behave as proton-donors [7].

To give insight into the electrolyte/electrode interface, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) [8] was used to monitor reactive chemical species such as both gaseous and adsorbed CO<sub>2</sub> and CO on a SOFC Au/zirconia electrode by tuning the temperature and applied voltage. Moreover, by applying a negative potential it was possible to trigger surface reconstructions of Ge crystals in acidic medium by using ATR-IR [9].

### Raman spectroscopy

Activity, stability and selectivity of electrocatalysts can be considerably affected by transformation of the catalyst surface structure and changes in the chemical species involved in reactions. By monitoring *operando* Raman spectra at different pH values and by tuning the potential during CO<sub>2</sub> electrochemical reduction, Dutta et al. [10<sup>•</sup>] reported that a SnO<sub>2</sub> catalyst showing high Faradaic efficiency (FE) toward formate production steadily reduced to metallic Sn under reaction conditions, with a corresponding decline in the FE toward formate, Figure 1. These results demonstrated that the oxidation state of the catalyst controlled the product yield and catalytic performance. Another example is the dissolution of an anatase TiO<sub>2</sub> crystal employed as a Na-ion battery electrode, in which the diminishing working potential and battery capacity was tied to the discharge of Na ions by simultaneous Raman analysis [11]. In addition, since the organic products (C<sub>x</sub>H<sub>y</sub> species) strongly adsorbing on the catalyst surface can inhibit catalytic reactions, recent studies have aimed to stabilize vulnerable electrode materials against poisoning by carbon species. By monitoring the

early stage of carbon deposition on Ni-based anodes of a SOFC, surface-enhanced Raman spectroscopy (SERS) analysis determined a higher tolerance toward carbon poisoning on the modified electrode (coated by gadolinium-doped ceria) as compared to a pure Ni foil [12].

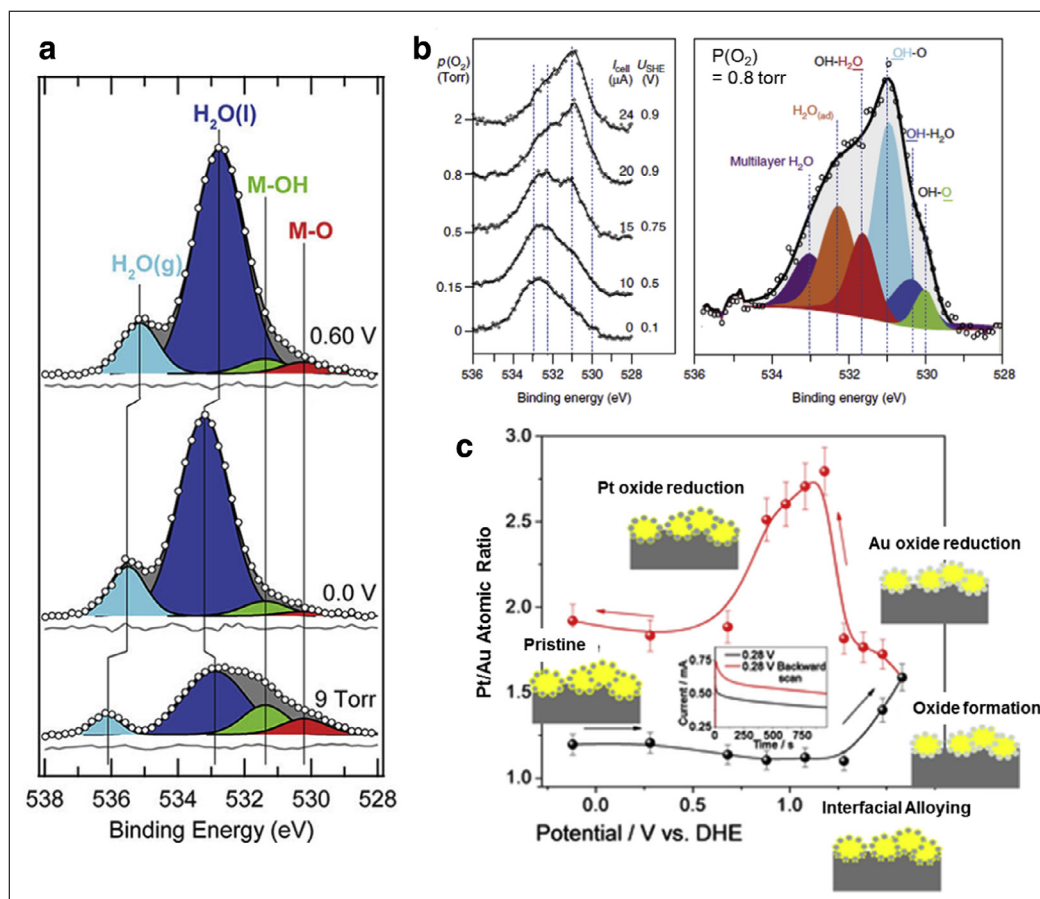
### Mössbauer spectroscopy

Fe- and Sn-based electrocatalysts can be investigated by Mössbauer spectroscopy, which detects absorption/emission of  $\gamma$ -rays from atomic nuclei. Using this technique with an *operando* electrochemical cell, Chen et al. [13] reported that Fe<sup>4+</sup> was produced on a NiFe hydroxide electrocatalyst during steady-state oxygen evolution reaction (OER), and they explained that formation of Fe<sup>4+</sup> contributed to stabilizing the NiOOH lattice. This is in contrast to the Fe-only catalyst, where Fe<sup>3+</sup> is known as the active site. The generation of high-valent Fe ions (Fe<sup>4+</sup>) at defect sites such as edges and corners could minimize kinetical losses during water oxidation [13].

### X-ray photoelectron spectroscopy (XPS)

One technique in which tremendous advances have been made in the past few years to study liquid/solid interfaces is synchrotron-based ambient pressure X-ray photoelectron spectroscopy (AP-XPS). A challenge of measuring XPS under environmental conditions is the reduced inelastic mean free path of electrons from the sample due to scattering in gas or liquid environments. In addition, the electron analyzer must operate in ultra-high vacuum (UHV) conditions, which has been accomplished by reducing the aperture size to the analyzer lens system and through differential pumping before the analyzer [14,15]. For electrocatalyst measurements, there is the additional challenge to maintain a liquid electrolyte in a UHV chamber. One of the methods recently developed in order to accomplish this consists of dipping an electrode into a beaker of electrolyte within the XPS chamber leading to a

Figure 2



AP-XPS results during *operando* electrochemistry. (a) O1s spectra measured on a Ni-Fe catalyst during OER using the dip-pull method by Ali-Löyty et al. [17]. (b) O1s spectra of Pt fuel cell catalysts during ORR measured in a PEM style by Sanchez-Calalongue et al. [23]. (c) Pt/Au atomic ratio under high temperature in a PEM cell with a phosphoric acid loaded membrane used by Papaefthimiou et al. [24], to study Pt catalysts *operando* during ORR. Each panel is reprinted with permission of refs. [17,23,24], respectively.

thin electrolyte layer across the surface after the sample is withdrawn. An ambient pressure of above 20 torr  $\text{H}_2\text{O}$  is introduced into the chamber to prevent evaporation of the aqueous electrolyte. Tender X-rays are also used to optimally probe the interface between the electrode and electrolyte [16]. Using this setup, the oxidation and reduction behavior of Ni-Fe [17] (Figure 2a) and Pt [16] OER electrocatalysts was followed. In addition, this method can be used with standing wave AP-XPS to gain depth-resolved information about the chemical species in a sample, as demonstrated recently for the electrochemical oxidation of Ni [18]. Alternatively to measuring through a liquid layer, a closed cell containing a liquid electrolyte was developed which is sealed by an ultra-thin Si film, thin enough that hard X-rays irradiated from the vacuum side can probe the solid/liquid interface, which may allow more realistic electrochemical conditions at the interface [19]. This system was used to follow the electrochemical oxidation of Si by applied potential [19]. Developments using graphene and graphene-oxide membranes to seal

such a cell will allow for *operando* measurements of working electrocatalysts in this type of system [20–22].

Other setups used for *operando* XPS analysis of fuel cell electrocatalysts have involved a polymer electrolyte membrane fuel cell (PEMFC) cell configuration with water vapor or liquid inside the cell (counter electrode compartment), the working electrode outside the cell (catalyst facing the irradiated X-rays) in a low pressure water vapor environment, and with a membrane separating the two electrodes [23,25–27]. Using this setup and supporting their experiments with density functional theory (DFT) calculations, Sanchez Casalongue et al. detected the OH intermediate during oxygen reduction reaction (ORR) on the surface of a Pt cathode, and determined that changing the hydration of these OH species could be used to tune the ORR activity, Figure 2b [23]. In another study, they correlated the increase in activity for the hydrogen evolution reaction (HER) of  $\text{MoS}_3$  nanoparticles to the reduction of their

surface to highly active MoS<sub>2</sub> edge sites [25]. Saveleva et al. have used a similar style cell to unravel the role of Ir in stabilizing Ru oxide catalysts for OER [28]. They have also studied Pt-based catalysts in high temperature PEM cells with phosphoric acid loaded membranes. They found that under oxidizing conditions, O/OH species first form on the Pt surface, then at more positive potentials, simultaneous formation of PtO and PtO<sub>2</sub> occurs [29]. Under ORR conditions, they observed the redistribution and migration of phosphoric acid to the Pt surface using AP-XPS [30]. Furthermore, they took advantage of the depth profiling capability of synchrotron XPS to study PtAu NPs under applied positive bias. They proposed that a thin film of Au coats the Pt NPs, then at higher potential, both Pt and Au are oxidized and Pt segregates to the surface, as shown in Figure 2c [24].

### X-ray absorption spectroscopy (XAS)

XAS is a technique that lends itself to measurements under realistic reaction conditions, since unlike XPS, it does not require UHV conditions at the detector, and hard or soft X-rays can be used to probe metal catalyst atoms and adsorbed intermediate reaction species. Extended X-ray absorption fine-structure (EXAFS) spectroscopy can probe the local environment of atoms in a working catalyst (coordination, bond lengths, etc.), while X-ray absorption near-edge structure spectroscopy (XANES) can give information about the chemical state and NP/adsorbate and NP/support charge transfer phenomena. Several groups have used a sandwich-style *operando* cell in which the anode and cathode are parallel with a thin electrolyte layer in between for transmission measurements. One of the challenges of this technique in an electrochemical environment is the absorption and attenuation of the incident beam in liquid. Therefore, measurements of operating solid catalyst/liquid electrolyte interfaces are often performed in fluorescence geometry, with the catalyst supported on an X-ray transparent, conductive film which may also act as the X-ray window, avoiding X-ray attenuation due to the electrolyte. Several recent studies have used *operando* XANES and EXAFS to reveal drastic transformations in the structure and oxidation state of the active electrocatalyst, which were not apparent in their *ex situ* state [2•,31–34••]. Using *operando* XAS, Rosen et al. showed that Zn dendrite CO<sub>2</sub> electroreduction catalysts deactivate at potentials less negative than –0.7 V vs. RHE due to oxidation of Zn at these potentials, Figure 3a [31]. Conversely, for the same reaction, Mistry et al. detected Cu<sup>+</sup> species in an operating plasma-oxidized Cu catalyst, which were critical for improving production of ethylene, Figure 3b [32••]. The active site of Ni–Fe(OOH) catalysts was also unraveled through careful analysis of *operando* high energy resolution fluorescence-detected (HERFD) XANES and EXAFS to be Fe<sup>3+</sup> sites substituted into  $\gamma$ -NiOOH [33]. The transformation of a partially oxidized CoS<sub>x</sub> HER catalyst to active CoS<sub>2</sub>-like clusters was also observed by combining *operando*

XAS (Figure 3c) with complementary *operando* Raman measurements in the same reaction cell [34••].

A limitation of XAS for nanostructured thin film catalysts is that it is a bulk sensitive technique and may not resolve important changes occurring at the catalyst surface which differ from the bulk. However, for small NP catalysts, this is less of a problem, since a higher fraction of atoms which are probed are at the catalyst surface. A good example is a recent study from Choi et al., who used *operando* EXAFS to study size-dependent changes in Au NPs during 2-propanol electrooxidation [2•]. They found that surface oxides were reduced during the reaction, and that there was an increase in NP size due to sintering during the reaction, as shown in Figure 3d, which explained the deactivation of the catalysts. In contrast, many real electrocatalysts are bulk-like films or nanostructures grown on bulk metallic surfaces, which are not optimal for XAS due to self-absorption effects. Catalysts synthesized for *operando* XAS may require altered synthesis methods or alternative support materials to minimize XAS thickness effects, which may not have the same reactivity as the real catalyst. Additional effort is needed in the years to come to develop reactor cells and measurement geometries compatible with the investigation of liquid/solid surfaces for industrially relevant materials.

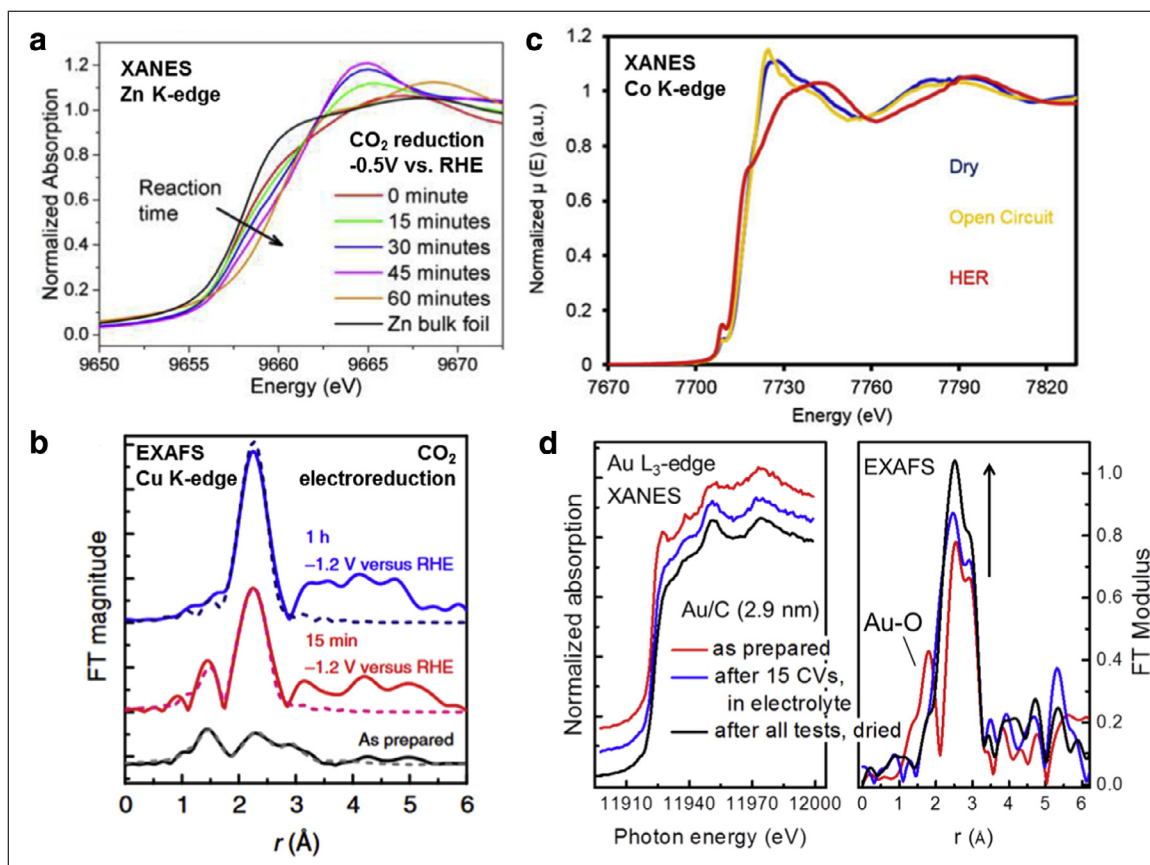
In addition to doing XAS with hard X-rays, soft X-rays have also been used to measure the L and M edges of some metals and also the K edges of lighter elements in catalysts mounted in *operando* liquid cells. Cusinier et al. studied S cathodes in a Li–S coin cell at the S K-edge to unravel the oxidation state of sulfur under electrochemical cycling and the mechanisms behind precipitation and dissolution of S and Li<sub>2</sub>S at the electrode [35]. In order to gain sensitivity to the electrode/electrolyte interface, a new XAS cell has been designed for use in a UHV chamber, in which secondary and Auger electrons from the interface region, which have very short mean free path and therefore are sensitive to the interface, can be collected and measured in total electron yield mode. The cell contains a Si<sub>3</sub>N<sub>4</sub> window which seals the liquid cell to UHV thin enough for incident X-ray penetration and which also serves as a current collector for the emitted photoelectrons of interest. Velasco-Velez et al. have used this setup to unveil the structure of the electrical double layer at the surface of a gold electrode under applied potential [36••].

### Microscopic techniques for the characterization of electrocatalysts

#### Atomic force microscopy (AFM)

AFM is a commonly used technique to characterize the surface morphology of catalysts on flat substrates before and after a reaction. Nevertheless, this technique can be integrated with specially designed electrochemical cells which are now widely available commercially in order to probe catalysts in liquid environments and under poten-

Figure 3



(a) Zn K-edge *operando* XANES of a Zn dendrite catalyst during CO<sub>2</sub> electroreduction [31]. (b) Grazing incidence Cu K-edge EXAFS data of plasma-oxidized Cu films during CO<sub>2</sub> electroreduction [32••]. (c) Co K-edge XANES data measured *operando* on a CoS<sub>x</sub> catalyst during HER [34••]. (d) Au L<sub>3</sub>-edge XANES and EXAFS of 2.9 nm Au nanoparticles before, during and after 2-propanol oxidation [2•]. Each panel is reprinted with permission of refs. [2•, 31, 32••, 34••], respectively.

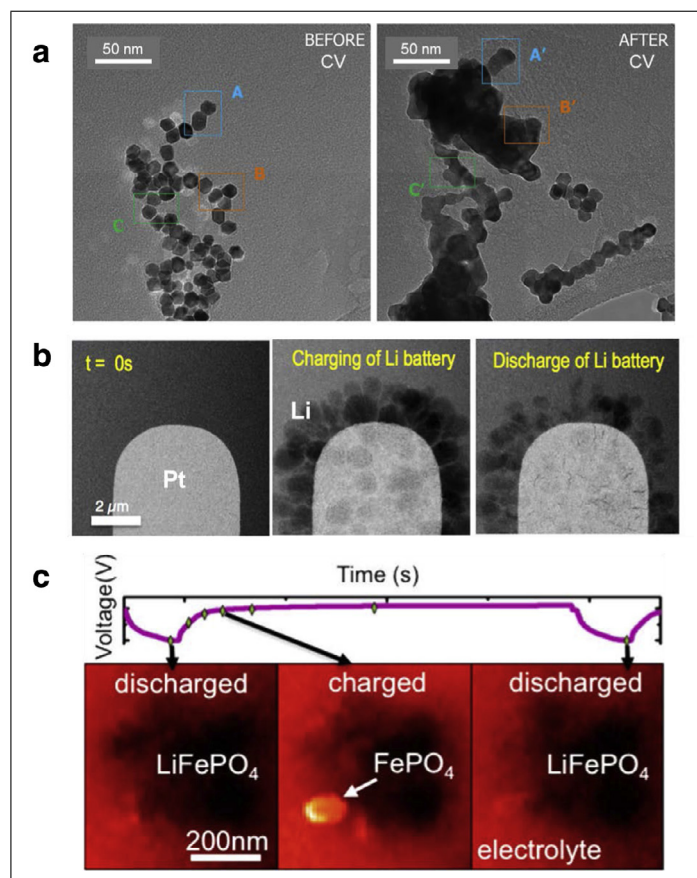
tial control. Such setups have been successfully used to study deposition and stability of electrocatalytic materials. However, it can often be challenging to reach true *operando* conditions during these measurements, due to the small volume of the electrochemical cells and the sensitivity of the AFM probe to reactant or product gas evolution. Since relatively flat substrates are needed to resolve small nanostructures using AFM, *in situ* electrochemical AFM (EC-AFM) studies are often restricted to model systems supported on flat electrodes such as highly oriented pyrolytic graphite (HOPG). In a recent work, Khalakhan et al. studied PtCo ORR films supported on HOPG during cyclic voltammetry (CV) under harsh conditions, finding growth in the particle grain size and decrease in activity with increasing number of cycles from EC-AFM, which was correlated to leaching of Co and Ostwald ripening [37]. EC-AFM has also been widely applied to study Li-based battery electrodes. Liu et al. studied a gold electrode in dimethyl sulfoxide LiClO<sub>4</sub> solution, observing deposition and growth of Li<sub>2</sub>O<sub>2</sub> particles under ORR con-

ditions, and dissolution of the particles under OER conditions [38].

### Scanning tunneling microscopy (STM)

Similar to AFM and STM can be outfitted with electrochemical cells to study the morphology and electronic properties of model surfaces, but with atomic resolution. *Operando* EC-STM measurements may also be restricted to avoid conditions of gas evolution or oxidation of the metal catalyst surface. Kim et al. have studied Cu surfaces for CO<sub>2</sub> electroreduction, finding that polycrystalline copper can reconstruct to different surface facets over time [39]. In another study of a CO<sub>2</sub> electroreduction catalyst, Cu monolayers on Pt(111) were measured under mild potentials in a CO-saturated electrolyte to reveal severe CO-induced reconstructions in the surface [40]. For fuel cell reactions, EC-STM can be extremely useful for following dissolution, degradation, and sintering phenomena of catalysts under potential control. Paoli et al. used EC-STM to show the stability of Ru<sub>2</sub>O particles under OER potentials, in contrast to metallic Ru particles which

Figure 4



(a) TEM image of hexagonal Pt particles before and after 1000 CVs in H<sub>2</sub>SO<sub>4</sub> [45]. (b) High-angle annular dark field (HAADF) TEM images of Li deposition and dissolution on a Pt electrode in LiPF<sub>6</sub>/PC electrolyte [46]. (c) Lithium removal and insertion during charging and discharging of a LiFePO<sub>4</sub> cathode [47]. Each panel is reprinted with permission of refs. [45–47], respectively.

dissolved under reaction conditions [41]. In addition, Ostermayr et al. studied hydrogen electrooxidation (HOR) and HER over Pt islands deposited on Au(111), finding much higher activity for Pt on defect-rich Au(111) [42].

### Transmission electron microscopy (TEM)

Electrochemical transmission electron microscopy (E-TEM) is a technique which promises to bring exciting new insights into the morphological properties of working electrocatalysts. E-TEM is extremely challenging since the system requires UHV, so well-sealed *in situ* liquid cells must be used. In recent years, great progress has been made in the design and commercialization of liquid TEM holders using MEMS technology which feature thin SiN windows and thin electrolyte layers which can be used for *operando* electrochemistry. Electron beam induced damage to the sample and its interaction with the electrolyte can significantly affect E-TEM measurements, and the small volume of the cell and close proximity of the working and counter electrodes can cause inhomogeneities in the electrochemical conditions at the catalyst surface, all

of which add further challenges to these measurements [43]. Despite this, some recent studies have gained interesting insights into electrocatalysts under potential bias using E-TEM. Zhu et al. used a technique known as identical location TEM, in which the same regions of the sample are measured over time, to study changes in Pt–Fe nanoparticles during CV, finding non-uniform coarsening of the particles over time [44]. Arán-Ais et al. also used the identical location TEM to reveal the structural degradation of hexagonal Pt PEMFC catalysts over time after a CV conditioning treatment, as shown in Figure 4a [45]. Other recent studies have focused on battery materials, such as a study by Mehdi et al. who revealed how the image contrast could be used to understand Li deposition on a Pt electrode, its operation during electrochemical cycling, and the subsequent degradation of its structure and performance, shown in Figure 4b [46]. Figure 4c shows the charging and discharging of a LiFePO<sub>4</sub> cathode in a study by Holtz et al., in which the de-lithiation of the cathode can be observed in TEM acquired during charging [47]. An exciting development would be the coupling

of *operando* TEM, a local probe of catalyst structure, with other techniques such as *operando* XAFS, which provides information on the average local structure across the entire sample. Recently, Li et al. have developed a reaction cell for gas phase catalysis which is compatible with both TEM and XAFS measurements, demonstrating how both techniques are necessary to unravel the structural changes in Pt catalyst during ethylene hydrogenation [48]. Development of a multi-functional *operando* electrochemical cell for TEM and XAFS could similarly allow great insight into local and global structural changes in working electrocatalysts.

### X-ray diffraction (XRD)

By employing *operando* XRD, several groups have studied electrode materials, their intermediate phases and effective parameters for Li-ion batteries (LIB) extensively for use in portable applications [49,50]. While the charging/discharging rate of Li ions can significantly affect the performance of LIB, the parameters and mechanism which determine the performance of LIB are still disputed. Through *operando* XRD coupled with EIS, Hess et al. [49] reported that phase separation reduced the electrochemically active surface area by tracking non-equilibrium intermediate phases on LiFePO<sub>4</sub> LIBs. Another reason for limited cell operation is rapid changes of volume and particle fracture during Li-ion charging/discharging. Controlling the composition of alloyed electrode materials containing Li, Sb and Ti could resolve this problem and improve the safety of LIB through tracking of the phase evolution [50]. In addition, Kim et al. [51] introduced the possibility of Na rechargeable batteries as an alternative system to LIB by investigating Na intercalation on graphite, which is widely used as the anode material of LIB. To investigate their operation as batteries with sufficient performance, XRD was used to study Na–O<sub>2</sub> batteries, revealing that humidity of the gas phase can be controlled as a key factor contributing to cell reaction and growth of the electrode crystal [52].

### Concluding remarks

*Operando* analysis can be used to characterize nanostructured electrocatalysts by observing their structural and chemical properties while in their working state, giving phenomenal insight into their mechanistic behavior during important energy conversion processes. While some lab-based techniques, such as Raman and IR spectroscopy, have lent themselves more easily to studying operating electrode/electrolyte interfaces, others such as AP-XPS have required significant technological developments, and further advancements are expected to allow unprecedented breakthroughs in understanding the operating surface of an electrocatalyst. Further insight will also be gained in the years to come by combining multiple analyses in the same setup, such as combining Raman, IR and XAS in the same *operando* cell, and making such cell compatible with microscopy analysis

such as TEM. Finally, as the examples given in this review make clear, insights from theoretical methods are critical for understanding the results and interpreting their mechanistic implications on reactivity. On the basis of these research trends, versatile aspects of nanostructured electrocatalysts can be investigated to gain new understanding into their reactivity.

### References and recommended reading

Papers of particular interest, published within the period of review, have been highlighted as:

- of special interest.
- of outstanding interest.

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### References

1. Tada M, Murata S, Asakoka T, Hiroshima K, Okumura K, Tanida H, Uruga T, Nakanishi H, Matsumoto SI, Inada Y, Nomura M, Iwasawa Y: **In situ time-resolved dynamic surface events on the Pt/C cathode in a fuel cell under operando conditions.** *Angew Chem Int Ed* 2007, **46**:4310–4315.
2. Choi Y, Sinev I, Mistry H, Zegkinoglou I, Roldan Cuenya B:
  - **Probing the dynamic structure and chemical state of Au nanocatalysts during the electrochemical oxidation of 2-propanol.** *ACS Catal* 2016, **6**:3396–3403.
 This study used operando XAFS to follow the reduction of surface oxides on Au nanoparticles and the sintering of the nanoparticles during 2-propanol oxidation.
3. Lira E, Merte LR, Behafarid F, Ono LK, Zhang L, Roldan Cuenya B: **Role and evolution of nanoparticle structure and chemical state during the oxidation of NO over size- and shape-controlled Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts under operando conditions.** *ACS Catal* 2014, **4**:1875–1884.
4. Grunwaldt JD, Wagner JB, Dunin-Borkowski RE: **Imaging catalysts at work: a hierarchical approach from the macro- to the meso- and nano-scale.** *ChemCatChem* 2013, **5**:62–80.
5. Bañares MA: **Operando methodology: combination of in situ spectroscopy and simultaneous activity measurements under catalytic reaction conditions.** *Catal Today* 2005, **100**:71–77.
6. Zandi O, Hamann TW: **Determination of photoelectrochemical**
  - **water oxidation intermediates on hematite electrode surfaces using operando infrared spectroscopy.** *Nat Chem* 2016, **8**:778–783.
 This paper discovered the intermediate species contributing to the photochemical water-oxidation reaction on hematite electrodes through operando IR spectroscopy.
7. Köck E-M, Kogler M, Klötzer B, Noisternig MF, Penner S: **Structural and electrochemical properties of physisorbed and chemisorbed water layers on the ceramic oxides Y<sub>2</sub>O<sub>3</sub>, YSZ, and ZrO<sub>2</sub>.** *ACS Appl Mater Interf* 2016, **8**:16428–16443.
8. Cumming DJ, Tumilson C, Taylor SFR, Chansai S, Call AV, Jacquemin J, Hardacre C, Elder RH: **Development of a diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) cell for the in situ analysis of co-electrolysis in a solid oxide cell.** *Faraday Discuss* 2015, **182**:97–111.
9. Nayak S, Erbe A: **Mechanism of the potential-triggered surface transformation of germanium in acidic medium studied by ATR-IR spectroscopy.** *Phys Chem Chem Phys* 2016, **100**:25100–25109.

10. Dutta A, Kuzume A, Rahaman M, Veszteg S, Broekmann P:  
 • **Monitoring the chemical state of catalysts for CO<sub>2</sub> electroreduction: an in operando study.** *ACS Catal* 2015, **5**:7498–7502.
- By changing the pH and electrode potential, a correlation between the oxidation state of SnO<sub>2</sub> electrodes and their Faradaic efficiency for CO<sub>2</sub> electroreduction towards formate was revealed.
11. Louvain N, Henry A, Daenens L, Boury B, Stievano L, Monconduit L: **On the electrochemical encounter between sodium and mesoporous anatase TiO<sub>2</sub> as a Na-ion electrode.** *CrystEngComm* 2016, **18**:4431–4437.
12. Li X, Liu M, Lee J, Ding D, Bottomley LA, Park S, Liu M: **An operando surface enhanced Raman spectroscopy (SERS) study of carbon deposition on SOFC anodes.** *Phys Chem Chem Phys* 2015, **17**:21112–21119.
13. Chen JYC, Dang L, Liang H, Bi W, Gerken JB, Jin S, Alp EE, Stahl SS: **Operando analysis of NiFe and Fe oxyhydroxide electrocatalysts for water oxidation: detection of Fe<sup>4+</sup> by Mössbauer spectroscopy.** *J Am Chem Soc* 2015, **137**:15090–15093.
14. Starr DE, Liu Z, Hävecker M, Knop-Gericke A, Bluhm H: **Investigation of solid/vapor interfaces using ambient pressure X-ray photoelectron spectroscopy.** *Chem Soc Rev* 2013, **42**:5833–5857.
15. Frank Ogletree D, Bluhm H, Hebenstreit ED, Salmeron M: **Photoelectron spectroscopy under ambient pressure and temperature conditions.** *Nucl Instrum Methods Phys Res Sect A Accel Spectrom Detect Assoc Equip* 2009, **601**:151–160.
16. Axnanda S, Crumlin EJ, Mao B, Rani S, Chang R, Karlsson PG, Edwards MOM, Lundqvist M, Moberg R, Ross P, Hussain Z, Liu Z: **Using “Tender” X-ray ambient pressure X-ray photoelectron spectroscopy as a direct probe of solid-liquid interface.** *Sci Rep* 2015, **5**:9788.
17. Ali-Löyty H, Louie MW, Singh MR, Li L, Sanchez Casalongue HG, Ogasawara H, Crumlin EJ, Liu Z, Bell AT, Nilsson A, Friebe D: **Ambient-pressure XPS study of a Ni-Fe electrocatalyst for the oxygen evolution reaction.** *J Phys Chem C* 2016, **120**:2247–2253.
18. Karslioglu O, Nemsak S, Zegkinoglou I, Shavorskiy A, Hartl M, Salmassi F, Gullikson E, Ng M-L, Rameshan C, Rude B, Bianculli D, Cordones-Hahn A, Axnanda S, Crumlin E, Ross PN, Schneider CM, Hussain Z, Liu Z, Fadley CS, Bluhm H: **Aqueous solution/metal interfaces investigated in operando by photoelectron spectroscopy.** *Faraday Discuss* 2015, **180**:1–19.
19. Masuda T, Yoshikawa H, Noguchi H, Kawasaki T, Kobata M, Kobayashi K, Uosaki K: **In situ X-ray photoelectron spectroscopy for electrochemical reactions in ordinary solvents.** *Appl Phys Lett*, vol 103 2013 111605.
20. Kraus J, Reichelt R, Günther S, Gregoratti L, Amati M, Kiskinova M, Yulaev A, Vlassiok I, Kolmakov A: **Photoelectron spectroscopy of wet and gaseous samples through graphene membranes.** *Nanoscale* 2014, **6**:14394–14403.
21. Wu CH, Weatherup RS, Salmeron MB: **Probing electrode/electrolyte interfaces in situ by X-ray spectroscopies: old methods, new tricks.** *Phys Chem Chem Phys* 2015, **17**:30229–30239.
22. Weatherup RS, Eren B, Hao Y, Bluhm H, Salmeron MB: **Graphene membranes for atmospheric pressure photoelectron spectroscopy.** *J Phys Chem Lett* 2016, **7**:1622–1627.
23. Casalongue HS, Kaya S, Viswanathan V, Miller DJ, Friebe D, Hansen HA, Nørskov JK, Nilsson A, Ogasawara H: **Direct observation of the oxygenated species during oxygen reduction on a platinum fuel cell cathode.** *Nat Commun* 2013, **4**:2817.
24. Papaefthimiou V, Diebold M, Ulhaq-Bouillet C, Doh WH, Blume R, Zafeiratos S, Savinova ER: **Potential-induced segregation phenomena in bimetallic PtAu nanoparticles: an in situ near-ambient-pressure photoelectron spectroscopy study.** *ChemElectroChem* 2015, **2**:1519–1526.
25. Casalongue HGS, Benck JD, Tsai C, Karlsson RKB, Kaya S, Ng ML, Pettersson LGM, Abild-Pedersen F, Nørskov JK, Ogasawara H, Jaramillo TF, Nilsson A: **Operando characterization of an amorphous molybdenum sulfide nanoparticle catalyst during the hydrogen evolution reaction.** *J Phys Chem C* 2014, **118**:29252–29259.
26. Sanchez Casalongue HG, Ng ML, Kaya S, Friebe D, Ogasawara H, Nilsson A: **In situ observation of surface species on iridium oxide nanoparticles during the oxygen evolution reaction.** *Angew Chem Int Ed Engl* 2014, **53**:7169–7172.
27. Arrigo R, Hävecker M, Schuster ME, Ranjan C, Stotz E, Knop-Gericke A, Schlögl R: **In situ study of the gas-phase electrolysis of water on platinum by NAP-XPS.** *Angew Chem Int Ed* 2013, **52**:11660–11664.
28. Saveleva VA, Wang L, Luo W, Zafeiratos S, Ulhaq-Bouillet C, Gago AS, Friedrich KA, Savinova ER: **Uncovering the stabilization mechanism in bimetallic ruthenium-iridium anodes for proton exchange membrane electrolyzers.** *J Phys Chem Lett* 2016, **7**:3240–3245.
29. Saveleva VA, Papaefthimiou V, Daletou MK, Doh WH, Ulhaq-Bouillet C, Diebold M, Zafeiratos S, Savinova ER: **Operando near ambient pressure XPS (NAP-XPS) study of the Pt electrochemical oxidation in H<sub>2</sub>O and H<sub>2</sub>O/O<sub>2</sub> ambients.** *J Phys Chem C* 2016, **120**:15930–15940.
30. Law YT, Zafeiratos S, Neophytides SG, Orfanidi A, Costa D, Dintzer T, Arrigo R, Knop-Gericke A, Schlögl R, Savinova ER: **In situ investigation of dissociation and migration phenomena at the Pt/electrolyte interface of an electrochemical cell.** *Chem Sci* 2015, **6**:5635–5642.
31. Rosen J, Hutchings GS, Lu Q, Forest RV, Moore A, Jiao F: **Electrodeposited Zn dendrites with enhanced CO selectivity for electrocatalytic CO<sub>2</sub> reduction.** *ACS Catal* 2015, **5**:4586–4591.
32. Mistry H, Varela AS, Bonifacio CS, Zegkinoglou I, Sinev I, Choi Y-W, Kisslinger K, Stach EA, Yang JC, Strasser P, Roldan Cuenya B: **Highly selective plasma-activated copper catalysts for carbon dioxide reduction to ethylene.** *Nat Commun*, vol 7 2016 12123 This study used operando EXAFS, combined with other ex situ characterization techniques, to discover cationic Cu<sup>+</sup> species and subsurface oxygen which were found to strongly affect the selectivity of plasma-oxidized Cu films during CO<sub>2</sub> electroreduction.
33. Friebe D, Louie MW, Bajdich M, Sanwald KE, Cai Y, Wise AM, Cheng MJ, Sokaras D, Weng TC, Alonso-Mori R, Davis RC, Bargar JR, Nørskov JK, Nilsson A, Bell AT: **Identification of highly active Fe sites in (Ni,Fe)OOH for electrocatalytic water splitting.** *J Am Chem Soc* 2015, **137**:1305–1313.
34. Kornienko N, Resasco J, Becknell N, Jiang CM, Liu YS, Nie K, Sun X, Guo J, Leone SR, Yang P: **Operando spectroscopic analysis of an amorphous cobalt sulfide hydrogen evolution electrocatalyst.** *J Am Chem Soc*, vol 137 2015 7448–7455 This study used operando Raman spectroscopy and XAFS in the same electrochemical cell to unravel the chemical and structural changes occurring in an operating CoS<sub>x</sub> HER catalyst. This is an example of how two operando techniques can be used to study the same system under realistic electrochemical conditions, giving phenomenal insight into the catalyst active site.
35. Cuisinier M, Cabelgouen PE, Evers S, He G, Kolbeck M, Garsuch A, Bolin T, Balasubramanian M, Nazar LF: **Sulfur speciation in Li-S batteries determined by operando X-ray absorption spectroscopy.** *J Phys Chem Lett* 2013, **4**:3227–3232.
36. Velasco-Velez J-J, Wu CH, Pascal TA, Wan LF, Guo J, Prendergast D, Salmeron M: **The structure of interfacial water on gold electrodes studied by X-ray absorption spectroscopy.** *Science* 2014, **346**(80):831–834.
- This study revealed the structure of water molecules at the surface of a gold electrode under potential control using soft X-ray absorption spectroscopy.
37. Khalakhan I, Vorokhta M, Václavů M, Šmíd B, Lavková J, Matolinová I, Fiala R, Tsud N, Skála T, Matolín V: **In-situ electrochemical atomic force microscopy study of aging of magnetron sputtered Pt-Co nanoalloy thin films during accelerated degradation test.** *Electrochim Acta* 2016, **211**:52–58.



38. Liu C, Ye S: **In situ atomic force microscopy (AFM) study of oxygen reduction reaction on a gold electrode surface in a dimethyl sulfoxide (DMSO) based electrolyte solution.** *J Phys Chem C* 2016, **120**:25246–25255.
39. Kim YG, Baricuatro JH, Javier A, Gregoire JM, Soriaga MP: **The evolution of the polycrystalline copper surface, first to Cu(111) and then to Cu(100), at a fixed CO<sub>2</sub>RR potential: a study by operando EC-STM.** *Langmuir* 2014, **30**:15053–15056.
40. Varela AS, Schlaup C, Jovanov ZP, Malacrida P, Horch S, Stephens IEL, Chorkendorff I: **CO<sub>2</sub> electroreduction on well-defined bimetallic surfaces: Cu overlayers on Pt(111) and Pt(211).** *J Phys Chem C* 2013, **117**:20500–20508.
41. Paoli EA, Masini F, Frydendal R, Deiana D, Schlaup C, Malizia M, Hansen TW, Horch S, Stephens IEL, Chorkendorff I: **Oxygen evolution on well-characterized mass-selected Ru and RuO<sub>2</sub> nanoparticles.** *Chem Sci* 2015, **6**:190–196.
42. Ostermayr C, Stimming U: **Electrocatalytic activity of platinum submonolayers on defect-rich Au(111).** *Surf Sci* 2015, **631**:229–234.
43. Hodnik N, Dehm G, Mayrhofer KJJ: **Importance and challenges of electrochemical *in situ* liquid cell electron microscopy for energy conversion research.** *Acc Chem Res* 2016, **49**:2015–2022.
44. Zhu G-Z, Prabhudev S, Yang J, Gabardo CM, a Botton G, Soleymani L: **In situ liquid cell TEM study of morphological evolution and degradation of Pt–Fe nanocatalysts during potential cycling.** *J Phys Chem C* 2014, **118**:22111–22119.
45. Arán-Ais RM, Yu Y, Hovden R, Solla-Gullón J, Herrero E, Feliu JM, Abruña HD: **Identical location transmission electron microscopy imaging of site-selective Pt nanocatalysts: electrochemical activation and surface disordering.** *J Am Chem Soc* 2015, **137**:14992–14998.
46. Mehdi BL, Qian J, Nasybulin E, Park C, Welch DA, Faller R, Mehta H, Henderson WA, Xu W, Wang CM, Evans JE, Liu J, Zhang JG, Mueller KT, Browning ND: **Observation and quantification of nanoscale processes in lithium batteries by operando electrochemical (S)TEM.** *Nano Lett* 2015, **15**:2168–2173.
47. Holtz ME, Yu Y, Gunceler D, Gao J, Sundararaman R, Schwarz KA, Arias TA, Abruña HD, Muller DA: **Nanoscale imaging of lithium ion distribution during in situ operation of battery electrode and electrolyte.** *Nano Lett* 2014, **14**:1453–1459.
48. Li Y, Zakharov D, Zhao S, Tappero R, Jung U, Elsen A, Baumann P, Nuzzo RG, Stach EA, Frenkel AI: **Complex structural dynamics of nanocatalysts revealed in operando conditions by correlated imaging and spectroscopy probes.** *Nat Commun* 2015, **6**:7583.
49. Hess M, Sasaki T, Villevieille C, Novák P: **Combined operando X-ray diffraction–electrochemical impedance spectroscopy detecting solid solution reactions of LiFePO<sub>4</sub> in batteries.** *Nat Commun* 2015, **6**:8169.
50. Villevieille C, Ebner M, Gómez-Cámer JL, Marone F, Novák P, Wood V: **Influence of conversion material morphology on electrochemistry studied with operando X-ray tomography and diffraction.** *Adv Mater* 2015, **27**:1676–1681.
51. Kim H, Hong J, Yoon G, Kim H, Park K-Y, Park M-S, Yoon W-S, Kang K: **Sodium intercalation chemistry in graphite.** *Energy Environ Sci* 2015, **8**:2963–2969.
52. Pinedo R, Weber DA, Bergner B, Schröder D, Adelhelm P, Janek J: **Insights into the chemical nature and formation mechanisms of discharge products in Na–O<sub>2</sub> batteries by means of operando X-ray diffraction.** *J Phys Chem C* 2016, **120**:8472–8481.