REVIEW

The EQCM: electrogravimetry with a light touch

A. Robert Hillman

Abstract In its simplest manifestation, the electrochemical quartz crystal microbalance (EQCM) is a relatively new device for executing a classical technique, electrogravimetry. The advantages it brought were in situ applicability (notwithstanding prior misconceptions regarding damping by a contacting fluid), exceptional sensitivity and dynamic capability, thereby permitting real-time monitoring of changes in surface populations of species during electrochemically driven processes. The basis of the method relies on the storage and dissipation of energy injected into the interfacial region by a high frequency (megahertz) acoustic wave; the latter is generated by a piezoelectric (generally quartz) resonator. From modest early aspirations, largely associated with the deposition/dissolution of simple adsorbates and thin metal films, the technique has expanded in three strategic respects: materials, phenomena and methodology. In the first instance, extension to thick electroactive films (notably metal oxides and polymers) has generated considerable insight. Second, the sensitivity of the EQCM to viscoelastic phenomena, stress and interfacial slip has been recognized. Considerable attention has been given to viscoelastic processes in redox and conducting polymers: these have been parameterized in terms of shear moduli, whose variation with polymer structure and imposed conditions provides insight into polymer dynamics. Procedures exist for characterizing film stress in harder materials, but this is less well exploited. Interfacial slip remains a poorly understood area. Third, application in the context of diverse electrochemical control functions and integration with other in situ techniques provide many as yet unexploited opportunities. The extent to which these are realised will probably depend on the level of interpretation of the resultant data, which presently underuses the library of modelling protocols available.

Concept and context

The quartz crystal microbalance (QCM) is one of a family of acoustic wave devices [1] based on piezoelectric resonators whose frequency responses are sensitive to the nature of the contacting environment, whether this be a fluid, a surface film or some interaction between these two. The particular attribute—not universal amongst high frequency acoustic wave devices—that has made the QCM such a major contributor to electrochemical science is its ability to operate in situ (i.e. in a liquid medium) with one of its electrodes under electrochemical potential control. The notable feature from a historical perspective is the startling rate of

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integration of the technique into electrochemistry: the technique has gone from inception to acceptance—or, in the phraseology of the hype cycle (see below), from technology trigger to the plateau of productivity—in an unusually short time. In sharp contrast to the development of classical electrogravimetry, as discussed in a related article in this issue [2], it has only taken approximately three decades since its inception for the electrochemical variant of the QCM (the EQCM) to become such an established part of the electrochemist's armoury of techniques that its use is often not overtly expressed through the titles or keywords of research articles. From the perspective of any review, this has two immediate consequences. First, any literature search inevitably underestimates its significance. Second, rather than a linear development of the methodology and its application to complex chemical and physical systems, there have been parallel pursuits of fundamental and applied aspects. This has the interesting feature of methodological development both providing the opportunity for new insights and being driven by demand for them.

Looking back, the decade in which it first appeared, the 1980s, was one in which a number of chemical and structural probes were either conceived or technically enhanced to the point where they could be used in situ for electrochemical purposes. It is therefore reasonable to ask why the EQCM should have had such impact. The answers are rather simple. First, like any other gravimetric probe, it has universal sensitivity: everything weighs something. Second, there is an unambiguous (and commonly trivial) relationship between the measured quantity and the change in surface population. The absolute nature of the assay (based on molar mass) contrasts with that of many spectroscopic probes, for which such factors as solvent, presence of a field or molecular orientation can influence the response. Third, the technique is accessible to all in economic, technological and interpretational terms. In this respect, there may be occasions when non-specialist application results in under-exploitation of the capability of the technique, but it does lead to enrichment of the literature through application of the EQCM to more exotic chemical systems.

Given the long-standing availability of electrogravimetric methods, it is worth asking how long the EQCM's arrival had been anticipated. This is neatly addressed by a quote from Lingane [3]: "Imagine how much more rapid and convenient electrogravimetric determinations would be if some means could be devised to weigh the metal deposit precisely without removing, washing and drying the cathode". It is the goal of this article to see how and to what extent this dream has been realised. In this respect, like any good reporter, the author had the fortuitous advantage of being in the right place at the right time: a sabbatical period in the laboratory that generated one of the most highly cited EQCM publications [4] and laboratory interaction with the student who made the relevant measurements.

Historical perspective

In electrochemistry and, more widely, analytical chemistry, there is a long history of gravimetric methods [5, 6]. The underlying reasons are that the method is absolute (requires no calibration), is generic (everything weighs something), does not suffer from matrix or environmental effects (in contrast to the vulnerability of many spectroscopic methods to variable sensitivity factors) and is very directly interpretable. Put simply, the facility to weigh a sample provides a very direct route to the amount of a substance that is present: knowledge of the sample composition and molar mass immediately yields the number of moles.

The classic experiment of Michael Faraday involving the electrolysis of a solution of a silver salt and comparison of the mass of elemental silver deposited with the charge passed provides an early quantitative example; the continuing relevance of Faraday as a role model in correlating the data will be made later. In the early part of the twentieth century, the development of electrogravimetric methods for the determination of a range of metals provides further evidence of the value of being able to weigh an electrode before and after executing an electrodeposition process [2, 3, 5, 6]. Generally, in this latter example, the charge passed is not used in the assay—the requirement is the absence of co-deposition processes—and one simply determines the mass (number of moles) of analyte present in a known volume of solution. Nevertheless, the concept of driving an electrochemical reaction and measuring the mass of a film deposited on the electrode is still present.

Moving to the last two decades of the twentieth century, one sees an explosion of research activity and published work on electrode surfaces modified with thin films, where "thin" in this context indicates a film ranging from nanometre (essentially monolayer) to micrometre in thickness. It is not the purpose of this article to review this well-documented area [7, 8], but simply to note that almost every conceivable type of material has been used in this context including, but not restricted to, metals (pure and alloyed), metal (hydr)oxides, inorganic complexes, redox polymers, conducting polymers, insulating polymers, self-assembled monolayers and a range of "host" materials from calixarenes and dendrimers to antibody–antigen systems. Dependent on the application in view, one may seek to harness the (bio)chemical, electrical, optical or other properties of the surface-bound species. Inevitably, whether in pursuit of fundamental insights or device performance, one requires some correlation of observed physicochemical effect with the surface population of species generating that

effect. In principle, gravimetry holds the promise of direct assay of the latter.

Three challenges emerge from the above aspirations. First, how can one get the desired sensitivity? Second, since the majority of interesting phenomena are based on controlling the relevant process and/or its rate via the applied potential, can one make the measurements in situ? Third, given that many practical devices involve the imposition of some change, i.e. a switching process, can one make the measurements dynamically? To summarize the challenge three decades ago, how can one measure surface population changes at the nanogram level under water (more generally, solvent) at sub-second intervals?

The first of these challenges had been successfully addressed in the 1950s through the development of the QCM—frequently referred to as a thickness monitor—widely used in diverse gas phase deposition processes. The concept here was to use a piezoelectric quartz resonator and exploit the sensitivity of its resonant frequency to the inertial mass of the system, i.e. the resonator and any accumulated surface loading. The underlying technology had been widely used in a range of oscillators, frequency control/timing applications and radio devices, so the physics was generally well understood [9]. However, it was "well known" that the presence of a contacting liquid would so severely damp the oscillation of the crystal as to prevent its oscillation or, at least, render it sufficiently weak to preclude reliable measurement of its frequency. This would appear to have been fatal for in situ application of the QCM and indeed, had this widely known fact been universally known and accepted, an entire field of endeavour would not have existed and this article would cease at this point.

The fortunate situation is that several groups of researchers in the 1980s were undeterred by this perceived wisdom. In 1978, Glassford [10] made some approximate calculations for the effect of liquid droplets or a liquid film on the surface of a QCM resonator, of the type commonly used for monitoring deposition from the gas phase. The declared goal was not the derivation of a quantitative theory for the response to a liquid per se, but rather the relative effect of a deformable liquid rather than a rigid solid film on the resonator surface. While the paper is candid about the use of some apparently sweeping assumptions in the theoretical analysis, the possibility of operation in the presence of a contacting liquid is clearly envisaged. The model arrives at the prediction that damping will be significant but the experimental observation (for the oscillator system used) was that higher liquid loading only precludes oscillation of the quartz crystal above a certain point. With the benefit of history, it is interesting to see in this early study—which was not at all aimed at an electrochemical audience—the presence of some central

tenets of the fundamentals of the EQCM technique: the concept of equal resonator and liquid velocity at the interface (now expressed as the "no slip" condition); a viscosity-dependent decay length in the fluid, in turn leading to an independence of response to the amount of fluid present beyond a thickness about twice the acoustic decay length; and the effect of damping on the resonant frequency.

Whether or not one argues cause and effect, the fact is that a short time later, there appeared a report of the piezoelectric detection of Ag deposition [11] and then the first description of practical circuitry for use of a QCM with one electrode contacted by an electrolyte solution and subject to an electrochemical control function [4]. The description by Bruckenstein and Shay of this methodology and exploration of its capability as an EQCM has now become a citation classic. From the perspective of development of the field and exploitation of the attributes of the EQCM, it had the important feature of providing practical details that made the technique accessible to all on both technical and economic bases, features not universally true of interfacial characterization techniques, notably many spectroscopies.

The consequences of these attributes can be seen in the dramatic expansion of the literature for the QCM and EQCM techniques. It is interesting to point out that, although some early reviews appeared [12–17] in response to the growth of the EQCM, approximately three quarters of the published work using the technique has appeared since the year 2000. In reality, this may be an underestimate, since the technique is now routinely used by many goal-oriented researchers for whom the methodology is of lesser importance and not cited in keyword listings. One might also argue that it is not the volume of published work that is important, but rather its impact. There are numerous measures of this—and no doubt the bibliometricians could write a review on their relative merits—but citations provide a simple, if crude, impression. The approximately 2,800 published outputs in which EQCM is sufficiently central to be a keyword have attracted ca. 49,600 citations to date. The current annual citation rate is ca. 6,000. That the EQCM has made an impact on electrochemical science cannot be in doubt.

It is also interesting to note that the number of QCM papers prior to the appearance of the EQCM was relatively small, with the QCM simply being an established enabling technology, but the development of the EQCM has stimulated non-electrochemical exploitation of the basic methodology, whether in situ or ex situ. This is evidenced by the fact that the numbers of QCM and EQCM publications rise in parallel. This highlights the fact that the development of the QCM for the electrochemical "market" has had the effect of generating many applications

involving liquid systems in the absence of electrochemistry; biological [18], biosensing [19] and biomedical [20] applications illustrate the point.

Attributes

Having noted that the EQCM has been widely used by the electrochemical community, it is worthwhile assessing the attributes that triggered this. At its simplest, the EQCM (like its QCM parent) is an absolute interfacial gravimetric probe of generic nature and exceptionally high sensitivity. In its early phase, this was how the technique was exploited, although in fact (for reasons that will shortly emerge) the selection of conceptually simple processes such as oxide monolayer formation on noble metal surfaces (Au) leads to technically rather demanding experiments [21]. In overview, the universality of detection brought about by the fact that everything weighs something is hugely attractive: one does not require a chromophore/fluorophore as, for example, is necessary in spectroscopic measurements. It is also the case that possession of (or change in) charge is not required for observation of a species. These features make the technique sensitive to the entrapment (whether on physical or chemical grounds) of solvent in surface films or surface features. The facility to "see" a species that has been carefully selected to be invisible in electrochemical and spectroscopic terms has certain attractions, but carries the penalty that it is another unknown component in the overall observed response. This is of course the downside of universal detection, namely absence of selectivity. The other interesting feature is that charge passage may often involve the movement of protons, which will contribute negligibly to a gravimetrically based response. This has been likened to "the curious case of the dog that did not bark in the night", in which the fictional detective Sherlock Holmes [22] notes that the absence of a response can be a unique indicator of the culprit.

In an era when superlatives dominate, the drive to ever greater sensitivity of detection is easily understood. However, the reality is that the ability to measure frequency changes on the order of 1 Hz about an operating frequency on the order of 10 MHz (quantified below) provides the opportunity to measure short-term surface mass changes on the order of 1 ng (without taking particular precautions for temperature control). Dependent on the species involved, i.e. molar mass and/or molecular geometry, this corresponds to ca. 10 pmol or 1–2% of a monolayer. Even for a monolayer system, this is more than adequate sensitivity, since any practically interesting or useful system will harness chemistry that involves at least this level of change. It is worth noting that, when the usual uncertainties about background corrections are taken into consideration, the practical sensitivity of

many coulometric assays is ca. 1 µC, which also corresponds to ca. 10 pmol; thus the sensitivities of the two components of the EQCM signal are well matched. For multilayer systems, most commonly studied in the form of polymeric materials, the surface population (and changes therein) and the charge associated with them will be correspondingly larger.

These considerations show that, although greater sensitivity is never without value, this is a problem that was solved essentially from the outset for the EQCM. Instead, the challenges—and opportunities—generally arise from other attributes of the EQCM. Classic examples include responses to other physical parameters such as temperature, fluid density and viscosity, viscoelastic phenomena and mismatch of acoustic impedance between the resonator and the surface film.

The issue of temperature sensitivity seems to be commonly misinterpreted. It is certainly true [9] that the QCM resonant frequency is temperature dependent. However, for the most commonly used resonators using the so-called AT cut of the quartz crystal, the variation of resonant frequency with temperature is relatively small around 25 °C, the temperature at which most electrochemical measurements are made. In contrast, the variations in fluid viscosity and density, which in turn determine the amount of viscously coupled fluid (the decay length) and the density of that layer, result in rather larger variations in the effectively coupled mass of fluid. Thus, temperature fluctuations result in a moving "baseline" on which the electrochemically driven interfacial changes are measured. To give some perspective of scale, the frequency change associated with immersion of a smooth crystal in a typical aqueous solution is on the order of 3 kHz, so a 1% change due to fluid viscosity and/or density changes would generate a ca. 30 Hz change in resonant frequency, which is more than an order of magnitude larger than the intrinsic sensitivity of the EQCM. A way out of this problem, though not widely exploited, is the dual crystal method in which the "reference" resonator is exposed to the same solution, such that the difference in crystal resonant frequencies automatically compensates for variations in liquid density and viscosity [23].

Considering the EQCM as an analytical tool, even if the application is not explicitly analytical in nature, the other critical attribute is selectivity. This is readily described: there is none. One cannot a priori distinguish between a small population change of a heavy species and a large population change of a light species. All the selectivity has to be generated by other means, notably via applied potential to drive reactions selectively, by selective chemistry (for example, through suitable host–guest or antibody–antigen chemistry) or by physical "sieving" (for example, based on charge type or some combination of molecular size and geometry).

Principles

In a historical, rather than overtly technical, review of the kind presented here, detailed exposition of the physical principles and their mathematical description are not the focus of attention; these are described in a number of reviews and specialist articles [12–17]. Nonetheless, some brief coverage of the principles is helpful to understand how these have guided the development and exploitation of the technique.

The quartz crystals used in the EQCM are generally of the so-called AT-cut type (although other cuts may be used; see below) and oscillate in the *thickness shear mode* (TSM); consequently, they are frequently referred to as TSM resonators. This mode of oscillation, with motion parallel to the electrode surface, is illustrated in Fig. 1a. The general assumption made is that the material immediately contacting the exciting electrode (commonly, but not always, Au) moves synchronously with the surface; this is the *no-slip condition*, shown schematically in Fig. 1b. A rigid material deposited on the surface also moves synchronously (across its entire width) with the electrode. As a first approximation, one can then treat the loading (the surface film) as an extension of the quartz resonator, with the result that the resonant frequency changes linearly with film thickness. This is the basis of the well-known Sauerbrey equation [24] relating the quartz crystal resonant frequency change (Δf/Hz) arising from the mass change per unit area (ΔM/g cm^{-2}) associated with a spatially uniform surface attached film:

$$\Delta f = -\left(\frac{2}{\rho_q v_q}\right) f_0^2 \Delta M = -S \Delta M \qquad (1)$$

where ρ_q is the density of quartz, v_q is the velocity of the acoustic wave in quartz and f_0 is the resonant frequency of the unloaded crystal; the minus sign signifies the fact that an increase in mass (i.e. an increase in film thickness) leads to an increase in wavelength and thus a decrease in frequency. For a 10 MHz resonator, the constant $S = 4.426 \times 10^{-9}$ g cm^{-2} Hz^{-1}. For a typical electrode area of 0.22 cm^2, this gives the convenient rule of thumb that a 1-Hz frequency change is generated by a surface mass change of ca. 1.1 ng. This is the basis of the traditional QCM "thickness monitor" for deposition from the gas phase. The linear approximation fails when the film thickness can no longer be regarded as small compared to the quartz resonator thickness, since equating the acoustic properties of the film with those of quartz is no longer tenable. For a 10 MHz TSM resonator, the quartz wafer thickness is 166 μm, so films of thickness 2 μm or less readily satisfy this constraint; above this, the effect may be

minimal or significant, dependent on material properties, but for most practical purposes it can be ignored [9].

The presence of the liquid introduces another "layer" to the system [25]. In the simplest case (see Fig. 1c) of a smooth resonator (in practice, surface roughness of physical dimension much less than acoustic decay length in the liquid) exposed to a liquid at perfectly maintained temperature, the end result is simply a shift in resonant frequency "baseline" by an amount corresponding to the mass of the viscously coupled fluid layer. Early work by Kanazawa [26] showed that the effective coupling of fluid was described by a liquid layer of thickness:

$$x_L = \left(\frac{\eta_L}{\pi \rho_L f_0}\right)^{1/2} = \left(\frac{2 v_L}{\omega}\right)^{1/2} \qquad (2)$$

where η_L is the liquid viscosity, $v_L = \eta_L / \rho_L$ is its kinematic viscosity and $\omega = 2\pi f_0$ is the angular frequency of the resonator. For a typical (aqueous) fluid at $f_0 = 10$ MHz, $x_L \sim 180$ nm. The "smoothness" criterion thus becomes the absence of surface roughness features larger than ca. 20 nm. In practice, this is not too problematical, since liquid trapped within such surface "valleys" cannot move freely in a lateral direction so, although obviously not an intrinsically rigid material, it behaves as though it were. This situation is shown schematically in Fig. 1d, representing any rigidly coupled mass on a resonator immersed in solution. The end result is an additional baseline shift determined by the volume of trapped fluid (valley depth and aspect ratio) and its density. Thus, to a good approximation, although the fluid damps the oscillation through the viscous dissipation of energy, the in situ EQCM functions essentially as the ex situ QCM. This issue has been explored at varying levels of complexity, from a simplistic gravimetric approach [14], through one considering variable fluid entrapment and surface energetics [27], to a full fluid dynamics treatment [28, 29]. The damping (dissipation) effects associated with surface roughness have been explored experimentally using acoustic admittance spectra [30].

The requirement for the potential of the (E)QCM to be realised in the above situation is a suitable oscillator system. The type of circuit originally described by Bruckenstein [4] has the practical advantages of being battery powered—thereby removing issues associated with ground loops resulting from connecting the working electrode to two sets of control circuitry (electrochemical and piezoelectric)—and of delivering a simple voltage output (from a frequency-to-voltage convertor) that can be stored in parallel with the electrochemical signal. Although not often exploited, such a device has the advantage of portability. Alternatives of a more sophisticated nature are

Fig. 1 Cartoon representations of motions of a TSM resonator and loading(s) under various conditions: **a** unloaded, in air; **b** loaded with a rigidly coupled mass, in air; **c** immersed in a liquid; **d** loaded with a rigidly coupled mass, immersed in a liquid; **e** loaded with a visco-elastic film, in air; **f** loaded with a viscoelastic film, immersed in a liquid
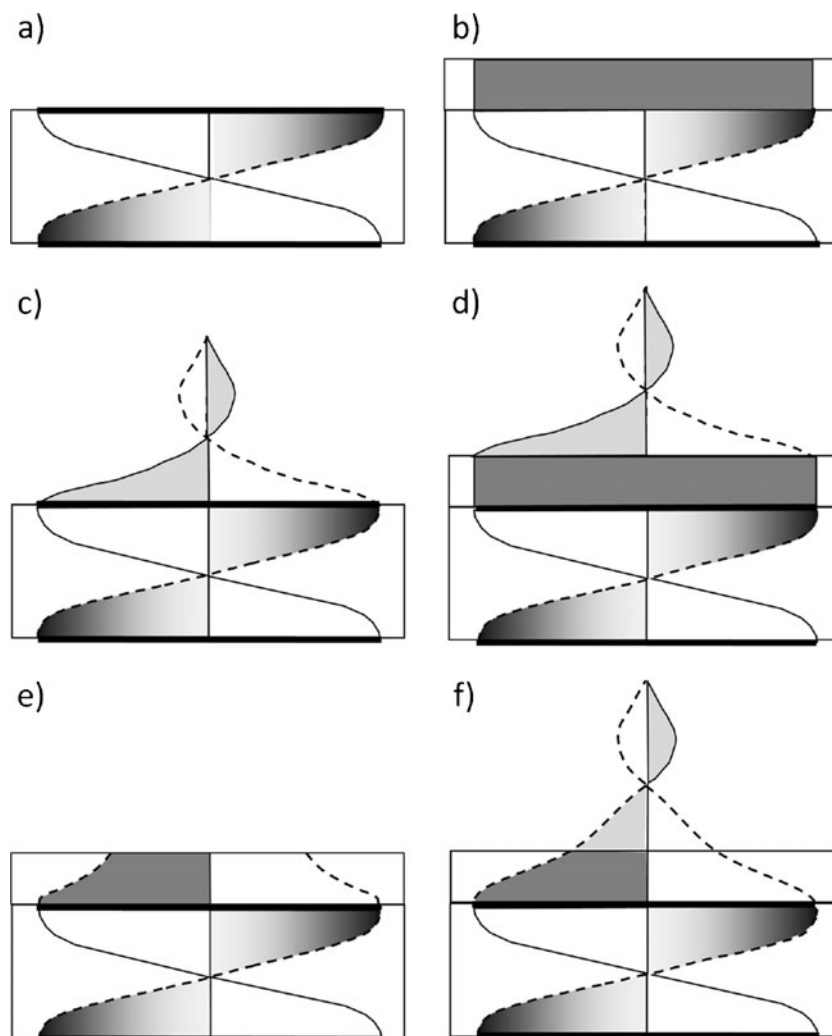
network analyzers and relaxation methods, in which the crystal is actively driven by the input of sufficient energy to overcome the damping effect. Both these latter types of device also permit the measurement of damping (in somewhat different ways) and the mechanical energy they input to the system may in fact be necessary for highly viscous liquids or for films that do not satisfy the rigidity criterion, as discussed below.

Complications and opportunities

With the benefit of hindsight it is interesting to see how different triggers and impediments have contributed to the development of the EQCM. In a recent article on nano-chemistry [31], Ozin referred to the "hype cycle" (see Fig. 2), in which a technology trigger leads to a peak of inflated expectations, followed by a trough of disillusion-ment, a slope of enlightenment and finally a plateau of productivity. The EQCM has gone through several such

sub-cycles—ultimately overlapping in time—as different aspects have promised new insights, and found to be more complex than imagined and finally been resolved and exploited. This can best be appreciated by recognizing a number of bêtes noires. After some early dramatic successes, notably with metal-based systems at both bulk [4, 32, 33] and UPD monolayer [34–36] levels, for some other systems anomalies appeared: gravimetric interpreta-tion of frequency changes according to the Sauerbrey equation (see above) gave outcomes greatly at variance with expectation based on the coulometric data. This tended to be more common for polymer systems—so-called soft matter—so these were almost universally attributed to viscoelastic effects, to the extent that *viscoelasticity* became almost synonymous with a result that failed to correspond to expectation. Subsequently, both experimental methodol-ogy [37] and theoretical analyses [38, 39] were developed to diagnose, measure and quantify viscoelastic phenomena, e.g. in terms of film shear moduli. The mechanical approach of Kanazawa is particularly helpful in revealing

the distance scales associated with motion of the various components in the system. Together, these theoretical descriptions removed viscoelasticity as an expedient justification for ignoring inconvenient data, though some anomalies still remained.

Other culprits were at various times postulated, but one can note with satisfaction that EQCM practitioners have risen to the challenge and, as in the case of viscoelastic phenomena, developed means to identify and quantify them. One notable example is mechanical stress developed within a film. This is more common for metallic and other rigid films, in which the physical motions underlying viscoelastic phenomena and the relief of stress are prevented. It is possible to separate and quantify both mass and stress contributions to the frequency response using the so-called double resonator technique [40]. The concept here is based on the fact that AT- and BT-cut crystals both respond to film mass and stress with known, but different, coefficients. Thus, by conducting replicate experiments on resonators using both crystals, one can solve the simultaneous equations (two measured resonant frequencies and two unknown parameters) to extract the film mass and stress. While this technique has not been widely applied, the methodology exists. A rather neat example in which its potential has been demonstrated is the uptake of hydrogen by Pd: the gravimetric effect is of course rather small, so stress effects are highly visible in the EQCM response [40].

Another potential complication is the phenomenon of interfacial slip [41]. As indicated above in Fig. 1, the standard models of the (E)QCM presume that the first layer of material contacting the surface moves synchronously with the exciting electrode; what happens beyond that is dependent on film or fluid material properties. Violation of this assumption, i.e. interfacial slip, is known for rather more exotic systems, such as sub-monolayers of inert gas atoms condensed on TSM resonators at very low temperature [41], with the result that the surface loading is mechanically de-coupled from the resonator. The chemistry (bonding and intermolecular forces) of such systems is so different from that generally encountered in electrochemical studies that one has to question the relevance of this precedent in the context of the EQCM. Nonetheless, this is an area that would benefit from more data and greater clarity.

The power and generality of the EQCM

Since electrochemistry is essentially an interfacial science, it is not surprising that a large fraction of electrochemical phenomena involve the exchange of species (beyond electrons) between the electrode and the electrolyte. Possession of a technique to measure such exchanges, ideally with generic capability and known sensitivity factor, is an entirely natural desire. Historically, gravimetric methods have occupied this niche in analytical chemistry at the *macroscopic* level, so the opportunity to make the quantum leap from the *milligram* to the *nanogram* level is irresistible. Coupling this with the facility to make the measurements under electrochemical control creates a compelling argument for developing the EQCM. The purpose of this section is to show how this aspiration has been satisfied for materials that span the periodic table from insertion of the cations of alkali metals in the *s*-block, through elemental deposition and redox chemistry of *d*-block metals and their complexes, to chalcogenide semiconductors, C-based polymers, oxides and halide adsorption in the *p*-block elements. The associated spectrum of physical and (electro)chemical properties is correspondingly broad. The examples selected below to illustrate this huge array are

Fig. 2 The hype cycle, as represented by Ozin [31] (adapted from reference [31]; permission applied for)
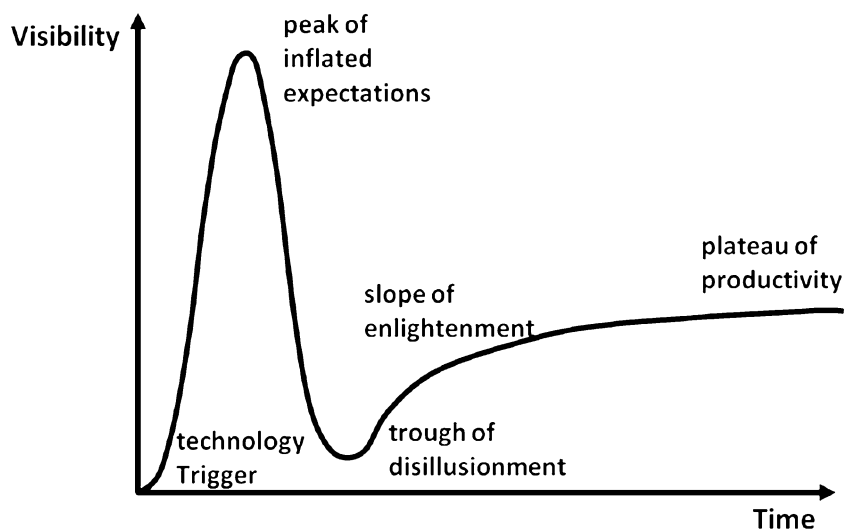
admittedly idiosyncratically selected, but they give an impression of the breadth of materials and phenomena upon which the EQCM has shed light; an equitable treatment of worthy examples would be the role of a more traditional review at least an order of magnitude greater in length.

Unsurprisingly, early examples of EQCM studies tended to focus on a combination of classical adsorption systems and metal deposition. The obvious reasons at the time were twofold: they are amenable to known calibration and they provide known electrochemistry with which to compare the EQCM outcomes. More mature reflection provides a slightly different perspective and perhaps a belated realisation of the challenges of such experiments. The formation of oxide on Au exposed to aqueous electrolytes illustrates the point. Prior knowledge suggested that, in a electrolyte free of specifically adsorbing ions, the outcome towards the positive end of the solvent potential "window" should be an increase in mass that corresponded to the formation of a monolayer of oxide; any debate about whether this should best be discussed in terms of a monolayer of adsorbed "O" atoms or the formation of an "oxide" per se is not relevant, since the EQCM is *not* a structural probe. When one conducts and interprets such an experiment, represented in Fig. 3 [21], three factors emerge. First, the mass change involved is small—above the detection limit of the EQCM but not by orders of magnitude—so modest contributions by other (electro)chemical processes can complicate the response. Adsorption/desorption of ions in the compact layer can give a potential-dependent baseline upon which one must measure oxide formation and if, as is generally the case, these ions are rather heavier than oxide then minority chemical processes can significantly alter the response. Rather more mundanely, adsorption of impurities from solution can have a similar—albeit less predictable—complicating effect. Second, small drifts in solution temperature can (as described above) generate a drifting baseline. Consequently, this conceptually simple experiment is in fact technically demanding—a good test to assign to new EQCM users. The third point is a rather more positive one. As discussed below, sufficiently thick surface films of "soft" matter give responses. However, adsorbed monolayers are so thin—both physically and acoustically—that viscoelastic effects are negligible. Historically, this problem was not appreciated at the time, so awareness of this simplification was not widespread. Other adsorption processes studied included those of halides [42], for which the issue of partial charge transfer had long been a topic of debate. The EQCM was able to address this through separate determinations of the charge passed and the change in surface population, then comparison of the two.

While such studies undoubtedly showcase the exceptional sensitivity of the EQCM, there is an argument that—at least in some instances—they are backward looking to long-studied systems. It transpired that the arrival of the EQCM was timely for a range of modified electrodes and materials designed with new applications in view. For practical reasons—more material generates a larger effect—the films studied tended to be much thicker; for convenience, one may use the term "multilayer", but this is not intended to signify any particular organization or structure at the surface.

With this last point in mind, it is interesting that the structurally "blind" EQCM has on several occasions revealed structural changes within surface-bound electroactive films. A striking example (see Fig. 4) of this is seen via the redox chemistry of Co-doped $Ni(OH)_2$ films [43]. The picture is complicated as a consequence of multiple ion and solvent transfer processes, but the simple overview is that the as-precipitated material behaves rather like the parent α-$Ni(OH)_2$ system: film oxidation leads to an increase in its mass due to the net ingress of mobile species. Upon repetitive cycling, the voltammetric i–E signature shows changes in peak height but little change in qualitative nature—certainly nothing to alert the experimentalist to dramatic changes in material characteristics. However, the ΔM–E signature evolves progressively, with the oxidation-driven mass increase diminishing in magnitude until the situation reverses to give a mass *decrease* upon film oxidation. This change is the consequence of a change in film structure, from the α-$Ni(OH)_2$ form to the β-$Ni(OH)_2$ form, which has a different capacity for accommodating mobile species, notably solvent. As a counterpart to the old adage that "ignorance is bliss", the EQCM would seem to reveal that "knowledge generates discontent".

A rather different example from inorganic chemistry concerns the deposition of $Cu_{(2-x)}Se$ films from a solution
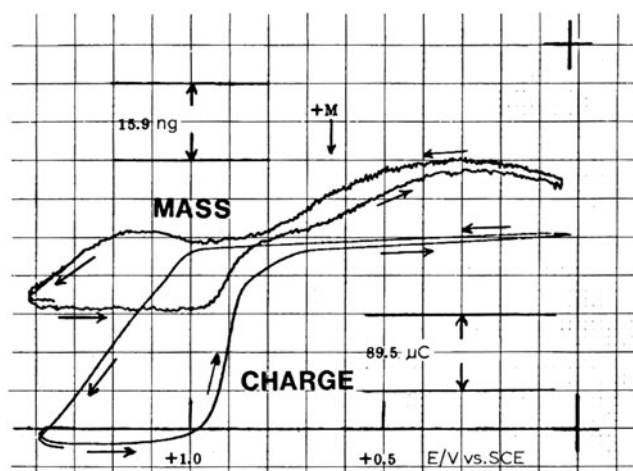
Fig. 3 EQCM mass and charge responses during potential cycling of an Au electrode in aqueous $HClO_4$ solution, showing the formation and removal of a monolayer of adsorbed O at anodic potentials (reproduced from reference [21]; permission applied for)
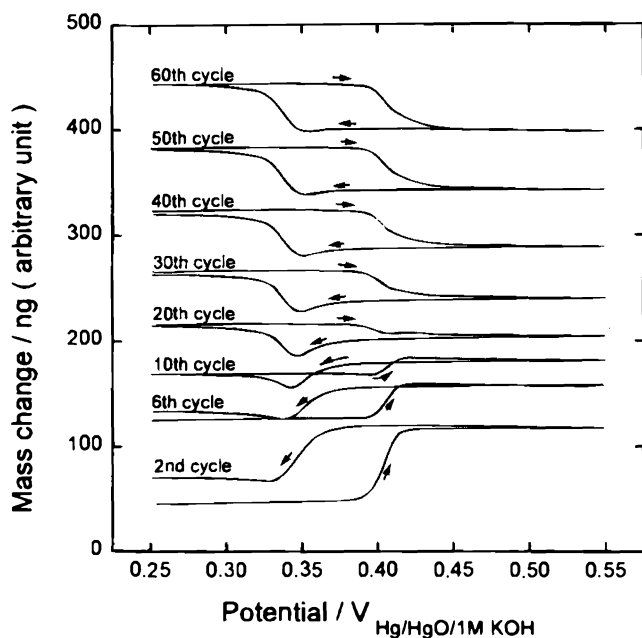
Fig. 4 EQCM-determined gravimetric response to multiple redox cycling in aqueous 1 M KOH of a Co/Ni(OH)$_2$ film (10.2% Co; electroprecipitated film) (reproduced from reference [43]; permission applied for)

in which Cu(SCN)$_4^{3-}$ is the source of the Cu and HSeO$_3^-$ is the source of the Se, in both cases by reduction [44]. The complicated set of redox processes can be unravelled by determination of the slopes of a ΔM vs Q plot; while this is not exactly mass spectrometry, the notion of identifying species based on the ratio of mass to charge obviously has precedent. As the potential is made progressively more cathodic, the slope of the ΔM vs Q plot changes from a value consistent with 4e reduction of HSeO$_3^-$ to elemental Se, to the formation of the desired Cu$_{(2-x)}$Se and eventually to deposition of elemental Cu. There were additional morphological subtleties to the central Cu$_{(2-x)}$Se deposition regime, which the interested reader might pursue, but the point is that simple correlation of mass and charge data is hugely revealing and shows how one can manipulate interfacial composition. The EQCM has also been used to follow the technologically important electroless deposition of Cu [45], a process in which there is no external electrochemical control but for which the component steps are intrinsically electrochemical.

The fundamental issues underlying the potential-driven exchange of charge balancing ions between an electroactive polymer film and the electrolyte solution to which it is exposed are well known, but the pivotal role of the EQCM in influencing the development of conducting polymers (i.e. polymers with extended conjugation, typified by the pyrrole-, thiophene- and aniline-based families) in particular is probably underappreciated. If one looks back to the early days of these materials, the notion of a material with an empirical formula relatively close to "CH" possessing high electronic conductivity was so novel that the electronic aspect became the near-total focus of interest. For steady state measurements and applications, in which electronic current was passed through a sample whose redox state was invariant, this was appropriate. However, when an electrochemical control function switches conductivity "on" and "off" by means of net charge change, the coupling of electronic and ionic motions renders the situation very different. The EQCM was perfectly poised to address such issues as the switching rate sensitivity to changing dopant ion size and/or charge, to introducing competing cation transfer and to changing the notionally inert solvent. Of these, the first of these might be considered to be fairly predictable and the other two not, but even the former has brought surprises. Changing dopant size in polypyrrole has the effect of altering the rate of anion transport in the film: this may be rationalised on the basis of classical solution chemistry behaviour, in which larger ions diffuse and migrate slower. Consequently, if one shortens the timescale of a measurement—exemplified by increasing scan rate in a voltammetric experiment—larger dopant anions will ultimately fail to keep pace with changing polymer electronic charge state. The system then seeks an alternative means of satisfying electroneutrality and, in most cases, the only other option is the transfer of suitably available and mobile cations in the opposite direction. As graphically illustrated using the classical *scheme-of-squares* mechanism, the EQCM can show how repetitive cycling can result in "pumping up" or "draining down" of the electrolyte concentration in the film [46], so that compositions far from equilibrium are accessed, until the system is allowed to relax back to equilibrium. Electrochemical responses, typified by i–E curves, to electron transfer alone could not have revealed such complexity. Far from being intellectual curiosities, such effects are highly relevant to multiple cycling and "memory" effects in devices. In the extreme, within certain potential regions cation participation may be the mechanism of choice for the system if the cation is proton—a highly mobile entity (particularly in aqueous media) with essentially no volume constraints or steric impediments. This has been alluded to above for poly (phenazine) [47] and is widely observed for polyaniline in a range of aqueous acid media [48, 49].

The third point is the involvement of solvent: this introduces a totally new dimension to the problem. Historically, solvents are selected on the basis that they play essentially no part in electroactive film electrochemistry. However, the crucial role of solvent in outer sphere electron transfer is the central tenet of Marcus theory [50], so perhaps one should not be surprised by the emergence of solvent as a key player. This happens at two related but distinct levels. When one considers the transport of ions

through a polymer film, the rate will be determined by the effective local viscosity. In a composite medium—such as a solvated polymer film—the viscosity will be some function of the volume fractions of the components and their dynamics; more of the polymer aspect of this follows shortly. Thus, we see a chain of events, in which electrochemistry measures the rate of electron transfer, which is coupled (in a sufficiently thick film) to the rate of an ion transfer (counter-ion or co-ion, as discussed above), which in turn is governed by the solvent content of the medium. Together, the "E" and "QCM" components of the EQCM respond directly (with known and high sensitivity) to the population changes of all four species—could one ask for a better technique? The other factor is that, if the film is sufficiently "soft", the TSM resonator will no longer give a gravimetric response, i.e. will no longer be a microbalance. Now, the resonator is a probe not of the mobile species populations but of the dynamics of the medium through which they move.

When the material of a surface-bound film is sufficiently soft as to deform under the shear motion of the underlying resonator (see Fig. 1e, f, representing the situations in the absence and presence of liquid, respectively), the central assumption of synchronous motion of the resonator and loading (see Fig. 1b) is violated. In the early literature, the phraseology used was of *materials* being "rigid" or "non-rigid", but this terminology is misleading in two respects. First, the underlying issue is whether or not the *film* behaves elastically. The absence of loss (manifested as damping) is associated with perfectly synchronous motion of the film, i.e. a zero phase shift of mechanical motion across the entire film. It is clear that deviation from this might occur for a relatively thin film of a very soft material or a rather thicker film of a stiffer material; in short, it is a feature of both the material and the sample. The criterion is whether the film thickness is greater or smaller than the acoustic decay length. This is an important issue when comparing coulometric, acoustic and topographic (e.g. AFM) assays of the amount of material on a surface [51]. Second, even when one focuses on materials properties, in an electrochemical context, a film will be perfused by solvent, to an extent that may vary dramatically from one solvent to another. A clear example [52] is the viscoelastic response seen for a polyvinylferrocene film during its deposition from CH_2Cl_2 but the complete absence of viscoelastic effects when this hydrophobic film is exposed to aqueous media. The progressive effect of damping by the growing film is dramatically illustrated by the crystal admittance spectra, as shown in Fig. 5; on transfer to aqueous media, where the film is poorly hydrated, there is negligible dissipation and frequency changes to redox-driven ion and solvent changes can be interpreted gravimetrically.

Physically, the atoms, molecules or, in the case of a polymer, chains within the film slide past each other and in so doing dissipate energy. Now, the film cannot be viewed as an *elastic* material that stores (but does not dissipate) energy. Neither is it a simple *viscous* fluid that only dissipates energy. Rather, it is a *viscoelastic* medium that both stores *and* dissipates energy, the relative contributions of which depend on intrinsic polymer dynamics (represented by a relaxation time, τ) and the observational timescale (here, represented by the angular frequency of the resonator, $\omega=2\pi f$). The TSM resonator response under these circumstances is a function of film thickness and materials properties, generally represented by the shear modulus, $G=G'+jG''$, where G' is the storage modulus and G'' is the loss modulus ($j=\sqrt{(-1)}$ indicates the phase relationship). The analysis is more complicated in that there is no longer additivity of the responses of multiple components (layer and liquid), but one can extract the shear modulus components from the TSM resonator response [25, 38]. Experimentally, the phenomenon can be explored using crystal admittance or pulsed methods, as elegantly set out by Kanazawa [53]. Interestingly, even if polymer dynamics are not so rapid as to be manifested via viscoelastic effects, slow(er) relaxation processes may result in apparent "drift" in gravimetrically measured ion and solvent transfers accompanying film redox switching. Such history effects have been rationalised by a multidimensional extension of the classical scheme-of-squares model [54].
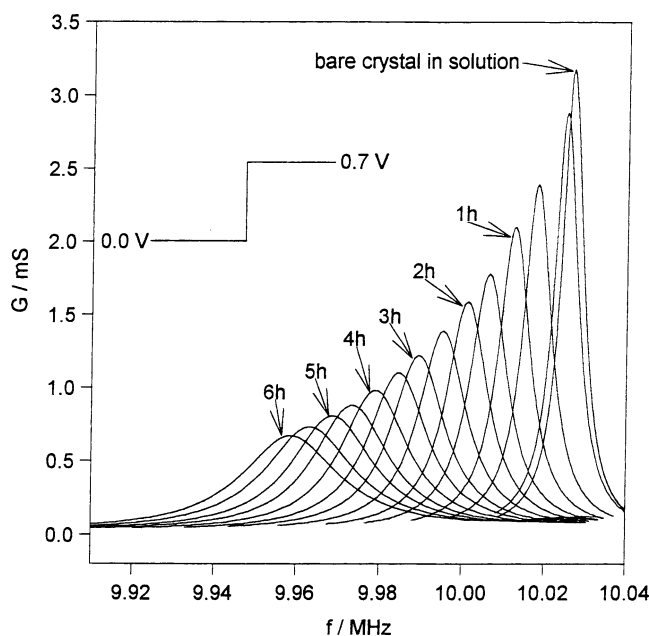
Fig. 5 Time-resolved crystal admittance spectra during electrochemically driven deposition ($E=0.7$ V) onto Au of a polyvinylferrocene film from PVF/TPA$^+$ClO$_4^-$/CH$_2$Cl$_2$ solution (reproduced from reference [52]; permission applied for)

Now, with the facility to determine film viscoelastic properties, users of the EQCM were gifted a huge opportunity, via the existence of a vast library of analogous data for bulk polymeric materials [55, 56]. Polymer dynamics are characterized by a relaxation time, τ; in practice, there may be multiple relaxation times, but a single relaxation time conveys the basic concept, as follows. On long timescales ($t > \tau$), the material appears soft: simplistically, the polymer chains have time to slide past each other freely, without substantial energy dissipation. As the timescale is shortened, the material becomes progressively stiffer and the increased frictional resistance to motion is manifested by energy dissipation. Continuing this trend, the stiffness (parameterized by the storage modulus) rises to a plateau: the polymer chains can no longer move past each other and the viscous dissipation (parameterized by the loss modulus) falls to zero. Thus, when viewed as functions of a normalized timescale $\omega\tau$, G' rises monotonically in sigmoidal form and G'' rises then falls. The two functions cross ($G' = G'' = 1/2 G'_\infty$, where G'_∞ is the short timescale limiting value of G') at $\omega\tau = 1$. The relaxation time is dependent on temperature, in a manner determined by polymer energetics. By determining the variation of shear modulus with temperature and timescale (via the use of resonator harmonics), using the *time–temperature superposition* principle, it is possible to construct a stress master relaxation curve. From the viscoelastic signature, one can infer likely molecular origins of the polymer dynamics [57, 58]. This type of insight was certainly never anticipated when the QCM was first introduced to electrochemistry.

Integration with other techniques

In the previous section, the universal sensitivity of the EQCM has been expressed as a great strength. A more negative way to present this would be as a lack of selectivity. The natural response to this would be combination with a technique possessing some form of species selectivity. Spectroscopy is the obvious class of methods, with the complementary attributes of molecular selectivity and lesser certainty of sensitivity factor. Surprisingly, although the benefits of using the EQCM in conjunction with visible spectroscopy [59], FTIR [60], ellipsometry [61] and even mass spectroscopy [62] have been elegantly demonstrated, these are relatively rare examples; no doubt, this is an opportunity for the future.

An interesting tripartite combination is electrochemistry-quartz crystal microbalance–probe beam deflection (EQCM-PBD) [32, 34]. Conceptually, the QCM and PBD are natural complements, since the QCM probes (gravimetrically) population changes on the "dry" side of the electrode/

solution interface and the PBD probes (optically, via refractive index gradients) population fluxes on the "wet" side of the interface. Practically, they are also excellent teammates in terms of their sensitivities to different species: for example, the QCM readily detects solvent entry into/exit from a film but has difficulty detecting proton transfer, while the probe beam has broadly the inverse sensitivity. The quantitative nature of this partnership has been demonstrated for silver deposition/dissolution [32] and proton vs anion transfer discrimination has been demonstrated during redox switching of hydroxyphenazine [47] and poly-o-toluidine [63] films.

It is also worth noting that the "E" in EQCM has been explored quite widely. From the perspective of electrochemical control function, there is no surprise at the dominance of (cyclic) voltammetry. Extension to impedance methods has also been demonstrated [49]. Visualizing the physical situation of a high frequency (megahertz) mechanical resonance modulated by the gravimetric consequences of a low frequency (hertz) electrochemical oscillation is non-trivial. Nonetheless, by expressing the response in terms of an electrogravimetric transfer function, this sophisticated methodology can discriminate between and quantify the interfacial transfers of different species in a truly impressive fashion.

In a typical EQCM experiment, the situation is very well controlled *at* the interface but the supply of reactant or partitioning species *to* the interface is commonly poorly controlled. Elsewhere in electrochemistry, this has been addressed using controlled hydrodynamic methods, notably the rotating disc electrode (RDE) and the wall jet electrode (WJE). EQCM practitioners have been quick to spot this and to develop the EQCM-RDE [64, 65] and EQCM-WJE [66, 67] hyphenated methods.

State of the art

Having explored a range of factors, phenomena and feats of accomplishment, it is appropriate to take stock. Given the diversity of chemical systems studied and the disparate ways in which they have been pursued, this will be somewhat superficial but one can nonetheless see some generic features. Looking first at the initial expectations of the EQCM as a gravimetric monitor of electrochemically driven surface/solution exchange processes, the technique has been successful beyond even the most optimistic aspirations of its early pioneers. For major classes of materials—including metals (and their oxides, salts and complexes), semiconductors, simple adsorbates and polymers—substantive information and insights have been acquired for film fabrication and subsequent (electro)chemical manipulation. If there were

a disappointment, it would not be in the acquisition of the data but its appraisal. The concept of correlating the gravimetric and coulometric responses ("E" and "QCM" component responses) dates back to classical electrochemical times, yet only a minority of reports appear to make such correlations in any detail. The quantitative nature of the technique at this level is clear, so there would appear to be no impediment to progress.

Several of the bêtes noires in terms of interpretation have now been demystified and rationalised. These include viscoelastic phenomena, stress effects and acoustic impedance mismatching. Invoking them without justification as an explanation for otherwise uninterpretable data is no longer tenable: a clear diagnostic exists for determining their presence (or otherwise). The one demon that has not been slain is the issue of interfacial slip. If there is a downside to all this progress, it is the fact that the technique is commonly used in "black box" mode; that is to say that there are occasions when non-expert users consider it sufficiently straightforward that firstly, it can be applied without consideration of the physical nature of the sample and, secondly, the data may be interpreted gravimetrically without ambiguity or error. In most cases, this may—however unknowingly—be appropriate, but the dangers abound. This faith in the method is a curious measure of success. At a grander level, the EQCM has clearly been accepted into the fold of electrochemistry through the appearance of an IUPAC report [68].

Unquestionably, the major *unanticipated* success has emerged from what in the early development phase was a problem, namely the phenomenon of viscoelasticity. This can be recognized at several levels, in both fundamental and technological aspects. The facility to understand materials properties is clearly valuable both in rationalizing film/device properties and in designing new materials for specific purposes. In particular, since essentially all electrode coatings have the requirement to control entry, exit and transport of selected species—from ion insertion into battery materials, through partition of analytes and catalytic substrates, to exclusion of corrosion enhancing species—the local viscosity of the medium is crucial. The latter is directly related to the loss modulus (G''), which may in turn be rationalised in terms of polymer structure and dynamics. In a number of cases, such as artificial muscles and other actuators, the mechanical properties per se may be the basis of the application. In others they may reflect its limitations, for example mechanical and consequent electrical "disconnection" from the electrode underlying the active component of a battery. The facility of an acoustic wave resonator—strictly, no longer a "microbalance"—to yield this information is indeed powerful.

Future prospects

Notwithstanding the rapid maturation of the EQCM as a technique, there is a spread of materials, methodological, phenomenological and technological opportunities that might be explored. In the first instance, application of the EQCM in both gravimetric and viscoelastic modes is essentially limited only by the imagination of the (electro) chemist to design new materials and to fabricate them into novel interfacial architectures. One area in which considerable opportunities exist is in the fabrication of multi-component structures. There has been some work done in this broad area, including use of gravimetric data to identify the electron source/sink in a bilayer via the associated cation vs anion transfers for the two materials [69]. In the viscoelastic regime, the inclusion of rigid elements such as carbon nanotubes [70] or nanodiamonds [71] also offers the possibility of tailoring mechanical properties. There would appear to be innumerable new opportunities in this area.

In terms of methodology, combination with other techniques should be exploited more widely. The natural candidates are those which possess species-specific capability, to complement the generic nature of gravimetric determination. Since a number of such techniques—notably of a spectroscopic nature—are routinely used in electrochemistry, the challenges are more instrumental than fundamental. Focusing on the EQCM alone, it is also worth pointing out that it is by nature a *differential* technique, i.e. one measures a *mass change* and has no a priori means of accessing the absolute mass and thus the absolute population. In cases of film deposition, where one can often ensure the absence of a film before the measurement is initiated, this brings no ambiguity. However, in cases of mobile species transfers into/out of electroactive films, there may be considerable value in knowing if the ion or solvent population change is a small or large perturbation on the overall population within the film. This issue has been addressed instrumentally via the dual QCM technique [23, 72], but the methodology has not been widely exploited.

Of the various phenomena to which the EQCM response is sensitive, the one that is most tantalising and least well understood is "slip". While often viewed as a more exotic topic, its investigation using acoustic wave devices may have considerable relevance to tribology and surface wetting applications such as superhydrophobicity.

Technologically, two areas where acoustic wave methods have been demonstrated to have value but have been least exploited involve mechanical properties of materials. For "soft" materials, most commonly polymers, determination of thin film shear moduli as functions of the relevant physico-chemical control parameters can reveal new insights and

assist with design of new materials. For harder engineering materials, as widely used in metal deposition and coating technologies, stress measurements should be of great value. Analogous arguments apply to the active materials in ion insertion batteries where continued redox cycling and repetitive insertion/ejection of species may result in stress-driven loss of electroactive material from the surface.

Final observations

In the context of the EQCM, what has history taught us? The first point is that received wisdom is not always a good source of truth. Had the early pioneers of the EQCM believed that damping by a contacting fluid would be fatal to resonator oscillation, they would never have embarked on the development of the technique at all. Second, we should remember that a plan and the outcome are not the same. Had the EQCM turned out to be a simple gravimetric probe of surface population changes, it would have been a useful but unspectacular addition to the suite of interfacial electrochemical techniques. However, its response to other phenomena—notably viscoelasticity, stress and slip—makes it a much more versatile and interesting tool. This leads to the third observation, namely that problems create opportunities. These last three phenomena were initially viewed as either a restriction on what the EQCM could do (with a blinkered view to use as a gravimetric probe) or as a convenient scapegoat for any undesirable or unanticipated outcome; they are neither of these things, but rather opportunities for novel science. From these, we learn to see history as an interesting set of prompts, but not as an infallible guide, and recognize that it cannot predict discovery or invention.

References

1. Ballantine DS, White RM, Martin SJ, Ricco AJ, Zellers ET, Frye GC, Wohltjen H (1997) Acoustic wave sensors. Academic, San Diego
2. Scholz FJ (2011) Sol State Electrochem. doi:10.1007/s10008-010-1234-2
3. Lingane JJ (1958) Electroanalytical chemistry, 2nd edn. Wiley, New York, pp 351–445
4. Bruckenstein S, Shay M (1985) Electrochim Acta 30:1295–1300
5. Skoog DA, West DM, Holler JM (1996) Fundamentals of analytical chemistry, 7th edn. Saunders College Publishing, Philadelphia, pp 431–459
6. Hillman AR (2005) Electrogravimetry. In: Worsfold PJ, Townshend A, Poole CF (eds) Encyclopedia of analytical science, vol 2, 2nd edn. Elsevier, Oxford, pp 317–323
7. Murray RW (ed) (1992) Molecular design of electrode surfaces. Wiley, New York
8. Hillman AR (1987) Preparation and properties of polymer modified electrodes. In: Linford R (ed) Electrochemical technology of polymers. Elsevier Applied Science Publishers, London, pp 103–239
9. Lu C, Czanderna AW (eds) (1984) Applications of piezoelectric quartz crystal microbalances. Elsevier, Amsterdam
10. Glassford APM (1978) J Vac Sci Technol 15:1836–1843
11. Nomura T, Iijima M (1981) Anal Chim Acta 131:97–102
12. Buttry DA (1991) Applications of the quartz crystal microbalance to electrochemistry. In: Bard AJ (ed) Electroanalytical chemistry, vol 17. Marcel Dekker, New York, pp 1–85
13. Buttry DA, Ward MD (1992) Chem Rev 92:1355–1379
14. Schumacher R (1990) Angew Chemie-Int Ed Engl 29:329–343
15. Bruckenstein S, Hillman AR (1995) Electrochemical quartz crystal microbalance studies of electroactive surface films. In: Hubbard AT (ed) Handbook of surface imaging and visualization. CRC Press, Boca Raton, pp 101–113
16. Hepel M (1999) Electrode-solution interface studied with electrochemical quartz crystal nanobalance. In: Wieckowski A (ed) Interfacial electrochemistry. Marcel Dekker, New York, pp 599–630
17. Hillman AR (2003) The electrochemical quartz crystal microbalance. In: Bard AJ, Stratmann M (eds) Encyclopaedia of electrochemistry, vol 3. Wiley, New York, pp 230–289
18. Ferreira GNM, Da-Silva AC, Tome B (2009) Trends Biotechnol 27:689–697
19. Casero E, Vazquez L, Parra-Alfambra AM, Lorenzo E (2010) Analyst 135:1878–1903
20. Hunter AC (2009) J Biomed Nanotechnol 5:669–675
21. Bruckenstein S, Shay M (1985) J Electroanal Chem 188:131–136
22. Conan Doyle A (1894) Silver blaze. In: Conan Doyle A (ed) The memoirs of Sherlock Holmes. Newnes, London
23. Bruckenstein S, Michalski M, Fensore A, Li Z, Hillman AR (1994) Anal Chem 66:1847–1852
24. Sauerbrey G (1959) Z Phys 155:202–222
25. Bandey HL, Martin SJ, Cernosek RW, Hillman AR (1999) Anal Chem 71:2205–2214
26. Kanazawa KK, Gordon JG (1985) Anal Chim Acta 175:99–105
27. Theisen LA, Martin SJ, Hillman AR (2004) Anal Chem 76:796–804
28. Urbakh M, Daikhin L (1994) Phys Rev B 49:4866–4870
29. Daikhin L, Gileadi E, Katz G, Tsionsky V, Urbakh M, Zagidulin D (2002) Anal Chem 74:554–561
30. Bund A, Schwitzgebel G (2000) Electrochim Acta 45:3703–3710
31. Ozin GA, Cademartiri L (2011) Small 7:49–54
32. Henderson MJ, Hillman AR, Vieil E, Lopez C (1998) J Electroanal Chem 458:241–248
33. Gollas B, Bartlett PN, Denuault G (2000) Anal Chem 72:349–356
34. Henderson MJ, Bitziou E, Hillman AR, Vieil E (2001) J Electrochem Soc 148:E105–E111
35. Hepel M, Kanige K, Bruckenstein S (1990) Langmuir 6:1063–1067
36. Hepel M, Kanige K, Bruckenstein S (1989) J Electroanal Chem 266:409–421
37. Bandey HL, Hillman AR, Brown MJ, Martin SJ (1997) Far Disc 107:105–121
38. Hillman AR, Jackson A, Martin SJ (2001) Anal Chem 73:540–549
39. Kanazawa KK (1997) Far Disc 107:77–90
40. Cheek GC, O'Grady W (1994) J Electroanal Chem 368:133–138
41. Mak C, Krim J (1998) Phys Rev B 58:5157–5159
42. Deakin MR, Li TT, Melroy OR (1988) J Electroanal Chem 243:343–351

43. Kim MS, Kim KB (1998) J Electrochem Soc 145:507–511
44. Kemell M, Saloniemi H, Ritala M, Leskela M (2000) Electrochim Acta 45:3737–3748
45. Feldman BJ, Melroy OR (1989) J Electrochem Soc 136:640–643
46. Bruckenstein S, Brzezinska K, Hillman AR (2000) Phys Chem Chem Phys 2:1221–1229
47. Miras MC, Barbero C, Kotz R, Haas O, Schmidt VM (1992) J Electroanal Chem 338:279–297
48. Hillman AR, Mohamoud MA (2006) Electrochim Acta 51:6018–6024
49. Gabrielli C, Keddam M, Nadi N, Perrot H (2000) J Electroanal Chem 485:101–113
50. Marcus RA (1968) Electrochim Acta 13:995–1004
51. Tedim JA, Freire AC, Hillman AR (2009) Phys Chem Chem Phys 11:268–277
52. Bandey HL, Gonsalves M, Hillman AR, Glidle A, Bruckenstein S (1996) J Electroanal Chem 410:219–227
53. Geelhood SJ, Frank CW, Kanazawa KK (2002) J Electrochem Soc 149:H33–H38
54. Hillman AR, Bruckenstein S (1993) J Chem Soc Far Trans 89:3779–3782
55. Ferry JD (1970) Viscoelastic properties of polymers, 2nd edn. Wiley, New York
56. Aklonis JJ, MacKnight WJ (1983) Introduction to polymer viscoelasticity. Wiley, New York
57. Hillman AR, Efimov I, Skompska M (2005) J Am Chem Soc 127:3817–3824
58. Hillman AR, Efimov I, Ryder KS (2005) J Am Chem Soc 127:16611–16620
59. Kim JM, Chang SM, Muramatsu H (1999) J Electrochem Soc 146:4544–4550
60. Shimazu K, Ye S, Sato Y, Uosaki K (1994) J Electroanal Chem 375:409–413
61. Rishpon J, Redondo A, Derouin C, Gottesfeld S (1990) J Electroanal Chem 294:73–85
62. Jusys Z, Massong H, Baltruschat H (1999) J Electrochem Soc 146:1093–1098
63. Henderson MJ, Hillman AR, Vieil E (1999) J Phys Chem B 103:8899–8907
64. Kern P, Landolt D (2000) J Electrochem Soc 147:318–325
65. Kern P, Landolt D (2001) J Electrochem Soc 148:B228–B235
66. Itagaki M, Tagaki M, Watanabe K (1997) J Electroanal Chem 440:139–143
67. Jusys Z, Stalnionis G (2000) Electrochim Acta 45:3675–3682
68. Buck RP, Lindner E, Kutner W, Inzelt G (2004) Pure Appl Chem 76:1139–1160
69. Hillman AR, Glidle A (2001) Phys Chem Chem Phys 3:3447–3458
70. Hillman AR, Dong Q, Mohamoud MA, Efimov I (2010) Electrochim Acta 55:8142–8153
71. Ispas A, Peipmann R, Adolphi B, Efimov I, Bund A (2011) Electrochim Acta (in press)
72. Bruckenstein S, Fensore A, Hillman AR (1997) Far Disc 107:323–336