



Review

Combinatorial electrochemistry – Processing and characterization for materials discovery



Paul J. McGinn*

Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, IN 46556, USA

ARTICLE INFO

Article history:

Received 4 August 2015

Received in revised form 22 October 2015

Accepted 25 October 2015

Available online 17 December 2015

Keywords:

Combinatorial discovery
 High-throughput experimentation
 Combinatorial electrochemistry
 Materials screening
 Electrocatalysis
 Combinatorial processing

ABSTRACT

Combinatorial materials science is a research methodology for accelerating the pace of materials discovery and optimization. This article reviews issues in combinatorial processing of materials for, and characterization of materials by, electrochemical methods. In particular the emphasis is on the discovery of electrocatalysts for energy uses, including batteries, fuel cells, and related applications. The article also discusses issues in analyzing and using the data obtained from such experiments. Finally, it is emphasized that for most applications it is necessary to confirm results obtained by rapid screening with more traditional approaches on bulk samples in “real world” environments.

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1. Introduction

The search for materials with improved properties for energy and other applications has traditionally been performed by

combinations of various compounds being mixed, reacted and characterized in serial experimentations. In the drug industry the field of combinatorial chemistry was pioneered as a means to permit *high throughput experimentation* for efficient and systematic exploration of various chemical families for signs of biological or chemical activity. About 20 years ago this approach was first adapted to the field of solid state materials [1]. Since that time combinatorial investigations have been utilized to attack a wide

* Tel.: +1 574 631 6151; fax: +1 574 631 8366.

E-mail address: pmcginn@nd.edu

variety of materials problems spanning many different technological areas. Several excellent books and articles have been published that provide comprehensive reviews of many of these developments [2–11].

A major attraction of combinatorial approaches to materials discovery is that they are faster, and generally less costly than traditional serial experimentation. Upfront costs for combinatorial experimentation can be high, such as for some types of sophisticated thin film deposition systems or certain characterization techniques. However, financial models employing discounted cash flow scenarios incorporating factors including decreased labor cost per experiment and product cycle time reduction suggest high throughput experimentation offer significant economic benefits [12].

In addition, data fidelity can be greater than with traditional methods since all of the library samples are ostensibly experiencing the same process and measurement conditions. Combinatorial materials experiments involve three main steps including (1) high speed automated materials synthesis, (2) automated serial or parallel characterization or screening and (3) processing and analysis of large data sets. Ideally, high throughput experimentation is complemented by computational methods to aid in the identification of candidate materials systems or compositions.

Combinatorial investigations have proven to be particularly well suited for development of improved catalysts for electrochemical energy conversion applications, including fuel cells, batteries, and photocatalysis. The present work discusses issues in processing materials for (step 1), and characterization of materials by (step 2) electrochemical methods, particularly with respect to the discovery of electrocatalysts for energy uses.

2. Materials synthesis for electrochemical studies

A wide variety of materials synthesis approaches have been used for combinatorial materials experimentation. They have in common the desire to synthesize many samples in a rapid manner while trying to vary only one parameter, which typically is composition. In fewer reported investigations, a constant composition is subject to varying process or use conditions [13–15]. Since composition investigations are the most common, they will be the focus of the discussion that follows. Furthermore, discussion will be confined to techniques used in generating libraries intended for electrochemical characterization.

Fabricated composition ‘libraries’ are either *discrete*, with many distinct regions of uniform composition, or *gradient* (also referred to in the literature as “composition spread”), where composition varies continuously across the library. Gradient libraries are typically easier to produce, as overlapping fluxes of constituents can be directed to a substrate, or through the use of opposing thickness wedges. They can also be readily produced through the use of diffusion couples or diffusion “multiples”, although these have not been used in electrochemical studies [5]. Various sample forms can be processed for combinatorial studies, with libraries from films, powders and bulks having all been reported. The preferred sample form is typically dictated by the property to be measured. For electrochemical and energy related research which is the focus here, films and powders are the most common sample forms, so synthesis of these will be discussed in more detail below.

2.1. Films

Well established physical (PVD) and chemical vapor deposition (CVD) processes have been adapted for combinatorial film processing. The use of CVD has been less widespread than PVD, but a number of different CVD approaches have been described

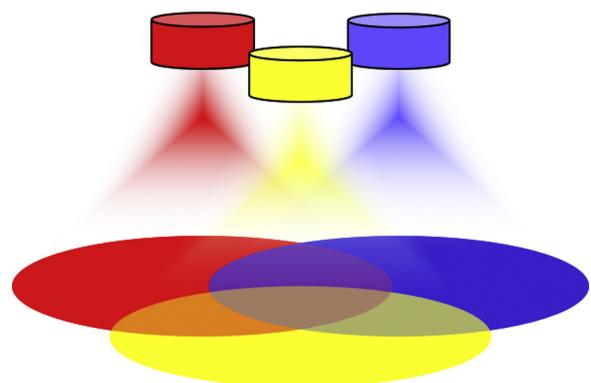


Fig. 1. Co sputtering with overlapping fluxes.

[16–19,14,20–22]. Far more widely reported are the use of PVD techniques including evaporation, sputtering and pulsed laser deposition (PLD), which are discussed below.

2.1.1. Gradient thin film libraries

2.1.1.1. Sputtering. In typical sputtering systems (i.e. those not designed specifically for combinatorial work) it is common to have the ability to simultaneously deposit from more than source onto a central spot, but this is less often the case in evaporation systems. This widespread capability in sputtering systems has resulted in this being the most commonly used technique to synthesize compositional gradient samples. Slight non-uniformities in these systems can produce samples with a continuous change in the ratio of the components in regions of the sample surface. The most straightforward means to achieve this is by using separate sources, as illustrated below (Fig. 1). Through simultaneous deposition from 2 or 3 sources, gradient composition binary or ternary films can be formed. In contrast, for PLD, although the application of analogous simultaneous dual laser PLD has been reported, it is a rare capability [23,24]. In the absence of multiple lasers, gradient films can be produced from a segmented target made from different materials [25], similar to the technique first pioneered for sputtering more than 40 years ago [26].

An attractive feature of co-sputtering is intimate mixing of the co-deposited constituents, eliminating the need for annealing to achieve interdiffusion, as is required for multilayered films. Brief anneals are only needed if the as-deposited films are amorphous, and crystalline alloys are desired. However, achieving precise spatial compositional control is a challenge in co-sputtering because of the large number of deposition parameters, including gun power, chamber background pressure, gun-substrate distance, carrier gas composition and gun-tilt. The distance and angle between the substrate and the deposition sources plays a significant role in determining the film thickness and distribution. Hence there has been interest in recent years in developing models to permit more precise compositional control [27]. One recent sophisticated combinatorial sputter system design incorporates deposition sources whose tilt with respect to the substrate can be robotically controlled to permit optimization of the deposition geometry for specific combinatorial synthesis experiments [28]. Lacking such models or sophisticated deposition capability, most researchers determine film composition after deposition by ex situ energy-dispersive X-ray spectroscopy, wavelength dispersive spectroscopy or X-ray fluorescence spectroscopy to map composition as a function of location on the substrate.

2.1.1.2. Evaporation. As with sputtering, overlap of fluxes from multiple evaporation sources can be utilized to synthesize libraries. Shadow masks positioned between the evaporation source and the

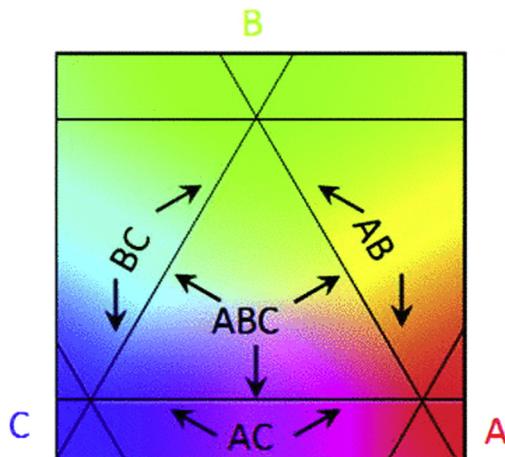


Fig. 2. Schematic representation of a composition spread generated by the use of a rotatable shadow mask containing the entire ternary alloy composition space. From [31].

substrate can give greater control over the gradient of a particular constituent, as some positions on the substrate are shadowed from portions of the flux [29]. A similar approach has been utilized in conjunction with Knudsen cells [30]. Using shadow masks, one can generate a linear gradient varying from a maximum in regions exposed to the entire flux to zero where the substrate is completely shadowed from the source. Use of rotatable shadow masks allows for more control [31]. It is possible to generate an entire ternary composition space as shown in Fig. 2. Alternatively one can rotate the substrate through successive 120° turns and achieve a similar result [32]. These approaches are applicable for sputtering, evaporation or PLD, which are all line-of-sight deposition processes, in contrast to CVD.

2.1.1.3. Sequential deposition. Sequential deposition from multiple sources (sputter, evaporation, PLD) combined with moving masks can be used to form thickness wedges. Wedges with linear thickness variation are obtained by combining constant velocity mask motion

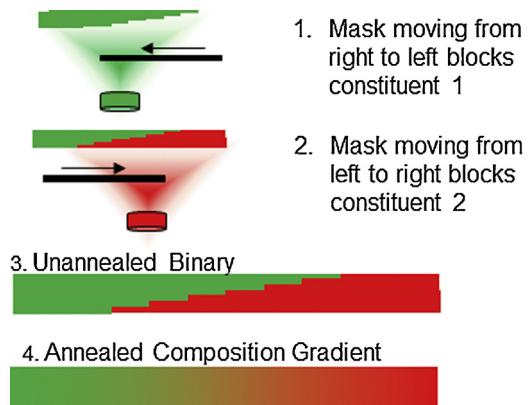


Fig. 3. Illustration of the use of a moving mask to generate a binary gradient library from thickness wedges.

with a constant deposition rate. The concept is shown in Fig. 3 for construction of a binary composition gradient.

More complex masks have been designed in the author's lab for fabrication of ternary gradients by sequential deposition. This is illustrated in Fig. 4. Fig. 4A shows a circular substrate covered by a contact mask with a triangular opening. To the right of the substrate is a moveable mask with three triangular openings colored red, blue and yellow, positioned vertically as close as possible to the substrate/contact mask while still permitting movement past the opening. The leading edge of each of the mask openings is denoted by an arrow. Fig. 4B shows a series of snapshots as the yellow mask opening passes over the substrate during deposition of a constituent. At step 1 the contact mask opening is still blocked by the mobile mask so no flux reaches the substrate. At step 2, one corner of the substrate opening defined by the contact mask begins to "see" the flux. In steps 3 through 5, more of the substrate is progressively exposed to the flux. As a result, the first corner of the triangle exposed is subject to the flux for the longest time so ends up being the thickest. The triangular wedge thins perpendicularly towards the opposite edge. The resulting wedge thickness gradients produced by the three openings are shown in Fig. 4C. The resulting gradient from three stacked wedges is portrayed in Fig. 4D.

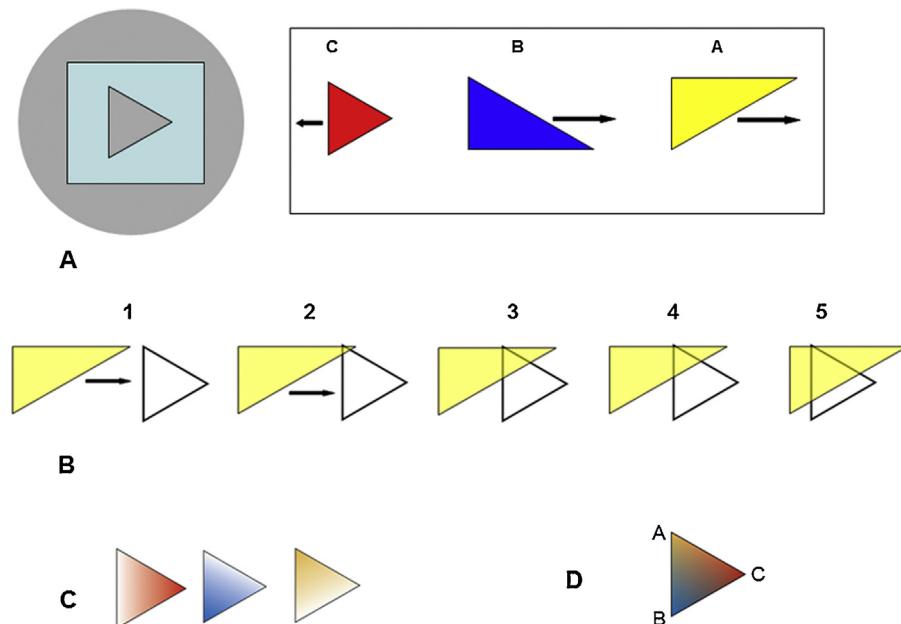


Fig. 4. Translatable mask for generating ternary gradients by sequential deposition of triangular thickness wedges.

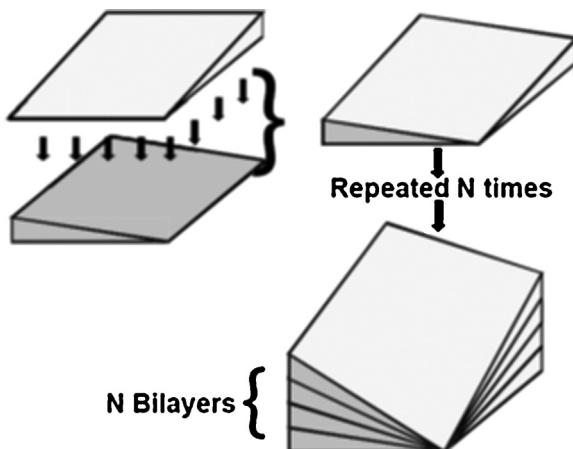


Fig. 5. Illustration of build-up of thickness wedges from deposition with rotating masks.

From [36].

An alternative approach that yields orthogonal thickness wedges involves rotation of a substrate on a table that is rotating beneath deposition fluxes from various sources [33,34]. As the substrate passes beneath various targets, it is continuously repositioned in a manner to yield thickness gradients (Fig. 5). This approach has even been used to generate slices from quaternary composition gradient libraries [35,36].

Moving mask approaches rely on repetitive deposition of very thin wedge layers so that, upon heating, vertical interdiffusion is complete before significant lateral diffusion occurs. For all sequential routes, control of the reaction pathway and the structure of the final products relies on the proper modulation of the reaction elements [37–40]. Layers need to be thinner than the critical nucleation radius of undesired intermediate phases, which is typically on the order of 2.5–5 nm.

As noted earlier, a significant advantage of co-deposition compared with sequential deposition is that the constituents are

intimately mixed as they are deposited, so no annealing step is required to promote diffusion. This means there is less concern with undesired interactions between the films and the substrate, which may eliminate the need for a diffusion barrier. Additionally, with co-deposition it is possible to prepare metastable phases that may not be able to be synthesized by other routes [41]. The continuous gradient techniques described above provide excellent coverage of phase fields, but for some characterization techniques it is advantageous to have independently addressable, discrete library elements.

2.1.2. Discrete thin film libraries

Synthesis of thin film discrete composition libraries is achieved through the use of multiple masks that expose different regions of the substrate to the incident vapor flux. The concept is illustrated in Fig. 6 for synthesis of a binary library. Constituents are sequentially deposited through masks with various openings. After deposition the library is annealed to produce regions whose composition is determined by the series of masks utilized during fabrication and the thickness of individual layers. Thus it is possible to know the precise composition as a function of position. Quaternary masks, i.e. n masks used in $4 \times n$ depositions to produce 4^n discrete compositions, have been used to create large libraries filled with combinations from large numbers of elements [42]. For testing where library elements are to be addressed through individual conductive traces, the masking and fabrication becomes more complicated, and incorporate lithographic techniques from micro-electronic fabrication [43]. An example is shown in Fig. 7 [44]. This is a library intended for parallel electrochemical characterization by cyclic voltammetry, where every pad needs to have a voltage applied, but be insulated from other pads. Hence, individual traces extend from each pad to the periphery of the wafer.

A unique approach described recently relies on serial co-deposition of discrete compositions that comprise an array [45]. A single aperture in a shadow mask is sequentially moved to positions over a substrate. Deposition can either produce up to 64 compositions on a 100 mm wafer, or deposit compositions directly onto as many as 16 glassy carbon electrodes. The advantageous feature

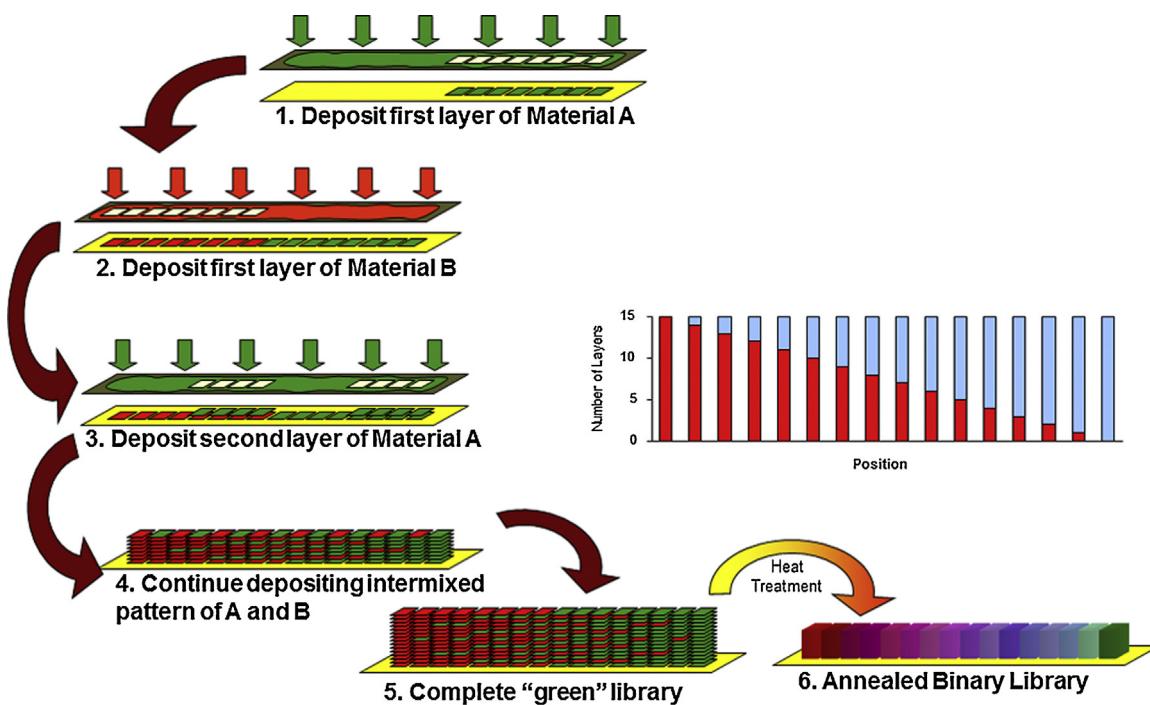


Fig. 6. Schematic sequence showing development of a thin film discrete composition library by deposition through contact masks.

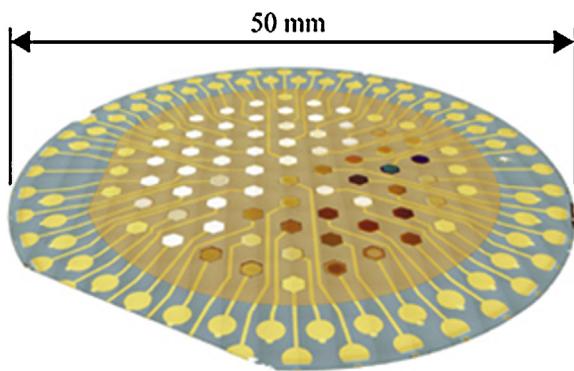


Fig. 7. Thin film library intended for parallel electrochemical characterization by cyclic voltammetry deposited on a 50 mm Si wafer.

From [44].

of this system is that after a thin film array is electrochemically characterized in parallel, specific compositions of interest can be reproduced atop electrodes for more detailed characterization and verification in rotating disk electrode (RDE) studies.

As the diverse approaches described above suggest, there is no best thin film processing route for all materials one might wish to investigate. Several factors will determine the preferred library fabrication technique(s) for a particular laboratory. Perhaps the most important factors are the materials application and the related characterization technique that will be employed. For example, the characterization technique may dictate the use of discrete compositions rather than gradient films.

The materials themselves may require a particular deposition process to be tested. For example, the stoichiometry of complex oxides can typically be controlled more readily by PLD than by sputtering, as exemplified by the high temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_7$. Sputtering of this compound is problematic due to

resputtering effects [46]. However, metals are not easily deposited by PLD, whereas they can be easily processed by sputtering or evaporation. Deposition of simple oxides is readily performed by sputtering, but poses more of a challenge for processing by evaporation, where oxide formation in the melt is to be avoided. For applications like battery materials, metallic Li is easily deposited by evaporation, but is challenging to deposit by sputtering because of low deposition rates. Hence, a particular set of materials, as suggested by the application, may favor one deposition technique. Finally, deposited thin films often exhibit texture, rather than the random orientation of planes as found in a powder. For applications like catalysis where activity can vary significantly between different (hkl) orientations this might be a concern, especially if films are textured such that they have only a low fraction of high activity planes. This is a case where the substrate choice might be important in order to influence the orientation of the film.

2.2. Liquid deposition of powders

Liquid deposition routes are widely used in combinatorial materials studies. They are attractive because implementation is usually relatively inexpensive and straightforward. Costly vacuum systems associated with thin film techniques are not needed, and in many cases consumer level printers can be converted for scientific use. Techniques based on dispensing of liquids (pipettes, inkjets) are typically used for the synthesis of discrete composition libraries. Less commonly, electrochemical processes have been used for synthesis purposes. McFarland and co-workers demonstrated combinatorial library synthesis through novel use of etching [47] to vary porosity in anodized alumina, and combinatorial electrodeposition of Pt-WO_3 catalysts was also reported [48]. However, by far the most common deposition techniques employed are inkjet printing and pipetting [49–52] which are discussed below, but ultrasonic misting [53,54] (Fig. 8) has also been used.

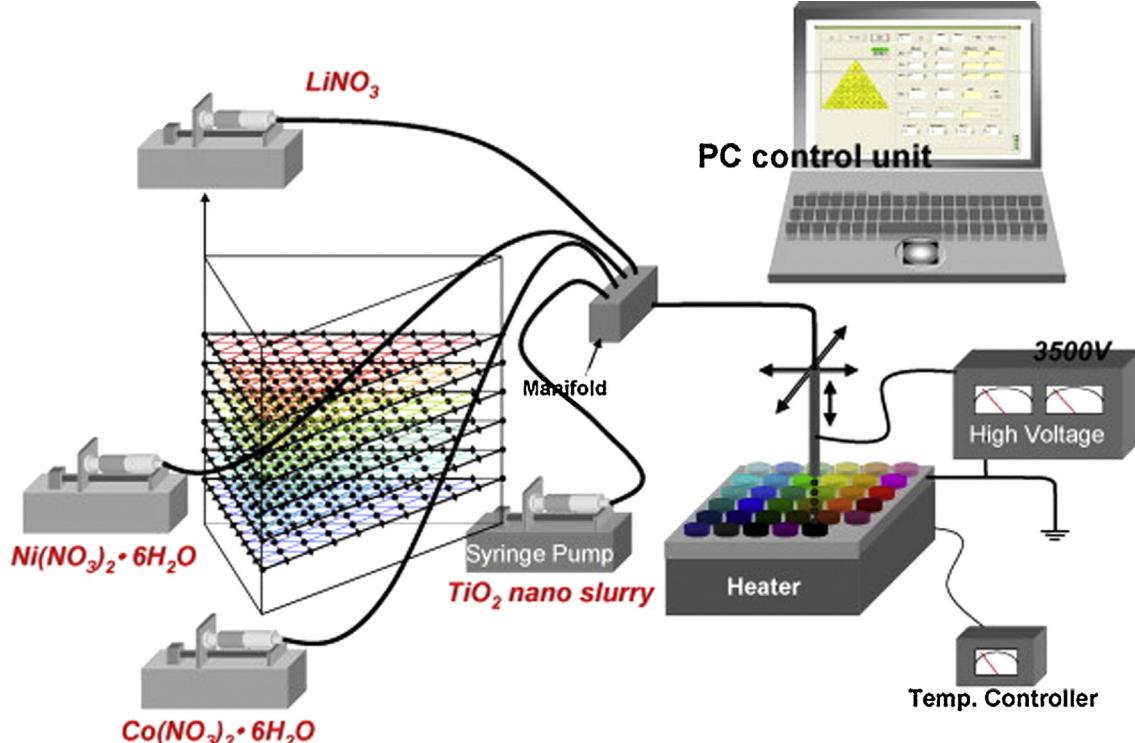


Fig. 8. Schematic of mist-based system for combinatorial powder synthesis from liquid precursors.

From [53].

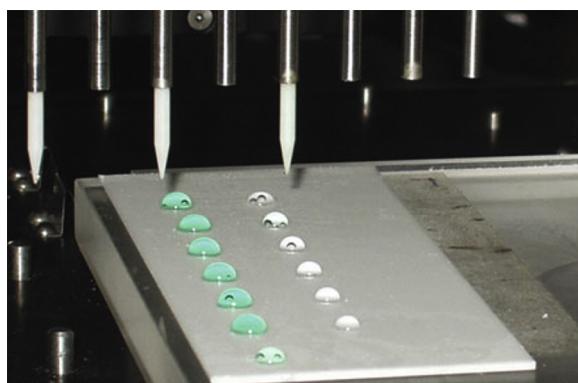


Fig. 9. Spinel precursors dispensed onto an alumina plate coated with stearic acid to control solution wetting.
From [58].

2.2.1. Inkjet

Inkjet dispensing of liquids is inexpensive and readily adapted to a variety of precursor chemistries. Both consumer and technical inkjet devices have been utilized by researchers. The application of inkjet technology for combinatorial oxide synthesis has been recently reviewed so will only be briefly recapped here [55,56]. Liquid precursors (e.g. nitrates, acetates) are dispensed into well plates, onto paper or other absorbing substrates, or coated glass, silicon or other bulk substrates. Inks made from both soluble and insoluble colloidal suspensions have been utilized. Polymers have also been printed, but are beyond the scope of this work. Inks are dispensed sequentially, but interdiffusion of the constituents occurs readily in the liquid state. After drying the printed dots are heated to produce the desired metal or oxide compounds, as is needed. The wetting of deposited drops on the substrate can be controlled to produce drops of preferred size [57,58] (Fig. 9). The final compounds may be of a particulate or cracked film nature, so are not suited for all types of characterization or screening. Inkjetting is a relatively high speed process, so large libraries can be rapidly synthesized [59,60], even if multiple passes are required to deposit

enough material to satisfy characterization needs. For libraries intended for electrochemical studies, conducting substrates (FTO-coated glass or carbon paper) are often used.

2.2.2. Powder slurry dispensing

Dispensing of powder slurries has also been utilized for discrete library synthesis in combinatorial research, but to a much more limited extent [61–65]. A significant challenge is insuring that the components are suitably mixed and that separation does not occur [66].

3. Electrochemical screening

Characterization or screening of electrochemical properties has generally involved one of four approaches that will be discussed below. These are: (1) parallel screening by optical detection of electrochemical activity, (2) parallel screening in multi-channel electrochemical cells, (3) serial electrochemical activity characterization by scanning electrochemical microscopy, and (4) serial characterization by scanning droplet cells. In many cases the screening technique will determine the best library format, as it may not be equally well suited for all types of samples. Screening/characterization techniques can be differentiated by several characteristics. A primary distinguishing factor is whether the technique permits parallel (simultaneous) screening of all library compositions, or is serial in nature. Additionally some techniques are specifically designed to characterize samples under actual or near operational conditions, while others only screen under approximate conditions. It is important to note that deviations from operational conditions can be particularly important in electrocatalysis studies as reactivity and catalytic mechanism can be sensitive to electrochemical conditions, in particular the solution pH.

3.1. Parallel screening

3.1.1. Parallel screening by optical detection of electrochemical activity

Optical detection methods are appealing for use in combinatorial studies because they tend to be fast, allowing large numbers

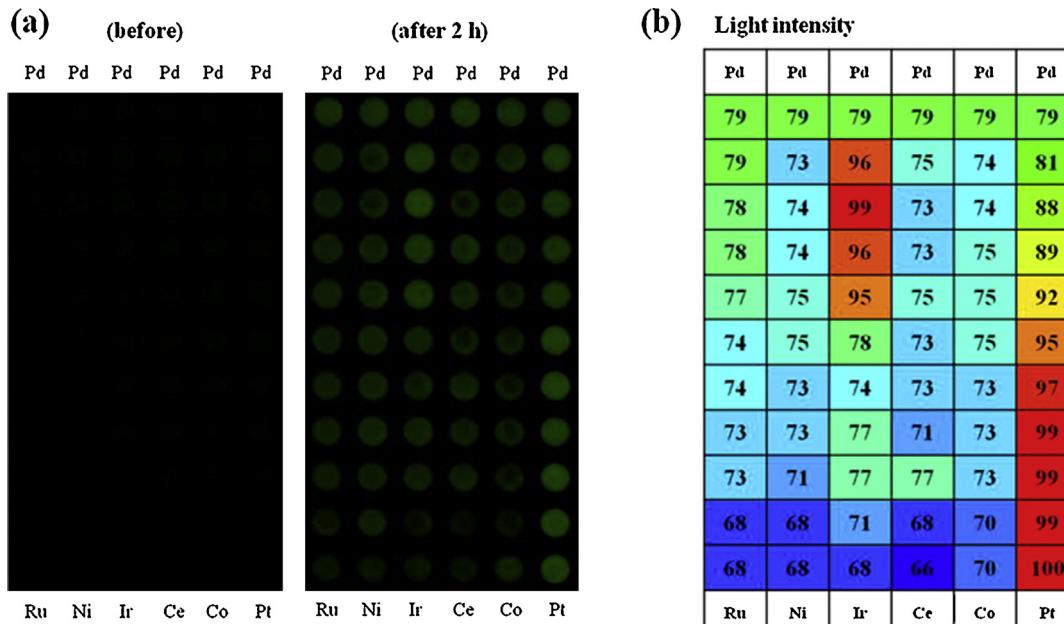


Fig. 10. (a) Images from optical screening for Pd based array at a constant potential of 0.8 V (vs RHE); before (left) and after 2 h (right). (b) Degree of brightness of catalyst spots.
From [70].

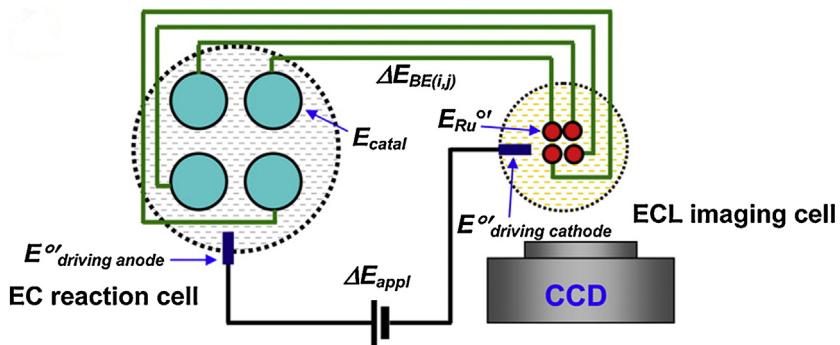


Fig. 11. Schematic diagram of an ECL imaging based screening platform for electrocatalysts used in fuel cells.

From [85].

of candidate compounds to be rapidly screened. They are most commonly based on the use of a fluorescent indicator to signal the presence or absence of ions in the diffusion layer near an electrocatalyst surface. This approach is equally suited for powders or films. In the pioneering work of Smotkin and Mallouk, compounds active for electrooxidation of methanol were screened using quinine as the fluorescent indicator. It fluoresces at a pH < 5, so was an indicator for the production of H⁺ by active electrocatalysts [49]. This approach has since been utilized in many other studies searching for electrocatalysts that promote the oxygen reduction reaction (e.g. Fig. 10) [67–71], methanol oxidation [72–79], ethanol oxidation [76,80] and oxygen evolution during electrolysis [81]. The popularity of this technique is because it is fast, low cost, and relatively easy to implement.

Photocatalysts have also been the subject of many combinatorial investigations, as they are well suited for optical screening [52,82,81,83]. In some cases, fluorescence indicators have been used for screening and then followed up by traditional electrochemical investigation of the most active compositions [81,84].

One variation on the fluorescent approach was described that uses a bipolar cell, where an electrochemiluminescence (ECL) reaction at the anode is used to image currents resulting from the reaction at the cathode [85]. This technique uses the ECL intensity of one system (Ru(II)+tripropylamine) to estimate the electrochemical reaction currents of another system (the system being screened). Hence, their test system has an electrochemical cell connected to the ECL cell (Fig. 11). The electrochemical cell has an array of glassy carbon electrodes on which candidate ORR catalysts are loaded. The ECL cell has a corresponding array of Pt anodes on which ECL reactions (Ru(II)+tripropylamine) can occur. When sufficient potential is applied to the system the ORR of the cathode array will drive the ECL reactions in the anode cell, yielding light that is detected by a CCD camera.

Another clever adaptation of the fluorescence approach was recently reported for screening potential water oxidation electrocatalysts [86,87]. This technique employs a fluorescence-based parallel screening method to directly detect electrolytic oxygen-evolution activity of catalyst arrays under alkaline conditions. A stainless steel mesh is coated with a commercially available paint, widely used to visualize air flow across aerodynamic surfaces, that contains a fluorescent compound that is sensitive to oxygen. Both the intensity and the fluorescence lifetime of the paint change in response to oxygen [88]. The coated mesh is positioned in the electrolyte parallel and close to the library (an array of oxide compounds deposited by pipetting onto FTO-coated glass) (Fig. 12). During electrolysis under constant-current conditions, the mesh was illuminated with an appropriate wavelength of light. Fluorescence changes due to the presence of oxygen could be detected by a camera.

A novel approach was described that used an electrochromic counter electrode as an optical screen for methanol oxidation on platinum-based catalysts [89]. Protons from the electrolyte are intercalated into the electrochromic counter electrode to balance the charge passed at the working electrode, causing a color change from colorless to blue in the counter electrode. The intensities of blue color across the counter electrode correspond to the electrocatalytic activity, with darker shades signifying more current corresponding to a more active catalyst. Either oxidation or reduction reactions can be screened, by starting the test with the counter electrode in the bleached or colored condition, respectively. This technique is limited to systems with intercalatable species, but that makes it well suited for fuel cells and Li-ion batteries.

A parallel technique that uses an optical, non-fluorescent technique was recently reported for evaluating electrocatalysts for the oxygen reduction [90,91] and hydrogen evolution reactions (HER) [92]. Candidate compounds are screened in a bipolar electrochemical cell where a pair of driving electrodes are used to produce an electric field in the electrolyte (Fig. 13a) [90]. Each of the electrodes on a glass slide (36–72 of them) is 4 mm long and has a cathodic pad that is 325 μm wide. The candidate compounds are inkjet deposited on these pads. The functional anode (opposite end) of each electrode is modified with 100 individual Cr microbands (5 nm-thick, 10 μm-long, 10 μm separation) (Fig. 13c). When a sufficiently high potential is applied across the driving electrodes, the HER will proceed at the cathode pad, which, by virtue of its electrical coupling, will cause anodic dissolution of the Cr microbands at the opposite end of the electrode. The highest overpotentials occur at the extreme ends of each bipolar electrode (Fig. 13b) so dissolution starts there. The better the catalyst, the greater the number of Cr microbands that will be dissolved (Fig. 13c). As bands are dissolved, the overpotential will decrease and the rate of dissolution becomes very small. The number of bands dissolved is easily determined by optical microscopy, so the relative performance of the electrodes can be quickly evaluated. By recording videos of the dissolution of the Cr bands, it is possible to obtain kinetic data about the catalysts, which may yield quantitative kinetic information.

Finally, an optical technique has been recently reported that uses detection of bubble evolution to screen of oxygen evolution reaction (OER) catalysts [93]. A camcorder records bubble development during screening in a compact cell (Fig. 14). This was demonstrated with a (Ni–Fe–Co)O_x electrocatalyst library that was successfully screened in less than 1 min. Independent screening of the same library using a scanning droplet cell showed good agreement between the two techniques. With proper data interpretation to eliminate false negatives, this parallel bubble screening method permits rapid identification of OER and HER electrocatalysts.

With fluorescence techniques the allowed pH value for the cell is narrow (e.g. 3–5) to be compatible with both the pH indicators

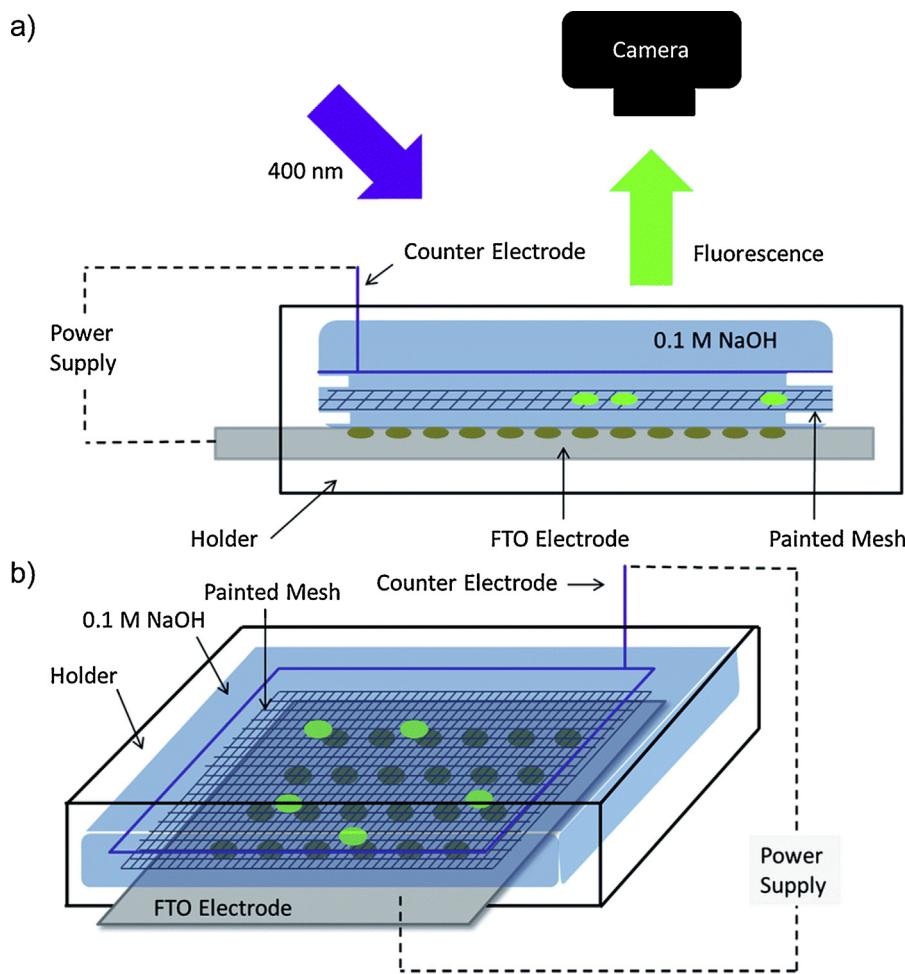


Fig. 12. Schematic drawings of the fluorescence cell to detect electrolytic oxygen-evolution activity of catalyst arrays under alkaline conditions. (a) Side and (b) perspective views of the screening apparatus.

From [87].

and catalysts. However, this may not be the optimum conditions for either the electrochemical reaction or for the fluorescent imaging, and will not be the same as the real conditions during use, such as for a fuel cell. The bubble detection technique has the advantage, that unlike the fluorescent techniques it is not limited to a narrow pH range. It can be applied in strongly acidic or basic environments, and it also can be used to screen H₂ bubbles so screening for HER catalysts is possible.

As noted above, the choice to use fluorescent detection often times is based on speed, cost, simplicity, etc. This is used as a screen to help identify regions of high activity, rather than produce archival data.

Many of the early studies utilizing fluorescent detection of electrochemical activity in combinatorial studies were aimed at electrocatalysts for use in PEM or DMFC fuel cells. This prompted a study comparing several high throughput screening techniques used for DMFC anode electrocatalysts, including fluorescence screening, voltammetry with a rotating disk electrode, a 25 electrode combinatorial array fuel cell with a common counter electrode, and a conventional DMFC [94]. It was noted that the conditions used in fluorescence screening, as well as other approaches (e.g. scanning electrochemical microscope) do not closely match the conditions used in an operating fuel cell. For example the electrolyte in the fluorescence studies is a liquid rather than a polymer (e.g. Nafion), a fuel cell typically operates at temperatures higher than room temperature unlike most testing, and

catalysts may not be on a support and are often not conditioned prior to screening as in real fuel cells. It was concluded that for fuel cells, fluorescence screening is reliable as a first level screen, but that such studies need to be followed up with a more precise testing technique [94]. This touches on a recurring issue in combinatorial screening studies regarding the quality of data one expects to generate, i.e. identifying promising leads or generating performance data such as might be used in data mining/materials modeling. Fluorescence-based techniques are well suited for the former, but not for the latter. Moreover, for all screening approaches, the further removed the conditions are from actual use, the more critical it is that follow-on studies by traditional techniques verify what conclusions can reliably be drawn regarding functionality under real conditions. In general one needs to realize the goal is generally to spot trends in data with variation of a parameter, which is the strength of these screening approaches. It is often more important to rapidly narrow down the number of possible candidate for in-depth examination, rather than to report the actual value of a particular property under specific conditions.

3.1.2. Parallel screening in multi-channel electrochemical cells

While optical screening electrochemical activity by techniques like fluorescent detection are quite rapid, screening of electrochemical activity by employing multi-channel potentiostatic measurements can offer better quantification. Both multichannel

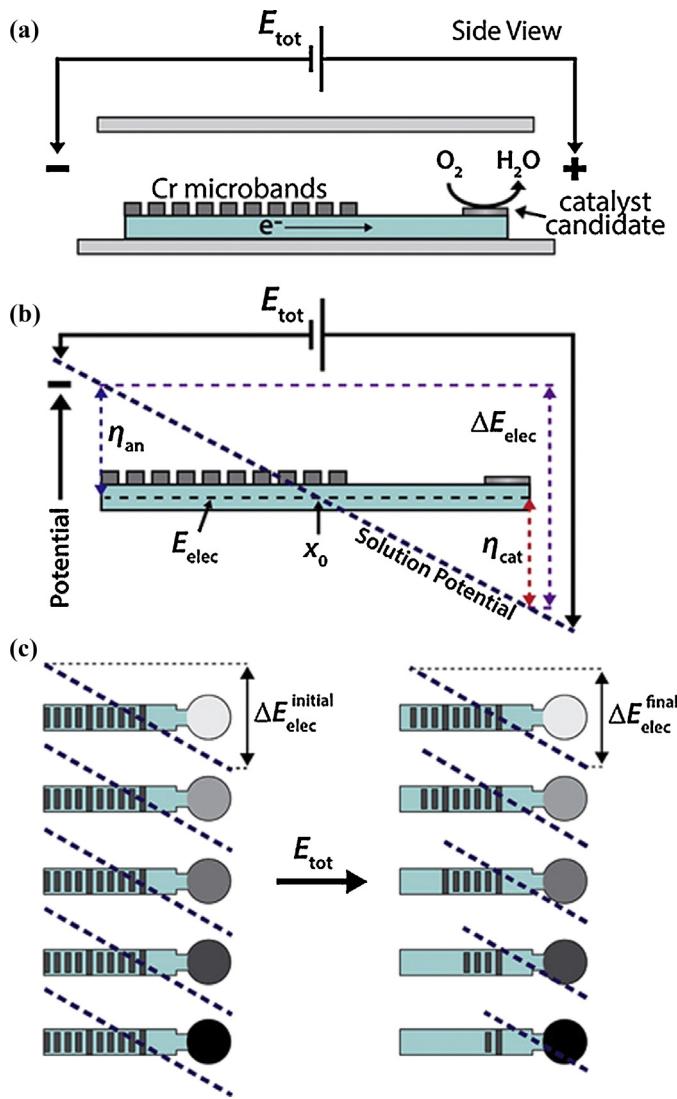


Fig. 13. Schematic diagram of the operational principles of a bipolar electrochemical cell for evaluating electrocatalysts for the oxygen reduction reaction.

From [91].

half-cell and multi-channel full-cell techniques have been utilized for samples in the form of thin films or powders.

In the parallel approach, electrochemical reactions in multiple cells, usually with small working electrodes, are simultaneously monitored. These parallel cells can either be isolated, or share a common electrolyte. In some studies multichannel cells are prepared but not monitored in parallel; this approach offers rapid preparation of electrolyte contact to an array of working electrodes, and then each electrode is addressed sequentially by the potentiostat while the remaining electrodes are idle [95].

Jiang developed an inexpensive electrochemical cell array employing a common air-electrode cathode that is suited for screening of both fuel cells using a polymer electrolyte membrane or metal/air batteries using a separator and a liquid electrolyte [96]. In both cases serial characterization was performed on ink-based particulate samples using a moveable probe designed around a graphite rod. Such an approach can be enhanced if the system is coupled with another analysis technique like differential electrochemical mass spectrometry [97,98]. What these serial approaches may lack in speed compared with parallel testing, they can make up for in the quality of data one can obtain. This is especially true if the material form and test environment is close to that of the real application conditions.

More rapid analysis is possible if the working electrodes of a multichannel array are all biased simultaneously by a potentiostat while the currents are continuously measured in parallel. If a common electrolyte is used, care must be taken in the cell design such that neighboring electrodes do not interfere with each other. While many expensive cells are designed specifically to accommodate samples from unique synthesis instruments, as discussed below, inexpensive planar multielectrode arrays are sold commercially for neuroscience research (e.g. ALA Scientific Instruments). These have been adapted for combinatorial materials studies, with a common electrolyte and electrodes being addressed sequentially [99].

More extensive studies have been published involving special cell designs to accommodate specific deposition or characterization equipment [44,45,100–103]. Researchers at Symyx, a pioneer in the development of combinatorial tools, developed a multielectrode microarray consisting of 64 titanium pads (each 1.7 mm in diameter) formed lithographically on a 3" quartz wafer [100]. The thin film catalyst compositions were deposited in thickness wedges utilizing moving shutters, as described above. They used the cell to simultaneously monitor the performance of ternary compositions of Pt–Ru–M (M = Co, Ni, W) in methanol electrolyte solutions. Strasser et al. also demonstrated the use of their multiarray system to examine oxygen reduction [104]. They reported a Pt–Co–Cr

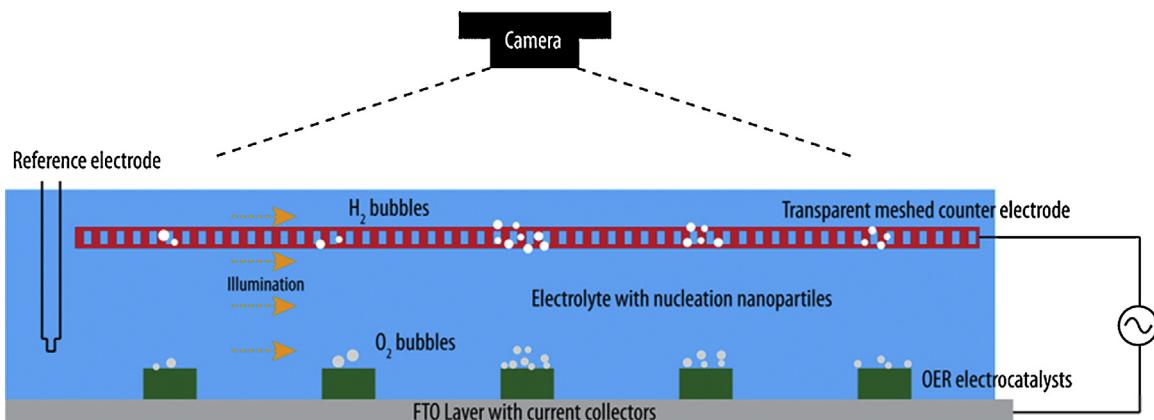


Fig. 14. Schematic cross-section of the bubble screening cell, where the green rectangles represent the material library under test and the red bars represent the mesh counter electrode.

From [93].

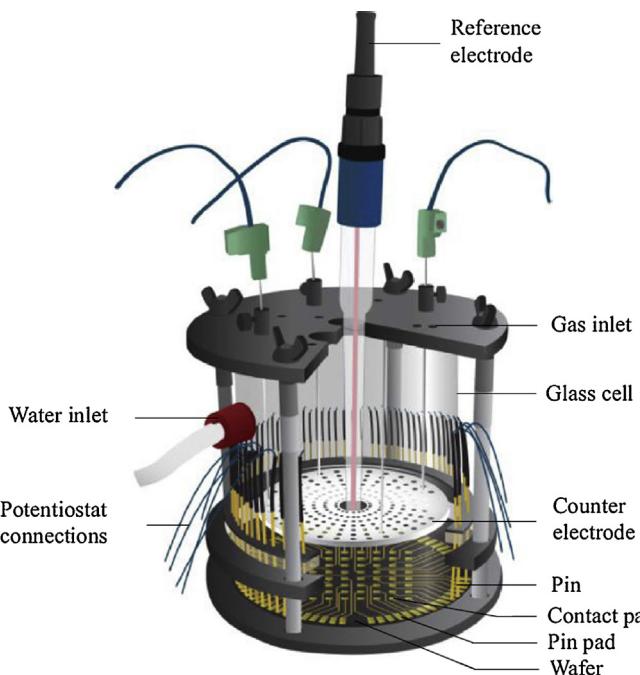


Fig. 15. Schematic of a cell designed for parallel screening of 64 member libraries deposited on 100 mm wafers.

From [45].

composition with very improved activity and verified its performance when fabricated as a high surface area powder and tested with a rotating disk electrode. A variation of this approach, using a cell designed around the use of 50 mm Si wafers has been used for HOR, ORR, and other applications [102,103,105]. A cell designed for 100 mm wafers coupled to a 64 channel potentiostat has also recently been described (Fig. 15) [45].

The Dahn group reported array test cells developed to characterize thin film libraries for both fuel cell and battery electrode applications (Fig. 16). Their cell design was based on 114 mm × 114 mm glass plate substrates [106,107]. A layer of Cu is sputtered onto the glass substrate and then etched into a pattern of leads and electrical contacts through photolithography. The combinatorial array is then sputtered onto the Cu contact pads using their moving mask system described earlier. The cathode composition is varied across the electrically addressable contact pads. For batteries the O-ring sealed cell is filled with liquid electrolyte, a separator is inserted, followed by a common lithium foil anode.

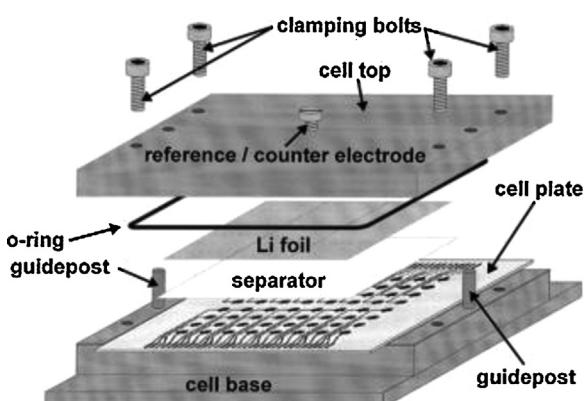


Fig. 16. Schematic of a combinatorial electrochemical cell for testing thin film Li-ion battery cathode compositions.

From [107].

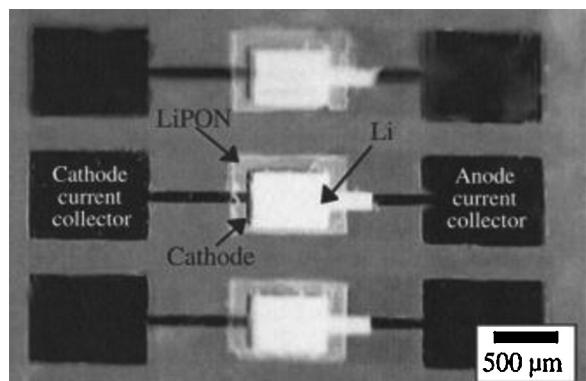


Fig. 17. Optical micrograph of solid state microbatteries comprising a thin-film test cell.

From [113].

In testing, the combinatorial electrochemical cell produced data comparable to coin-cells with identical active material, but with increased efficiency and data collection rate.

Guerin and Hayden and co-workers et al., in their earliest combinatorial studies fabricated a multiarray with 64 working electrodes and used it to investigate particle size effects on the ORR [108] and cathode candidates lithium batteries [109]. These first libraries were powder based materials, and they subsequently designed a 100 element cell for characterizing thin film samples synthesized by co-evaporation through a contact mask [110]. In more recent work they have described a number of innovative related cells for tackling different electrochemical related issues, and significantly ramped up their cell sophistication as part of work in a company they founded (Ilika Technologies Ltd; www.ilika.com). For example, they developed a cell to study solid electrolytes for Li-ion batteries [30]. Here they deposited an array of compositions in the $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ solid solution, which is a solid state lithium ionic conductor. Impedance spectroscopy measurements were made through an array of 0.25 mm platinum contacts deposited onto the library composition. The measurements were automated using a probe station. They also developed an approach for screening of the corrosion resistance of Ni-Cr [111] and Ni-W thin film alloys, using a (10×10) silicon nitride micro-fabricated array of independently addressable working electrodes for high throughput electrochemical screening of the alloys [112].

For any of the parallel cell designs it is important to characterize and understand any effects of cell geometry on measured signals. For example, in traditional 3-electrode cells ohmic losses due to resistance between the reference and working electrode ("IR drop") are monitored and corrected for. Some parallel screening cell designs involve parallel working electrode and counter electrode plates, creating a high aspect ratio electrolyte volume. With such an electrode geometry, it is challenging to ensure a properly sensed solution potential with a non-optimally positioned reference electrode, which is not always considered in multi-channel cell electrochemistry investigations.

Other researchers have reported novel microarrays to characterize solid-state microbatteries with varying $\text{Li}_y\text{Mn}_x\text{Ni}_{2-x}\text{O}_4$ cathode compositions ($0.2 \leq x \leq 1.8$ and $2.7 \leq y \leq 3.7$) (Fig. 17) [113]. These batteries were deposited by a combination of sputtering and evaporation. Lithium phosphorous oxynitride (LiPON) was sputtered as the electrolyte, while evaporated Li was the anode. The test cell substrate fabrication began with deposition of $590 \mu\text{m} \times 590 \mu\text{m}$ Pt current collectors. A composition gradient of cathodes was sputtered, followed by sputtering of LiPON evaporation of Li and a protective parylene layer. Electrochemical characterization was performed in parallel using a computer-controlled potentiostat.

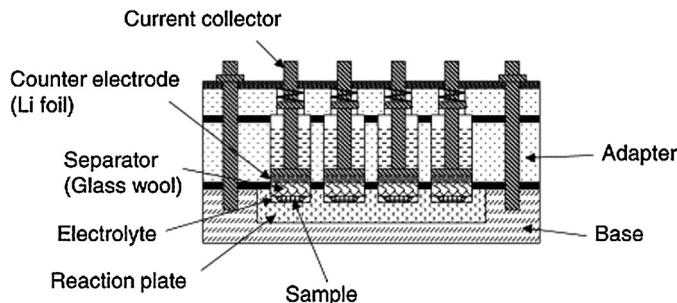


Fig. 18. Schematic cross-sectional view of the combinatorial electrode array for testing powder compositions for battery cathodes.
From [118].

It was found that the thin-film cathodes had similar structural and electrochemical performance parameters as their bulk counterparts, suggesting this is a viable approach to investigate novel cathode chemistries. Kawamura reported a combinatorial microbattery array with $\text{LiCoO}_2\text{-LiMn}_2\text{O}_4$ mixed cathodes prepared by PLD and characterized by parallel cyclic voltammetry [114,115].

In a later study Whitacre et al., described development of a 36 electrode microarray to study DMFC anode electrocatalysts (Pt/Ru and two compositional regimes of the quaternary Ni/Zr/Pt/Ru system) [116,117]. They developed a 36-channel pseudopotentiostat like that reported earlier by Dahn and co-workers [106]. The array was immersed in the electrolyte, along with a reference and counter electrode. A novel feature was the incorporation of a hot plate/stirrer permitting the solution to be heated up to 60 °C while also continuously stirring, approximating the conditions encountered with a rotating disk electrode [117]. The variability of oxygen flow between test electrodes was found to depend on the rate of stirring, the oxygen flow rate into the solution, and the cell geometry. Hence, results needed to be corrected for mass transfer effects. This illustrates the need with any combinatorial cell design to properly evaluate any possible geometric effects by measuring a single composition library, such that any variability in results can be attributed to cell geometry.

Takada et al. also developed a cell for characterizing combinatorial battery electrode materials in powder form (Fig. 18) [118]. Powder was synthesized and sintered in the reactor plate/cell, and subsequently electrolyte was added to each well. A piece of glass wool was used as a separator, and then Li foil was attached to the current collector as a counter electrode, completing the cell. Multi-channel potentiostats were used for characterization. Performance

was lower than typically processed materials because the materials were sintered and there was no carbon conductor in the electrodes. However, repeatability was good, suggesting that this combinatorial electrode array is well suited as a first-level screening of electrode materials.

Strasser co-authored studies with two different groups describing development of 16 cell 4×4 arrays for testing of powder versions of electrocatalysts [119]. The catalysts were deposited on polished glassy carbon working electrodes. The electrodes were isolated in individual electrolyte wells, with each sample being independently controlled by a multipotentiostat [119]. The systems were used to examine Ru-containing OER electrocatalysts [120] and Ni-based binary and ternary alloy catalysts for hydrazine electrooxidation for use in anion exchange membrane fuel cells.

As noted above, the cell described by Whitacre [117] used a stirred electrolyte to approximate the electrolyte convection of rotating disk electrode (RDE) studies. Rather than approximating RDEs, the approach of Honda researchers utilized 16 parallel RDE cells [121–123]. This apparatus was specially designed to use thin film samples deposited directly onto RDE electrodes in a combinatorial sputtering system. The obvious appeal of this approach is that one can directly compare thin film and powder versions of a composition using the same characterization technique. A similar approach using five parallel RDE units has also been described by Hatchard et al. for testing of thin film electrocatalysts [124].

Once the data acquisition and electronics are developed for one array cell design, a variety of other cells can be designed to attack other applications. For example, the Dahn group adapted the technology they developed for testing arrays of lithium-ion battery electrode materials to a 64-electrode fuel cell test platform [125]. In this cell individual contact is made to powder catalyst electrode gas diffusion layer disks by 6 mm graphite rods. The electrode block has a serpentine flow field to supply gases to the catalysts under test. The cell also incorporates a common counter/reference electrode. The advantage of such a cell is that it offers conditions closer to the actual operating conditions used in a fuel cell.

Finally, an improved fuel cell design offered commercially by Nuvant (\$21,000 US; <http://nuvant.com/products/fuel-cell-reactors/array-fuel-cell/>) has five independent flow field columns with five electrode spots each, allowing one to vary gas flow to particular sections of the array so that gas flow/humidification can be a variable under test in addition to composition. This is a good example of how specialized cells can be designed to attack specific industry problems. Of course, the size of an array that can be measured in parallel may be limited by the complexity and cost of the associated instrumentation. Hence complex, “real world” cells are

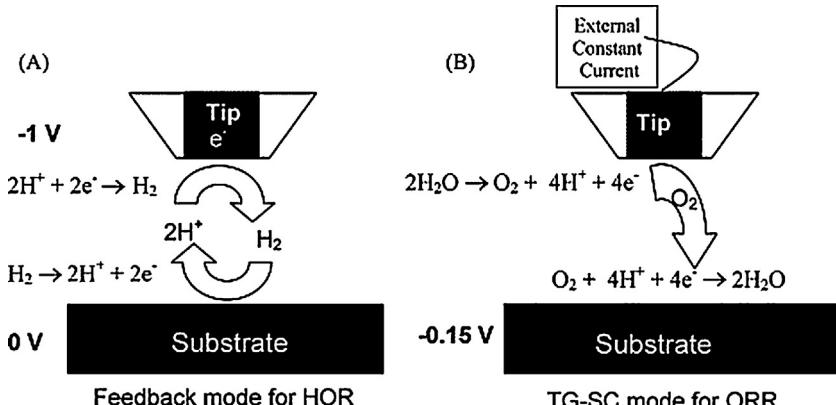


Fig. 19. Schematic diagrams of the SECM working under feedback mode for studying HOR (A) and under the current modified TG-SC mode for studying ORR in acidic media (B).
From [128].

more commonly found in industrial rather than academic settings. However, these are the types of cells needed in industry with actual operating conditions in order to have confidence in the applicability of the test results.

3.2. Serial electrochemical activity characterization

A few examples of serial characterization of electrochemical activity were mentioned above in the context of fuel cell testing. More extensive serial characterization has occurred through the application of two relatively new electrochemical characterization tools, scanning electrochemical microscopy (SECM) and scanning droplet cells. These techniques both make use of robotic positioning of an electrochemical probe across a sample surface. The most significant difference between these two techniques is that in SECM investigations the entire library is continuously immersed in the electrolyte, whereas in droplet cells the only composition/area under investigation is exposed to the electrolyte, and the electrolyte is replaced between measurements.

3.2.1. Scanning electrochemical microscopy

A scanning electrochemical microscope (SECM) consists of an xyz positioning system and an ultramicroelectrode (UME) tip. Characterization using a SECM involves the measurement of electrochemical currents as the UME tip is scanned across the sample surface while immersed in an electrolyte at a controlled separation distance. Hence it is easily adapted for use in characterizing combinatorial libraries. SECM has been used for screening potential electrocatalysts for ORR [126–128] and HOR [129–133] for PEM fuel cell applications, as well as OER for solar fuel applications [134,135]. Recent reviews detail much of this work [136–138].

Electrocatalysts screening is usually performed in one of two ways: feedback mode (tip collection) or tip generation-substrate collection mode.

The characterization of potential hydrogen oxidation catalysts for a fuel cell anode illustrates the use of feedback mode (Fig. 19A). Here one uses the proton/hydrogen redox couple as the tip reaction, with the substrate (combinatorial library) potential set at 0 V while the tip is held at a constant potential such that the tip reaction is the diffusion-limited reduction of protons to generate hydrogen. With very small tip-substrate separation, the hydrogen generated at the tip diffuses to the sample surface, where it can be oxidized if the sample surface is electrochemically active. The protons created by oxidation can then diffuse back to the tip surface, where they are reduced by the reverse reaction, resulting in additional tip current. The rate of hydrogen oxidation at the substrate determines their concentration near the tip, and hence the probe tip current. Variations in the tip current as the tip position is moved over different regions in a combinatorial library can be used to characterize the relative reactivity of the sample.

For reactions like the ORR in an acidic solution, the reaction cannot be studied efficiently in feedback mode. Since water is in the bulk electrolyte and plentiful around the tip, and is also the ORR product, its feedback diffusion to the tip will not cause tip current to change. In this case the tip generation–substrate collection (TG-SC) mode is used, as developed by Bard [126,127]. In TG-SC mode (Fig. 19B), a constant oxidation current is supplied to the tip from an external source so oxygen is generated at the tip (i.e. tip generation TG) which diffuses to the substrate. The substrate is held at a potential where oxygen is reduced on ORR active areas (i.e. substrate collection). In this mode, the substrate current is monitored instead of the tip current. Again, by comparing the current from different compositional regions, the ORR catalytic activity can be mapped.

A typical SECM has relatively high sensitivity, with a diffusion-limited current for a 1 μm radius tip in a 1 mM solution of a typical

redox species being approximately 200 pA [139]. The spatial resolution of a SECM depends on the tip diameter, which is not a concern for characterization of discrete libraries where the pad dimensions will far exceed a relatively large tip diameter (e.g. 50 μm). For continuous gradient libraries, the composition increment resolved will be governed by the tip dimensions. For feedback mode, precise control of the tip-substrate separation distance is critical and must be carefully controlled. This makes scanning over large areas challenging. Improved functionality has been reported with development of an exchangeable tip instrument that combines scanning differential electrochemical mass spectrometry with a SECM [140].

However, the biggest experimental challenge with using SECM for combinatorial characterization is that the entire library is submerged in the electrolyte for extended periods of time. This can lead to changes in surface properties of compositions due to adsorption or corrosion processes. Thus some library elements may be degraded in the electrolyte before they are characterized. Additionally, there is the possibility of tip fouling or passivation over long times in the electrolyte bath. Pipet- or droplet-based techniques can overcome many of these issues.

3.2.2. Serial characterization by scanning droplet cells

The primary characteristic of a scanning droplet cell or microcapillary cell is that it utilizes a standard 3-electrode configuration cell of a microliter volume that contacts only a small surface region at any time [141]. Like a SECM it relies on xyz positioning of the cell. However, the scanning droplet cell technique offers significant advantages compared to SECM for combinatorial work because only a certain confined location of the sample is exposed to the electrolyte at any time, and the electrolyte can be refreshed, or even analyzed downstream [142,143]. This is a real benefit for large libraries with hundreds of samples. Although the area sampled by a droplet cell may be larger than the smallest tipped SECMS [144], this is not a significant limitation for combinatorial studies, especially for discrete composition libraries. Among the experimental challenges with droplet cells is achieving a good seal to the sample surface, with silicone being the usual choice as a pliable gasketing material [145]. This is especially critical in combinatorial work where the tip will be repositioned numerous times in the course of characterizing a library. Recently, Gregoire reported a novel gasketless design [146]. It relies on pumping electrolyte outlet ports at approximately twice the inlet flow rate. This excess pump rate leads to a suction of ambient gas into the probe region, eliminating the need for a gasket. A variety of cell configurations have been reported, as discussed in a recent review [147]. An example of one cell design is shown in Fig. 20. As depicted, only a small volume of electrolyte (microliters) is needed to fill the cell. The most significant development, especially for combinatorial work is the evolution of flow-cell designs, which permit downstream analysis of gases or reaction byproducts [145,146,148]. With the ability to refresh the electrolyte between measurements, the possibility of cross sample contamination is greatly reduced. A flow-cell also has the added benefit that electrolyte flow over the working electrode mitigates mass transport effects, as in RDE experiments. With the use of 3D printing, cells can be customized to offer optimized fluid dynamics in cell designs that would otherwise be difficult to machine [149].

Haber et al. have demonstrated the power of scanning droplet cell screening in investigations of oxygen evolution reaction electrocatalysts [150,151], including one report where they scanned over 5456 (!) discrete compositions produced by inkjet printing [60]. Such screening has been extended by the same group. Shinde et al. characterized both the catalytic and the optical properties to better evaluate the characteristics required of photocatalysts for solar fuel generation, where the transparency of a catalyst is also important. Combined electrochemistry–spectroscopy

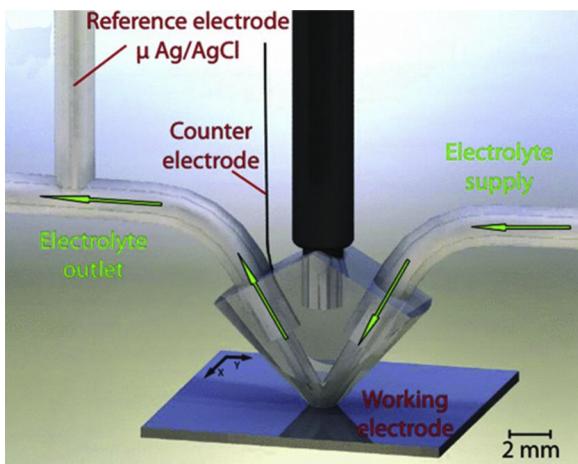


Fig. 20. Illustration of a flow-through scanning droplet cell design. From [145].

measurements were performed on over 1000 individual inkjetted compositions with a scanning drop cell with integrated optical illumination and detection [152]. In this application the catalyst is deposited on the surface of the light absorber, so the catalyst transparency controls how much light reaches the absorber.

4. Discussion

The majority of electrochemical combinatorial investigations have utilized either thin film deposition or inkjet/pipette synthesis techniques. As the survey of processing approaches describes, a library of samples may be processed to yield powders or films that may be either discrete or continuous in nature. For either thin films or powders, it is difficult to ensure that no property other than composition changes by small amounts. For example, in films there can be subtle changes in grain size or stress that accompany compositional variations [153], while in powders the surface area may change [154]. In most cases these will be relatively minor or can be minimized by process conditions, but it reinforces the emphasis on searching for changes in performance, based on some figure of merit, that exceeds any effects that minor materials variations might have. With a primary screen, the researcher is hoping to spot trends in a property with a parameter (e.g. composition) variation that can be further explored by more traditional routes, such as in real application conditions.

In screening of activity one desires to avoid both false positives (incorrect assessments of enhanced activity) and false negatives (incorrect assessments of activity, either none or reduced from the actual case). False positives will result in unnecessary work in subsequent testing, as one is testing a composition that in reality merits no further consideration. False negatives are potentially more undesirable if they result in missing a highly active catalyst. Hence it is a good experimental practice to design libraries that include a standard reference sample (i.e. a widely used, well characterized electrocatalyst), perhaps positioned at several locations in a library, as well as routine characterization of duplicate libraries. The use of reference samples allows better comparison between libraries in case a particular deposition run was marred by some undesired parameter variation (e.g. variation in background gas partial pressure during a thin film deposition).

Smotkin et al. [155] defined 4 criteria that a high quality combinatorial investigation of fuel cell catalysts should aim to include, comprising: (1) Inclusion of a relevant state-of the-art control composition. For a direct methanol fuel cell this would be a commercially available industry standard for methanol oxidation (e.g.

Pt50Ru50). (2) Catalyst fabrication should be by a scalable method: testing of a catalyst that cannot be mass produced is of less practical value. (3) The screening method should be decoupled from the catalyst fabrication technique. (4) The screening should be performed in as realistic conditions as possible.

The vast majority of combinatorial fuel cell investigations fail to meet several of the suggested criteria. These criteria are excellent for focusing an investigation and returning meaningful data, but they apply more to investigations that have already identified promising candidates and are at the stage of a secondary or tertiary screening investigation. More nimble screening techniques, perhaps farther from realistic conditions, can more rapidly sift through screening work thousands of candidate compositions. For example, the sample fabrication technique (criterion 3) may not be economically scalable, or not the preferred synthesis route for a particular application. In such a case, a combinatorial investigation needs to be followed up by an investigation of promising leads (compositions) in the final form and environment in which it will be applied.

Among the challenges for combinatorial experiments utilized for electrocatalysis applications is developing means to adequately assess catalyst stability. Material evaluation in combinatorial studies is designed to be rapid. Hence long term stability, of vital importance to manufacturers of batteries and fuel cells cannot be realistically evaluated. Some researchers have reported cursory evaluations of durability as part of their library evaluation [102], but such evaluations still need to be followed up by longer term evaluations. More recently, the need for durability characterization has been addressed in two studies using a cell design that permits extended stability measurements [156,157].

Assessing the selectivity of catalysts in complex reactions, such as the electroreduction of CO₂, is also challenging. The incorporation of downstream analysis of scanning droplet cell electrolyte helps to address this issue, but there is the possibility that such characterization may introduce a new bottleneck in the screening process.

Finally, many of the studies cited in this review identify new compounds that show superior properties to industry standard catalyst compositions (e.g. Pt for ORR). Reviewing all of these new compositions is not the subject of the present work, but it is worth noting that most of the novel materials resulted from studies that involved screening alloy systems with some prior known activity. In the future, the application emphasis of combinatorial electrochemistry experimentation may shift more towards verification of predicted materials properties rather than an emphasis on screening to accelerate materials optimization. This shift may be driven by a combination of the emergence of the Materials Genome Initiative (<https://www.mgi.gov>), wider availability of computational data bases such as The Materials Project (<https://materialsproject.org>) and continued improvement in materials modeling and simulation.

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