

Semiautomated Experiments to Accelerate the Design of Advanced Battery Materials: Combining Speed, Low Cost, and Adaptability

Published as part of the ACS Engineering Au virtual special issue "Materials Design".

Eric McCalla*



Cite This: *ACS Eng. Au* 2023, 3, 391–402



Read Online

ACCESS |

Metrics & More

Article Recommendations

	Traditional	Automated semi	Automated full
samples/yr	~500	15,000-45,000	8,000-72,000
cost	\$	\$\$	\$\$\$
structure	●	●	●
electrochem	●	●	✗

ABSTRACT: A number of methodologies are currently being exploited in order to dramatically increase the composition space explored in the design of new battery materials. This is proving necessary as commercial Li-ion battery materials have become increasingly high-performing and complex. For example, commercial cathode materials have quinary compositions with a sixth element in the coating, while a very large number of contenders are still being considered for solid electrolytes, with most of the periodic table being at play. Furthermore, the promise of accelerated design by computation and machine learning (ML) are encouraging, but they both ultimately require large amounts of quality experimental data either to fill in holes left by the computations or to be used to improve the ML models. All of this leads researchers to increase experimental throughputs. This perspective focuses on semiautomated experimental approaches where automation is only utilized in key steps where absolutely necessary in order to overcome bottlenecks while minimizing costs. Such workflows are more widely accessible to research groups as compared to fully automated systems, such that the current perspective may be useful to a wide community. The most essential steps in automation are related to characterization, with X-ray diffraction being a key bottleneck. By analyzing published workflows of both semi- and fully automated workflows, it is found herein that steps handled by researchers during the synthesis are not prohibitive in terms of overall throughput and may lead to greater flexibility, making more synthesis routes possible. Examples will be provided in this perspective of workflows that have been optimized for anodes, cathodes, and electrolytes in Li batteries, the vast majority of which are also suitable for battery technologies beyond Li.

KEYWORDS: Advanced battery materials, accelerated testing, automated synthesis, automated characterization, high-throughput experimentation, combinatorial synthesis

1. MOTIVATION FOR INCREASED EXPERIMENTAL THROUGHPUT

Advanced rechargeable batteries, thanks to state-of-the-art Li-ion batteries, have undergone monumental improvements in performance over the past 30 years in both increasing the amount of energy stored in the batteries and dramatically increasing the lifetime of batteries. Increasing the energy stored in the battery means increasing both the voltage (Li-ion batteries operate near 4 V, compared to about 1 V in aqueous rechargeable batteries such as lead acid) and the capacity (amount of charge transferred), which is limited by the amount of Li that can be transferred between the anode and cathode. Innovations made over those three decades have resulted in a 375% increase in

energy density in commercialized cells since Sony's first cells in 1990 (from 80 Wh/kg to over 300 Wh/kg), with another factor of 2 gain being seen in the lab-scale.¹ Some key materials innovations have been seen for the cathode active material, which have increased significantly

Received: August 1, 2023

Revised: September 27, 2023

Accepted: September 28, 2023

Published: November 4, 2023



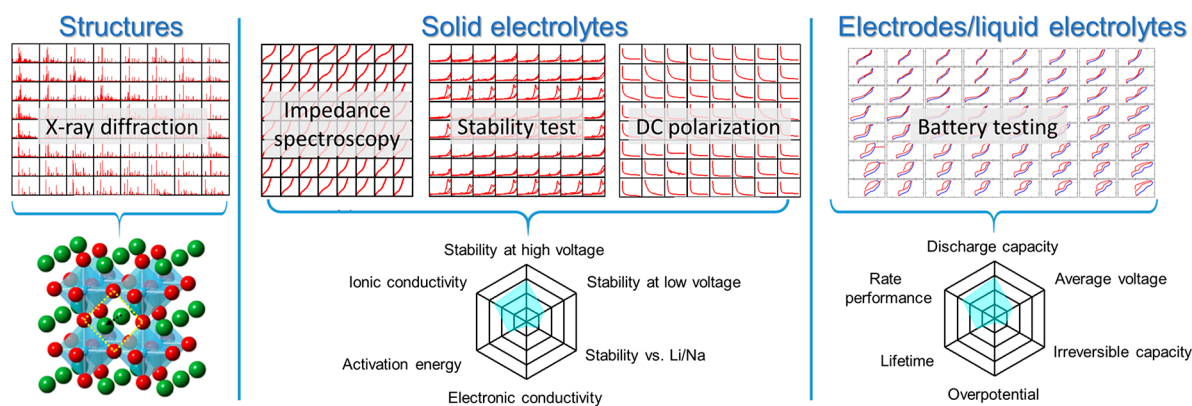


Figure 1. Illustration of the essential properties required to design new solid-state components for advanced secondary batteries. In all cases, structure must be determined, typically by X-ray diffraction. For solid electrolytes, multiple techniques are required to extract the essential electrochemical properties, while for electrode materials, battery testing is sufficient to extract the key properties. For liquid electrolytes, the methods are similar those used for electrodes in that battery testing is nominally sufficient; however, this testing must go on for very long periods of time (months) or have extremely high precision in order to discriminate with respect to state-of-the-art electrolytes. The sets of 64 illustrate the large quantity of data resulting from accelerated workflows. Portions reproduced from ref 30. Copyright 2022, the Electrochemical Society.

in complexity from simple LiCoO_2 to the far more complex $\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$, and these cathodes are now always coated with a different metal oxide to improve extended cycling.² Dopants are also often used to further improve the material's performance.³ This means that vast composition spaces need to be explored in order to identify the ideal composition for the cathodes in next-generation Li-ion batteries. Extended cycling has also been dramatically improved by exploring complex mixtures, with 5 or more different components in the liquid electrolytes being quite common, and even small changes (1% or less) in the amounts of each component can have significant consequences.⁴ Overall, these innovations have led to an extremely competitive battery chemistry that is enabling the widespread implementation of electric vehicles, and also very long-lived batteries with as many as 1 million miles of use being possible, though this depends heavily on the way the vehicle is used.⁵

Despite these impressive developments, it continues to be imperative to develop new battery chemistries with particular emphasis on more earth-abundant elements. Sustainability is expected to be a monumental challenge in going to full electrification of vehicles and to be even worse as we have built up energy storage in order to convert our grids to rely increasingly on intermittent renewable energy sources. In this regard, a high variety of strategies are being explored, including:⁶ all-solid Li batteries (this should improve safety remarkably by eliminating the flammable liquid electrolytes and potentially increase lifetime), Na-ion batteries to rely on more earth-abundant elements, Li-S batteries (both with solid and liquid electrolytes), and Li-air batteries. Each of these emerging battery technologies has serious drawbacks that are preventing commercialization. The solutions being sought once again lead us into more and more complex chemistries. For example: Na-ion cathodes with Na-Fe-Mn-O show promise^{7,8} but need at least one more element to help improve air stability.^{8,9} For solid electrolytes, a number of candidates show good ionic conductivity but are seriously limited by other properties.¹⁰ There is therefore a continuing need to look at vast composition spaces (varying both the elements present and their amounts) to further develop the key solid-state components in advanced secondary batteries (anode, cathode, and electrolyte).

A number of methodologies are currently being exploited in order to significantly increase the composition space that can be explored in the design of new battery materials. Traditional methods, where a few (5–10) compositions are made at a time, are an inefficient way to search through complex composition spaces. This need to explore complex compositions is exacerbated by the growing interest to use high entropy materials to further develop battery materials and in other energy applications.^{11–13} A recent series in *Nature Materials* highlights many developments in high-entropy materials and points to the need for further exploration.¹⁴ Thoroughly studying compositions where some

high-entropy combinations may be of benefit implies a requirement for a very large number of samples.

High-throughput computations coupled with machine learning have gained traction to screen rapidly across vast composition spaces.^{15–17} This is usually done by calculating a single necessary property (e.g., voltage in the case of cathodes) rather than determining all necessary properties (a number of which are impossible to compute, such as capacity retention in extended cycling). Such studies have been applied to each of the cathode, anode, and solid electrolyte in Li batteries. They typically yield extremely long lists of candidates that must be tested experimentally (e.g., a list of 572 potential cathode materials recently produced in ref 15), or they sometimes aggressively screen and risk overlooking viable candidates (e.g., computations reduced the candidate list of solid electrolytes from over 12,000 down to 21 in ref 16 by ignoring key properties such as kinetic stabilization of the electrolytes during battery operation). The long candidate lists generated in such studies certainly motivate accelerated experimentations, although the potential for overscreening by computation also suggests that casting a wide experimental net is justified. The need for large data sets is further enhanced when considering that low-level substitutions are often found to be extremely beneficial in battery materials (e.g., 1% substitution increased the capacity by 60% in ref 18), and this becomes prohibitive in computations due to the size of supercell required. Furthermore, DFT may not be sufficiently predictive for many battery properties. One simple example is electronic conductivity, which needs to be high in electrodes and low in electrolytes but is notoriously difficult to calculate as the band gap is often very sensitive to calculation methods and can also be strongly influenced by coatings and other inhomogeneities. These challenges with DFT limit its predictive power, especially where long-range interactions are at play, such that calculations where low-level substitutions are important may be particularly difficult. Thus, the example from ref 18 where 1% indium substitution triples the electronic conductivity could never have been predicted from DFT calculations.

Given the need for a large number of samples described above, it is also important to know the scope of characterization required to screen battery materials. Figure 1 illustrates the minimum list of properties that are required in order to develop state-of-the-art electrodes and electrolytes for secondary batteries. The biggest challenge in accelerating design, therefore, lies in the variety of methods that are required with high precision. Thus, automated laboratories are an attractive alternative in the design of battery materials to address this growing need for a larger amount of data to fill in the important gaps left by computations.^{19–23} Furthermore, this necessitates new experimental setups to perform the measurements either in high-throughput or combinatorial manners.^{24,25} Combinatorial here is used to refer to high-throughput approaches where the sample sizes are scaled down in order

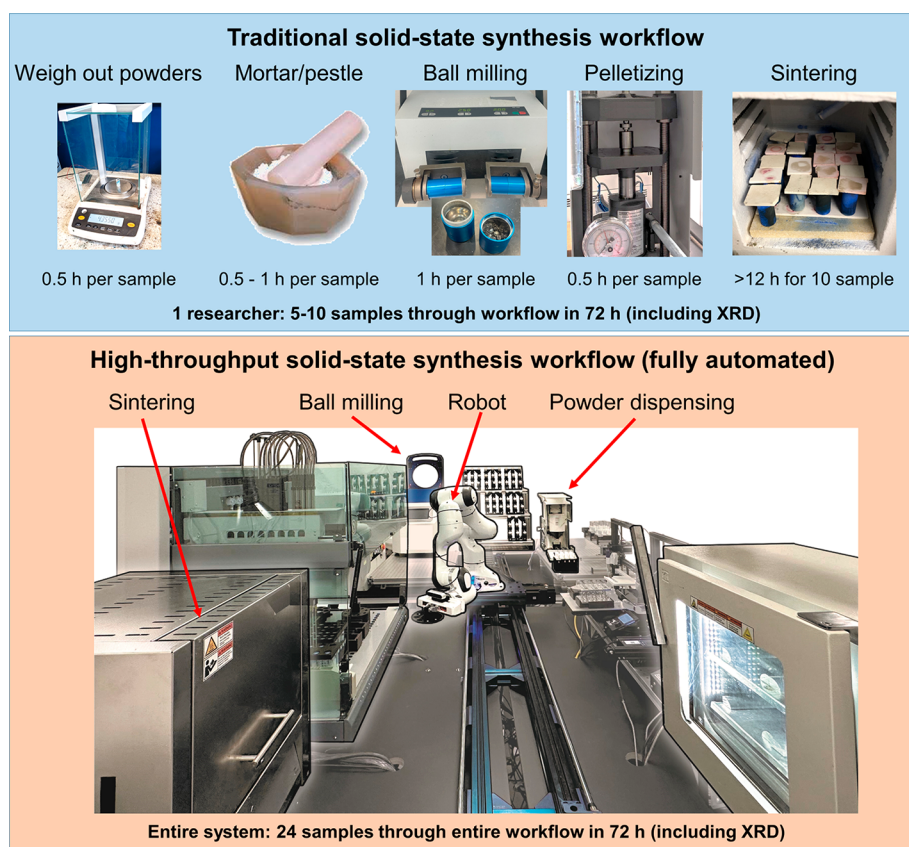


Figure 2. Comparison of traditional solid-state synthesis workflows to that obtained recently using a fully automated system (adapted from ref 22, reproduced with permission from the authors). Time estimates for the traditional workflow are based on the author's experience in various solid-state chemistry laboratories.

to permit parallelization of synthesis and measurements.²⁶ Examples of these exist for each of the anode,^{27,28} cathodes,²⁹ and electrolytes (both solid³⁰ and liquid³¹). Although a number of combinatorial approaches will be discussed in this article, they are not the main topic and they have been reviewed elsewhere.^{32–34} Rather, this perspective will focus on the potential roles of automation in the experimental workflows that utilize high-throughput methods. In particular, the aim is to highlight where automation is absolutely necessary in order to overcome certain bottlenecks in the workflow. By identifying steps where automation is not necessary, semiautomated workflows that avoid these steps may become more widely accessible to research groups as compared to more expensive, fully automated systems. Herein, I identify the most essential steps in automation as being related to characterization rather than synthesis. In fact, having steps handled by researchers during the synthesis is not prohibitive in terms of overall throughput and often leads to greater flexibility in the synthesis routes that can be considered.

2. ANALYSIS OF TYPICAL WORKFLOWS AND BOTTLENECKS

The first step in any of the workflows considered herein is the synthesis. Oftentimes, great efforts are made to increase the throughput of individual synthesis steps; here, we will evaluate the effect on the overall workflow of the system. The three most common synthesis routes for accelerated testing of solid battery materials are (1) solid-state synthesis, (2) solution-based synthesis, and (3) sputtering techniques to make thin film samples. Interestingly, the majority of electrochemical combinatorial investigations have utilized either thin film deposition or inkjet/pipet synthesis techniques.³³ However, for most battery components, thin-film results do not scale up particularly well to those obtained in bulk-scale synthesis as required for

commercial applications. For example, Si anodes for Li-ion batteries show outstanding performance in thin films,³⁵ while they show terrible capacity fade in powder samples where practical loadings are used due to large volume expansion, and this continues to prevent commercialization of high-Si-content anodes.³⁶ On the cathode side, it is very difficult to make arrays of samples with the correct oxygen content when sputtering, and XRD patterns tend to be quite different than those of bulk materials.³⁷ It is only in solid electrolytes that this synthesis route has proven particularly useful in developing practical materials; as such, it will be discussed in Section 2.4 (characterization of solid electrolytes). In the next two sections, I focus on the most common synthesis approaches used on the commercial-scale to make battery materials and discuss approaches to increase the workflow in each. It is worth noting that these synthesis routes are the foundation of numerous applied/fundamental fields that rely on solid-state chemical syntheses.

2.1. Solid-State Synthesis

This synthesis approach has been the workhorse of solid-state chemists for over 50 years. The most commonly used workflow for traditional syntheses is shown in Figure 2. First, solid precursors are weighed out in stoichiometric amounts. These precursors are typically simple solid powders such as metal oxides (e.g., Li_2O , NiO , ...), although recent work shows that more complex precursors may be valuable in obtaining the desired products more efficiently.²² The biggest challenge to solid-state synthesis is to obtain sufficient mixing between different elements (especially heavier transition metals in the case of most battery materials) such that the diffusion paths

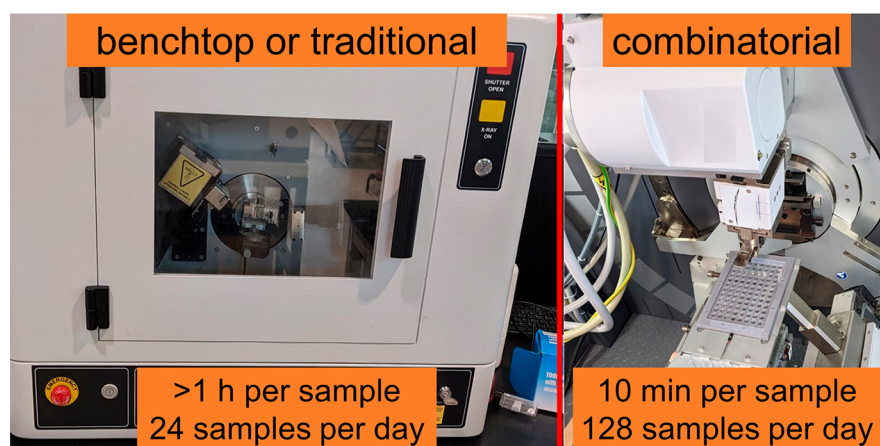


Figure 3. The ultimate limit to the throughput of both automated and semiautomated systems proves to be the X-ray diffractometer utilized. A traditional or benchtop XRD system typically takes about an hour with >100 mg of material to obtain a Rietveld-quality XRD pattern (needed to confirm single-phase materials) such that even an automated system is limited to 24 samples per day per XRD. By contrast, a combinatorial XRD system as described in ref 46 requires only a 10 min scan for a 2–10 mg sample to obtain Rietveld-quality patterns.

required to make the final products are as short as possible. For a long time, the mixing step was done for long periods of time with the researcher using a mortar and pestle. Now, there is usually a ball milling step added in a shaker mill or equivalent. Then, the powders are normally made into pellets to obtain as much contact between precursor particles as possible to further encourage mixing during the high temperature sintering step. As illustrated in Figure 2, the high temperature sintering step is typically at least 12 h, though much longer times may be required (up to a few days or even a week) depending on the target material. The time estimates in Figure 2 are based on the author's experience in various solid-state materials laboratories and gives an overall workflow of about 5–10 samples per researcher over a 3 day period, assuming a traditional X-ray diffractometer (XRD) is used for the structural characterization (Figure 3). The estimated throughput for a traditional XRD is 1 sample per hour; this is normally required to give a scan that will adequately constrain a Rietveld fit (based on a useful rule of thumb that the strongest peak should have at least 1000 counts). Such quality data is needed after synthesis in order to be able to determine whether or not the material is phase pure (i.e., quicker scans may hide secondary phases in the noise). This in theory gives a total throughput for the lab of 24 samples per day, though in practice this requires such automation either in the form of an autosampler or a sample handling robot.

Significant efforts are currently underway in a number of laboratories both in industry and academia to automate the solid-state synthesis process in order to increase the throughput.^{19–23} Samsung's Advanced Materials Laboratory, for example, has established a nearly fully automated system that aims to minimize the amount of human intervention needed (there are setup steps required such as applying grease to sample holders prior to XRD).²² This system uses a robotic arm to perform all the chemical and sample handling steps normally performed by researchers (Figure 2, details in ref 22). Such systems use the robot and automated powder dispensers but otherwise rely on the same equipment as used in the traditional workflow. Some research groups have also developed home-made powder dispensers in an effort to mitigate the cost of this combinatorial systems.²³ It should also be noted here that should semiautomation be tolerable, a powder dispensing pipet

is relatively affordable (about \$1000), and this would allow considerable acceleration of the preparation steps compared to the traditional workflow. The only step not included in the automated workflow demonstrated by Chen et al. (Figure 2, ref 22) that is in the traditional approach is pelletizing. Making pellets in an automated fashion is not trivial, with no commercial option currently available to the author's knowledge. Despite this, the system established by Samsung has been successful in preparing numerous complex target materials to validate the system by reproducing the literature and in making new materials. The biggest challenge again remains the need to overcome the elemental segregation in the precursors such that it is difficult to know if small amounts of secondary phases are in fact thermodynamically stable or simply a result of insufficient heating times. The workflow of the Samsung system is reported to be 24 samples through the system in 3 days,²² but one would presume that subsequent sets of samples could begin the workflow every 24 h (i.e., roughly 1 day for precursor mixing, 1 day for sintering, 1 day for XRD) such that the maximum throughput would likely be close to 1 sample/h or 8760 samples per year. Similarly, Berkeley's A-lab is in the process of going online with an automated solid-state synthesis system and has an expected throughput of 100–200 samples per day or 36,500–72,000 per year.²⁰ However, this system, and others like it to date, does not include automated electrochemistry; the workflow ends at the structural determination based on XRD such that likely candidates for battery materials can then be tested on an individual basis using the traditional electrochemical approaches to be discussed further on in this perspective. The power of these automated systems ultimately lies in their full utilization of XRD, which is the true bottleneck in the synthesis/structure workflow. As will be discussed further below, current fully automated solid-state synthesis systems are limited to using box furnaces such that sintering must be done in air with typical heating/cooling rates of 5–20 °C/min. Of particular significance, quenching does not seem to be possible in these systems; this limitation may prove cumbersome given that battery materials may reach a particular phase at high temperature and then transform to other phases during cooling.^{38,39} In such cases, quenching is useful to bypass the transformations and stabilize the high-temperature phase to give a near-thermodynamic product.



Figure 4. Comparison of traditional solution-based synthesis workflows to the semiautomated method used in the McCalla lab. Time estimates for the traditional workflow are based on the author's experience in various battery research laboratories where coprecipitation is performed in a tank reactor. The 1-step coprecipitation approach involves performing the coprecipitation rapidly in a beaker as described in ref 39. Portions reproduced from ref 46. Copyright 2022, Canadian Science Publishing.

2.2. Solution-Based Synthesis

To overcome the limitations of poorly mixed precursors that have plagued solid-state synthesis, a very common approach is to turn to solution-based methods such as coprecipitation or sol-gel.^{40,41} In coprecipitation, mixtures of precursor solutions are made, and a precipitator is added (often a base like NaOH) to cause coprecipitation of the precursor elements (usually transition metals). Figure 4 shows that in traditional approaches, this is normally done in a tank reactor over about 10 h or more such that the key conditions (temperature, pH, and stirring) are all carefully controlled.^{41,42} After rinsing, the rest of the synthesis proceeds in a manner similar to solid-state synthesis, where mixing with a Li (or Na for Na-ion) salt is done in a mortar and pestle prior to high temperature heating. This coprecipitation technique is the current state-of-the-art for commercial synthesis of cathode materials for Li-ion batteries. The workflow here is quite slow, limited by the use of the tank reactor, with 5 samples being made in 6 days being the maximum that one researcher could likely achieve. However, this can be increased to about 5–10 samples every 3 days (comparable to the solid-state synthesis approach) if researchers use a 1-step coprecipitation approach in a beaker.³⁹ The intimate mixing of the transition metals during coprecipitation means that sintering times generally do not exceed 10 h, and the correct phases are normally reached within 3–5 h.³⁹

In 2011, the Dahn group first published a combinatorial coprecipitation synthesis of Li-ion cathodes.⁴³ In this approach, 20–40 μL of solutions is dispensed using a robot, dried overnight, and then sintered at high temperature (Figure 4 without the sintering at moderate temperature or the pelletizing). The McCalla group has continued to optimize and use this approach to yield a workflow of 64 samples every 2 days (including synthesis and XRD).^{44,45} In the McCalla group, it is often found that the robot is in fact less efficient than a

researcher pipetting, particularly in cases where systematic composition changes occur between samples (e.g., same amount of different dopants or linear composition gradients). The solution-dispensing robots also require supervision, with droplets occasionally forming on the edge of pipet tips that need to be wiped off (this has been the case with both a \$100K solution-dispensing robot⁴³ and a \$5K Opentrons robot⁴⁶). Furthermore, all sample handling/transferring steps are handled by a researcher. As such, the combinatorial coprecipitation method developed by the Dahn lab and used heavily in the McCalla lab is a semiautomated approach, and yet achieves a very high throughput of 1.3 samples/h, slightly higher than achieved in the fully automated solid-state synthesis system from ref 22. The most important gains in throughput in these systems do not come from the synthesis; rather, they come from the XRD where combinatorial diffractometers are utilized. The system in the McCalla lab (Figure 3) uses Mo radiation in transmission in order to obtain Rietveld-quality scans in 10 min on as little as 2 mg of sample without loss of precision on extracted lattice parameters (details in ref 46). The standard approach used in the lab is to run 128 samples per day (two sets of 64), which yields a maximum throughput of 46,592 XRD patterns/year (i.e., the equivalent of about 5.5 traditional XRD instruments running nonstop, and is about 2–3 times the price of the least expensive traditional XRD). It should be noted that this semiautomated workflow therefore has a throughput within the range of the projected throughput of the fully automated solid-state-based systems in the previous section (100–200 samples per day²⁰).

The biggest limitation of using the coprecipitation method is that there must exist both a precipitator and conditions (pH, temperature) that cause all elements to precipitate at the same time. This is not universally possible. For example, in Na–Fe–Mn–O materials, it was found that phase-pure materials could

not be obtained with coprecipitation while a phase-pure material was obtained by a sol–gel approach (to be described below).⁴⁷ In an even more extreme case, Ti-containing solutions precipitate in water, and the resulting precipitate floats to the top of the water; as a result, it does not mix in the least with the other elements. As such, coprecipitation is not appropriate for broad screening of compositions involving elements from across the periodic table, in contrast to solid-state synthesis. As a result of this limitation, other solution-based approaches must be considered. The simplest is the sol–gel approach. This method has improved versatility over coprecipitation: doping studies have been performed with up to 52 different dopants on Na-ion cathodes,⁸ Li-ion cathodes,¹⁸ and solid electrolytes.⁴⁸ The initial step is similar to coprecipitation with mixtures of precursor solutions being mixed, but then a chelating agent such as citric acid is added.⁴⁹ During the subsequent drying steps, a gel forms, which maintains all elements well-mixed. Subsequent pelletizing and sintering lead to the formation of high-temperature phases. In traditional laboratories, the throughput of sol–gel synthesis is comparable to that of solid-state synthesis, i.e., 5–10 samples over a 3 day period. Figure 4 shows that the sol–gel-based combinatorial system has a throughput of 64 samples per researcher over 3 days, but a second set of samples can be started after day 2. The extra day compared to coprecipitation is a result of the time and care needed during the drying steps to ensure good gel formation and to avoid excessive swelling of samples that can result in neighboring samples mixing and contaminating each other. In all projects attempted to date in the McCalla lab using the sol–gel method, the results successfully reproduce the previously published phases obtained by solid-state synthesis. However, in doping studies, certain dopants (like Mo in ref 18) give very novel morphologies. In the case of Mo, it catalyzed particle growth to yield LCP particles 10 times larger than in the undoped case, and this of course has a very important impact on electrochemical performance with long-term cycling being particularly sensitive to specific surface area. Care must therefore be taken in comparing performances across different synthesis routes. To date, the workflow in the lab has not yet been limited by XRD, but typical researchers have sustained making about 1500 samples per year (with XRD and all electrochemical characterization to be discussed below). This infrastructure is capable of over 45,000 XRD per year and can therefore support a high number (on the order of 30) of high-throughput projects.

Unlike the high-throughput solid-state synthesis systems discussed in the previous section, there are no limitations on synthesis conditions for either of the combinatorial solution-based approaches discussed here: they have been used for various heating/cooling rates including quenching, as well as various atmospheres including air, oxygen, nitrogen, and forming gas (4% H₂, 96% Ar), with heating at temperatures as high as 1250 °C.^{18,39,47,50}

The above workflow describes the synthesis of electrode materials that can remain as powders. In the case of solid electrolytes, they must be pelletized at some point in the process in order to perform the characterization methods described later in this article. The high-throughput pelletizing, shown in Figure 4, uses a homemade die that allows 64 pellets to be made at once. However, it is impossible to press 64 pellets simultaneously (this would invariably result in the pellets with more volume being denser than the others); instead, they must be pressed one at a time in series. The high-throughput die therefore saves on time by eliminating the cleaning and loading steps needed between each sample, bringing the time down from about 15–30 min per

pellet to 2 h for 64 pellets (i.e., about 2 min per pellet). This yields an overall workflow very comparable to that of electrode materials, i.e., 64 samples through the workflow in 3 days.

In summary, Figure 4 reveals that the synthesis/XRD workflow is not slowed down by researchers being involved in sample handling/transport steps or even the dispensing. It is the long sintering steps and the XRD itself that result in bottlenecks. The key is to make as many of the synthesis steps as possible occur in parallel in order to increase overall throughput. In the McCalla lab, only the dispensing is automated, and all other synthesis steps are done in parallel (64 samples at once), but all handling/transferring of samples is done by researchers. Furthermore, as discussed above, since doing XRD in parallel is impossible, the other essential step to increase throughput is to automate the XRD. This can be accomplished by either using an autosampler (programmable XYZ sample stage in the case of the combinatorial system) or having a robot load the samples and operate the XRD (as in the fully automated system in Figure 2). In any case, with state-of-the-art diffractometers, throughputs on the order of 45,000 samples per year are achievable without full automation.

2.3. Characterization of Electrodes and Liquid Electrolytes

For both electrode materials and liquid electrolytes, the primary means to screen the materials is to perform electrochemical cycling on the test batteries. Figure 5 shows the typical steps in a traditional approach. First, the electrodes must be prepared as slurries and then spread with a doctor blade to make a uniform

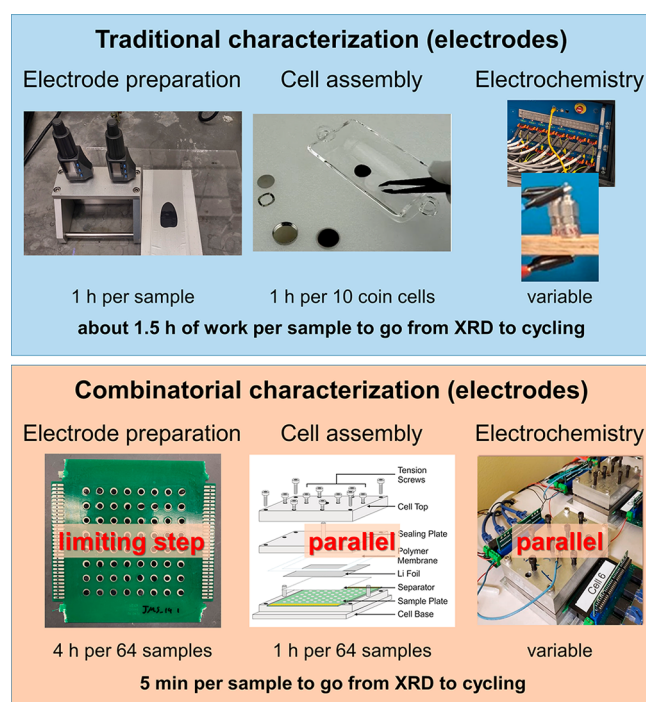


Figure 5. Comparison of traditional and combinatorial workflows for electrochemical cycling of electrodes made from powder samples. Such techniques are needed to develop new active materials for both anodes and cathodes. The time needed for the electrochemistry is variable, depending on the level of development of the material, but this is normally at least 2 weeks in order to obtain 10 cycles for preliminary screening. By contrast, the screening of electrolytes by traditional means is much more efficient as one electrode can be used to make many cells, and one simply varies the composition of the electrolyte mixture added to the cell.

thickness film (see ref 51 for specific details). This typically takes about an hour per electrode (steps include weighing out components, 15 min or more of mixing in a planetary mill, and spreading the inks on the current collector). Next, the electrode is transferred to a drying furnace, where it normally remains overnight. The electrodes are then punched, weighed, and transferred to the glovebox for assembly in a coin cell or Swagelok-style cell. Assembly in the glovebox typically takes 1 h for each of 10 cells. After the cell is removed from the glovebox, it is transferred to the cycling equipment to begin battery testing. A reasonable estimate is that a researcher spends roughly 1.5 h per sample after XRD is done in order to get the battery ready for testing. This number is assuming each battery contains a different electrode material, so this would be correct for studies screening either cathodes or anodes. Assuming sufficient channels are available in the lab, the throughput for traditional screening of cathodes is not limited by the electrochemistry (i.e., it is relatively easy for the electrochemistry to keep up with the 5–10 samples made per 3 days by the traditional syntheses described in Figures 2 and 4). This is particularly true now that there are suppliers of quality cyclers at affordable rates (e.g., 32 channels for coin cells for \$4K from Neware). Traditional characterization methods are, therefore, very well suited to the typical synthesis routes for traditional battery research.

However, this does not hold when we consider the throughputs generated from automated and semiautomated syntheses discussed previously. The 64 samples made in 2–3 days in Figure 4 would require a devoted researcher to work full-time for at least a week to prepare 64 coin cells or Swagelok cells. Some researchers have therefore used XRD as a first screening to select a few novel single-phase materials to test in traditional approaches (e.g., refs 22, 23, 39). Although this still has the potential of finding good performers, it has two very obvious downfalls: (i) there is certainly a risk of missing the best performers particularly if they happen to not be phase-pure (i.e., with follow-up, it could be made phase-pure and outperform all others), (ii) machine learning models require a large quantity of data including a high number of poor performers for models to be accurate and predictive. As a result, there have been numerous efforts to design electrochemical systems that keep up with the high-throughput synthesis workflows. One fairly affordable option is the pseudopotentiostat designed by the Dahn lab wherein Keithley voltage sources and Keithley current meters are assembled in-house to make a system that can perform cyclic voltammetry on 64 different samples assembled on a single printed circuit board (cell shown in Figure 6, details of the potentiostat in ref 52). The Dahn group has used this system extensively to test thin film anodes (e.g., ref 35). Given the limitations described above with regards to thin film electrodes, the McCalla group has developed methods to prepare 64 electrodes from 2 to 5 mg powder samples.^{18,44} Two methods are currently used in the group: (i) transfer the whole 2 mg sample after mixing with carbon black onto the pad, drop cast PVDF binder in an NMP solution, then dry to yield a loading of about 20 mg/cm²,⁴⁴ and (ii) mix the whole sample with carbon black, PVDF, and NMP in a small cup and then pipet a small volume of the slurry onto the pad to give a loading of about 2.5 mg/cm².¹⁸ As detailed elsewhere, both methods give acceptable reproducibility, and both are limited in terms of throughput by the time required to weigh 64 samples, which is needed to obtain specific capacities and energy densities, both considered crucial properties in the screening of electrodes. The electrode preparation of 64 samples for combinatorial electro-

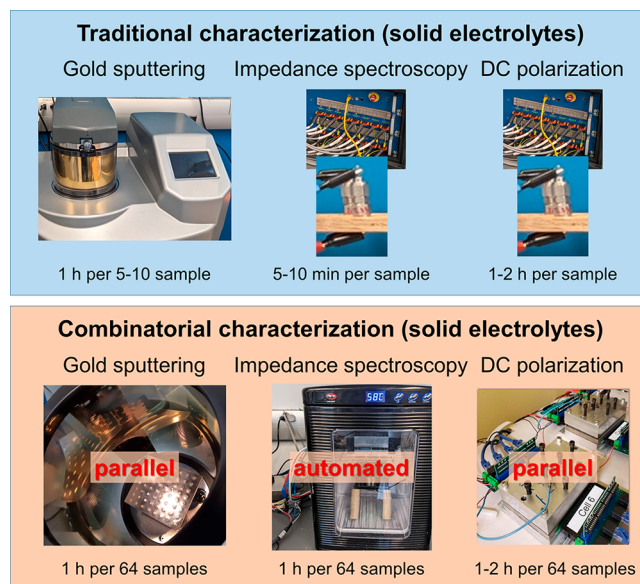


Figure 6. Comparison of traditional and combinatorial workflows for the screening of solid electrolytes. Oftentimes, the impedance spectroscopy is performed at multiple temperatures such that the time estimate is rough. The limit on DC polarization is the relaxation of the cell after the potential is applied, so this is roughly the same in a traditional cell as in a combinatorial cell.

chemistry takes a total of 4 h of researcher time and represents the limiting step in our electrochemical workflow. Although this is a significant time investment, it is still less than 4 min per sample and is followed by an overnight drying step such that it does permit researchers to keep up with the combinatorial synthesis. The overall workflow is still limited by the required overnight drying step rather than the steps performed by researchers. Therefore, although it would certainly be beneficial to the researcher's well-being to automate the weighing process, and the group is working on this, the gains in the overall throughput would be minimal. The assembly of the cell and cycling are then performed in parallel (all 64 samples tested at once). To the author's knowledge, this system remains the only combinatorial method to test the electrochemical performance of powder electrode materials (systems described below to test liquid electrolytes do not vary the electrode from cell to cell).

There have also been groups who have developed high-throughput testing systems for liquid electrolytes.^{53–55} Unlike the system described above to test electrodes, a common counter electrode and electrolyte cannot be used, such that the cell design must include multiple wells to keep each battery entirely distinct. However, since the same electrodes are used in all wells, the electrode preparation is very efficient: one electrode made by traditional methods can be punched a number of times to yield all electrodes needed for the high-throughput test. Then, during cell assembly, a different electrolyte mixture can be added to each well either by hand or using a solution-dispensing robot. As long as there are enough cycler channels, they can be tested in the same manner as those used in traditional tests. For state-of-the-art liquid electrolytes, very high-precision cyclers are required (or very long testing times), so the throughput is normally limited by the number of channels available rather than the throughput of cell preparation.^{4,5} For example, the Dahn group has utilized only traditional methods to develop electrolyte mixtures and have a throughput that is certainly competitive with the combinatorial papers published to date

(e.g., refs 4, 5) due to the availability of a high number of high-precision channels and a team that can maintain a workflow sufficient to fully utilize those channels, giving a bottleneck-free workflow. This is in sharp contrast to the electrode testing throughput described earlier, where traditional electrochemistry cannot keep up with the synthesis.

As described in detail here, traditional electrode testing workflows are not bottleneck-free and cannot keep up with the accelerated synthesis methods being developed to accelerate electrode material design. As such, it is imperative that combinatorial electrochemical techniques be increasingly utilized in order for the automated synthesis methods to be of true service in developing electrode materials rather than only being a tool to determine whether the solid-state synthesis of a target material is possible. The current capability in the McCalla lab is to test 9 cells of 64 samples each at once, assuming each cell is tested for 2 weeks; this gives about 15,000 cells tested per year, a throughput that is competitive with the synthesis throughputs described in previous sections.

2.4. Characterization of Solid Electrolytes

To function as a solid electrolyte, the material must conduct lithium (or Na, K, etc. for beyond Li batteries), must not conduct electrons, and must remain electrochemically inert throughout battery operation when in contact with either the anode or the cathode. The characterizations required to thoroughly test potential solid electrolytes are therefore extensive, as illustrated by the radar plot in Figure 1. Of course, ionic conductivity is a mandatory property, and as a result, it has tended to be the main/sole focus of many studies (both computational and experimental). The experimental determination of ionic conductivity is done using electrochemical impedance spectroscopy (EIS) after gold-coating both sides of a pellet made from the test material.⁵⁶ This allows extraction of both ionic conductivity in the bulk of particles and at the grain boundaries⁵⁷ (though these two contributions may be hard to distinguish in some samples). Measurements typically take about 5 min per sample; however, measurements are normally repeated at different temperatures in order to extract activation energies via the Arrhenius equation. Thus, in a traditional lab, it takes at least an hour per sample to perform EIS (Figure 6). However, automating EIS measurements is relatively straightforward, so it is sufficient to have a multiplexer (\$1000–5000) connected to any standard EIS channel.⁴⁶ A simple house-written program can then be used to coordinate the two instruments. The high-throughput EIS system in the McCalla lab is designed around sets of 64 samples such that the same PCB as used in the cycling are also used for EIS; however, the top plate of the cell contains spring-mounted pistons in order to make contact to 64 pellets that may vary slightly in thickness.³⁰ The resulting throughput is 64 samples in 1–2 h for room temperature conductivity, and in the case that activation energy is required, measurements can be done at a second temperature after letting the large cell equilibrate for several hours.³⁰

Beyond ionic conductivity, it is proving necessary to measure electronic conductivities because even a small electronic conductivity of 10^{-8} S/cm has been experimentally confirmed to yield Li dendrite formation within the solid electrolyte and rendering the material incompatible with all-solid batteries.⁵⁸ The same cell as used for EIS can then be used on a combinatorial cyler in order to perform DC polarization measurements in order to obtain electronic conductivity.³⁰ This

only requires a few hours, such that adding this measurement has no meaningful impact on the overall throughput.

The final essential solid-electrolyte test included in Figure 1 is the electrochemical stability window. The most precise way to determine this is to mix the test material with a conductive additive such as carbon black and assemble a cell with the mixture as the test electrode.⁵⁹ A stable electrolyte will show no current during electrochemical testing such that the end of the stability window is identified as the voltage at which the current first appears. It is important to mix the material with a conductive additive in order to ensure that the stability window is not overestimated by the poor electronic conductivity of the test material preventing the electrochemical reactions.⁵⁹ In high-throughput, this test can be achieved using the electrochemistry workflow discussed in Figure 5, except only 1–2 days of cycling is required because it is only the first cycle that is needed to determine stability window.

Thus, in its entirety, the electrochemical characterization of solid electrolytes in the semiautomated workflow can easily operate at 64 samples per day, with sets of samples going through the entire workflow in about 3–5 days. Other than the system in the McCalla lab, the author is not aware of another high-throughput system for the screening of multiple properties for solid electrolytes. However, there have been studies performing high-throughput conductivity measurements on combinatorial thin film arrays (e.g., ref 60). In such cases, the films are prepared by sputtering with multiple targets that are used to generate gradients with varying elemental compositions. Contact can then be made at multiple points along the film in order to obtain conductivities across films with various compositions. A similar setup could also be used to determine the electronic conductivity. Unfortunately, such sample sets are not suitable for measurement of the stability window, as mixing with a conductive additive is not possible. Nonetheless, such studies serve as excellent first screenings in order to down select compositions worthy of further studies. The difficulty lies in reliably making materials in the thin film form that are not biased by the particular sputtering technique utilized. Furthermore, the resulting structure determinations cannot be used by the general material community to know which compositions can be synthesized using bulk methods (scale-up to bulk syntheses is unreliable). Thus, in terms of informing the emerging wide-scale efforts in machine learning and computation-based predictions, it is important to utilize combinatorial syntheses that mimic best those methods used industrially as illustrated in Figures 2 and 4.

3. BENEFITS, COST, AND LIMITATIONS OF AUTOMATED STEPS

The obvious benefit of automation is to create bottleneck-free workflows. Thus, steps that limit the overall workflow need to be identified and improved either by making the step possible in parallel (preferred) or by continuing to do the step in series but using automation to improve the throughput. In the previous sections, analysis of the various workflows used in both traditional battery materials research and emerging accelerated workflows identified the automation of X-ray diffraction and parallelization of the electrochemical testing of electrodes as key solutions to bottlenecks needed to accelerate testing. With a combinatorial diffractometer capable of over 45,000 XRD patterns per year, it then becomes essential to make all steps in the synthesis parallel (e.g., 64 samples at once) such that the rest of the infrastructure (e.g., 4–5 furnaces) can keep up with the XRD. In no cases were the semiautomated workflows limited by

the nonautomated steps (Figures 4–6); the ultimate limits on throughput are either the time needed to do the chemistry (e.g., time required at high temperature) or the XRD characterization time. As such, the gains in fully automating are relatively small in terms of overall throughput, as can be seen by comparing Figures 2 and 4. However, automating the XRD is essential: either a robot is needed to handle the operation 24 h/day (estimated cost of about \$25,000), or a combinatorial XRD is required (5× throughput, 2–3× cost compared to a traditional diffractometer). Except for the diffractometer, traditional equipment is sufficient to yield a high throughput as illustrated in Figure 4 as long as care is taken in the design of the experiment (reduce sample size, maximize the number of samples at each step, as detailed further below), and no extra automation is mandatory. Similarly, the prices associated with increased throughput during electrochemistry are quite moderate (\$10,000 for 192 samples in the pseudopotentiostat described in ref 52, and only about \$4,000 for a multiplexer to change a single-channel EIS system into a 64-channel system as described in ref 46). The costs that are not so easy to estimate are (i) the time needed to design cells that allow the parallel measurements to be performed accurately and to assemble the systems in-house and (ii) the time required to write the programs/algorithms required to operate the automated equipment which are often custom-made or house-made.

In planning the overall workflow, it is also important to recognize that fully automated systems are limited in terms of synthesis methods accessible, and this choice is made when the automated lab is installed at the start of project. For example, the robot-based system in Figure 2 is limited to high-temperature synthesis in air at moderate heating/cooling rates, as discussed above. In solid-state chemistry, this can prove quite limiting; a few examples include:

- (i) Li and Na loss can be severe in air, such that synthesis in a tube furnace with flowing oxygen is required.⁶¹
- (ii) Materials made at high temperature can transform during cooling,^{38,39} such that quenching can be extremely informative. In the case of some materials, such as glasses, they can only be formed by quenching.⁶²
- (iii) Some materials, such as LiFePO_4 and carbon-coated materials, can only be synthesized in a reducing atmosphere such as Ar or H_2/Ar .⁶³ In such cases, heating in a tube furnace with these specific atmospheres is required.

Figure 7 illustrates a few cases where the above 3 examples would require the intervention of a researcher, at least with current self-driving laboratory setups. It therefore remains important to develop automated laboratories further in order to perform syntheses under various atmospheres. A partial vacuum may currently be achievable (this represents a weakly reducing atmosphere), but full automation of syntheses under a variety of atmospheres is needed to be broadly applied to all key battery materials. Quenching from as high a temperature as 1150 °C has been performed in high throughput in the McCalla lab in order to obtain glasses; it is difficult to envision using a standard robot for this step without risk of damage to expensive equipment, although this should be something to be developed. The added flexibility afforded by human intervention therefore makes semiautomated workflows easier to adapt to new chemistries. Figure 7 also shows two examples of unpredictable results encountered by the McCalla group that occur a significant number of times in the lab:

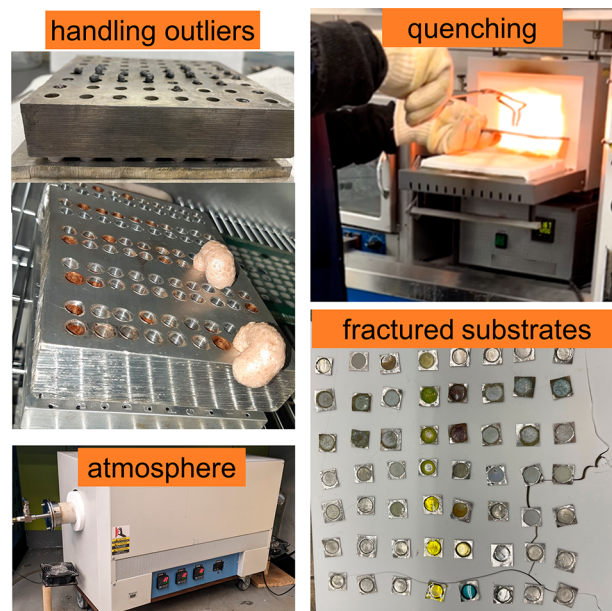


Figure 7. Illustrations of a few cases where flexibility supplied by researchers has proven invaluable in the semiautomated workflow. In the “handling outliers” images, we see two samples of V-doped LiCoPO_4 that have swollen so extensively during drying of the sol–gel samples that they have extruded extensively beyond the 1” deep wells, while all 94 other samples of the same volumes did not. The researcher was able to salvage both of these samples. The fractured substrate occurred during quenching from 900 °C; again, all samples were salvaged.

- (i) During the sol–gel drying process, some compositions swell dramatically while the vast majority do not. A robot would not struggle to adapt to such surprises and require human intervention to prevent contamination of neighboring samples and even damage to the equipment as loose powder may spread.
- (ii) Ceramic substrates needed to hold the high number of samples may often break during quenching processes. They shatter in a way that most/all samples can still generally be salvaged, but it requires human input for this to happen.

Such anecdotes illustrate that oftentimes the exciting part of exploring new materials yields completely unexpected outcomes that may often prove to yield the most valuable data, but preset protocols may not be sufficient to handle such unexpected outcomes. It is therefore my suggestion to maintain a certain level of researcher input at each stage of automated workflows in order to handle all of the varied outcomes that come from the exploratory materials discovery.

The above examples also help to give guidance as to what sample size reduction might be too severe to obtain meaningful results. In our quest for higher throughput, the ideal is to make the smallest samples that permit the characterization techniques required. For electrode materials, we have found that 2 mg is sufficient to make a combinatorial cell, but less than this proves difficult to manage (both in precisely weighing the active material and in mitigating Li loss). By contrast, for solid electrolytes, the smallest pellets we have been able to reliably make weigh about 10–15 mg. The question of throughput then becomes how many 15 mg (or 2 mg) samples can fit in our furnaces and other equipment during each synthesis step. It should also be highlighted that as described above, this ideal

cannot always be achieved. For example, samples sometimes swell excessively during drying, such that dense packing in the furnace is inadvisable. To date, 64 has proved to be a useful number of samples in the typical box and tube furnaces used in most battery laboratories, though this is by no means a hard limit; with care, a higher packing and hence a higher synthesis throughput may well be achievable.

The final important issue to consider with respect to efficiently automating laboratories is to ensure that data analysis tools are developed so that researchers can keep up with the large amount of data produced. For XRD data, the McCalla group utilizes automated phase identification and fitting in both commercial⁶⁴ and house-written⁶¹ software. This is ideal for cases where crystallographic databases have phases that are similar to the target phase, such as when a small amount of dopant is added and small changes in lattice parameters do not impact phase identification.^{8,18,48} However, such approaches may be limited when new materials are encountered or if full substitutions are tested, such that phase matching fails. In such cases, supplementing experimental databases with computational ones such as the Materials Project⁶⁵ becomes attractive and necessary. The Ceder group and Samsung's Advanced Materials Laboratory have both made significant efforts to further close the loop by automating the phase identification/quantification steps and use machine learning techniques to generate the next test composition/conditions.^{19,22} It is important to note that despite the significant progress in algorithms required for fully machine-operated syntheses, a recent review article highlights the many challenges remaining and suggests that concerted efforts are needed to make such methods outperform researcher-guided experiments.⁶⁶

Although these automated analysis methods need further validation and development, this author expects them to become far more widespread and widely beneficial to all groups with increased throughput. Currently, all analysis tools will fail should a completely new and unforeseen phase be synthesized; such cases must be flagged and followed up with a researcher who will most likely have to prepare single crystals to perform structure determination.⁶⁷ In terms of combinatorial electrochemistry, no commercial software exists, as such groups must write their own analysis codes to extract the necessary parameters from the large amount of data generated. As these techniques become more common, one imagines and hopes that commercial systems will become available.

4. CONCLUSION

Experimental accelerated design of anodes, cathodes, and solid electrolytes for Li and beyond Li batteries is increasingly seen as an essential approach in order to efficiently evaluate long candidate lists from combinatorial computational studies and also to improve machine learning models. Both fully automated and semiautomated workflows have been developed in various laboratories. Current fully automated laboratories seem to have a maximum throughput on the order of 10,000 samples per year with structural characterization only (though a system in the process of being launched was designed to study 36,000–72,000 samples per year). Some efforts are also underway to add electrochemistry to such systems, but for now, electrochemistry is done sample by sample using traditional methods after automated XRD is completed. By contrast, the semiautomated workflow in the McCalla lab has a maximum throughput of about 15,000 samples a year with both structural and electrochemical characterization with a team of 10 researchers,

and the infrastructure has a maximum throughput of 45,000 samples a year. Both the automated and semiautomated throughputs are orders of magnitude above what is typically achieved in a traditional materials research lab and therefore represent important steps toward accelerating the design of advanced materials. The semiautomated approach is also more widely accessible, with only the combinatorial diffractometer being an important cost addition over traditional workflows, though even fully utilizing a traditional diffractometer represents a significant acceleration. The author hopes that the current perspective encourages researchers to optimize their own workflows in order to increase throughput and support the growing efforts to screen widely. The semiautomated approach also currently offers greater flexibility during synthesis, such that researchers need not ask “what materials can my automated setup make?”, but rather, they can rely on their own experience and ask “how do I make these new materials?”

■ AUTHOR INFORMATION

Corresponding Author

Eric McCalla – Department of Chemistry, McGill University, Montreal, Canada H3A 0B8; orcid.org/0000-0002-0557-608X; Email: eric.mccalla@mcgill.ca

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acseengineeringau.3c00037>

Author Contributions

CReditT: Eric McCalla conceptualization, formal analysis, funding acquisition, methodology, writing-original draft, writing-review & editing.

Notes

The author declares no competing financial interest.

■ ACKNOWLEDGMENTS

This work was funded by NSERC under the auspices of a discovery grant.

■ REFERENCES

- (1) Li, Q.; Yang, Y.; Yu, X.; Li, H. A 700 Wh kg⁻¹ Rechargeable Pouch Type Lithium Battery. *Chinese Phys. Lett.* **2023**, *40*, No. 048201.
- (2) MacNeil, D. D.; Lu, Z.; Dahn, J. R. Structure and electrochemistry of Li [Ni x Co1– 2x Mn x] O 2 (0 ≤ x ≤ 1/2). *J. Electrochem. Soc.* **2002**, *149*, A1332.
- (3) Hebert, A.; McCalla, E. The role of metal substitutions in the development of Li batteries, part I: cathodes. *Materials Advances* **2021**, *2*, 3474–3518.
- (4) Ma, L.; Wang, D. Y.; Downie, L. E.; Xia, J.; Nelson, K. J.; Sinha, N. N.; Dahn, J. R. Ternary and Quaternary Electrolyte Additive Mixtures for Li-Ion Cells That Promote Long Lifetime, High Discharge Rate and Better Safety. *J. Electrochem. Soc.* **2014**, *161*, A1261.
- (5) Harlow, J. E.; Ma, X.; Li, J.; Logan, E.; Liu, Y.; Zhang, N.; Ma, L.; Glazier, S. L.; Cormier, M. M. E.; Genovese, M.; Buteau, S.; Cameron, A.; Stark, J. E.; Dahn, J. R. A wide range of testing results on an excellent lithium-ion cell chemistry to be used as benchmarks for new battery technologies. *J. Electrochem. Soc.* **2019**, *166*, A3031.
- (6) Dunn, B.; Kamath, H.; Tarascon, J. M. Electrical energy storage for the grid: a battery of choices. *Science* **2011**, *334*, 928–935.
- (7) Yabuuchi, N.; Kajiyama, M.; Iwatate, J.; Nishikawa, H.; Hitomi, S.; Okuyama, R.; Usui, R.; Yamada, Y.; Komaba, S. P2-type Na x [Fe1/2Mn1/2] O2 made from earth-abundant elements for rechargeable Na batteries. *Nat. Mater.* **2012**, *11*, 512–517.

- (8) Jia, S.; Yao, E.; Peng, R.; Jonderian, A.; Abdolhosseini, M.; McCalla, E. Chemical Speed Dating: The Impact of 52 Dopants in Na–Mn–O Cathodes. *Chem. Mater.* **2022**, *34*, 11047–11061.
- (9) Hijazi, H.; Ye, Z.; Zhang, L.; Deshmukh, J.; Johnson, M.; Dahn, J. R.; Metzger, M. Impact of Sodium Metal Plating on Cycling Performance of Layered Oxide/Hard Carbon Sodium-ion Pouch Cells with Different Voltage Cut-offs. *J. Electrochem. Soc.* **2023**, *170*, No. 070512.
- (10) Jonderian, A.; McCalla, E. The role of metal substitutions in the development of Li batteries, part II: solid electrolytes. *Materials Advances* **2021**, *2*, 2846–2875.
- (11) Sturman, J. W.; Baranova, E. A.; Abu-Lebdeh, Y. High-entropy materials for lithium-ion battery electrodes. *Front. Energy Res.* **2022**, *10*, No. 862551.
- (12) Ma, Y.; Ma, Y.; Wang, Q.; Schweidler, S.; Botros, M.; Fu, T.; Hahn, H.; Brezesinski, T.; Breitung, B. High-entropy energy materials: challenges and new opportunities. *Energy Environ. Sci.* **2021**, *14*, 2883–2905.
- (13) Kumbhakar, M.; Khandelwal, A.; Jha, S. K.; Kante, M. V.; Kefler, P.; Lemmer, U.; Hahn, H.; Aghassi-Hagmann, J.; Colsmann, A.; Breitung, B.; Velasco, L.; Schweidler, S. High-Throughput Screening of High-Entropy Fluorite-Type Oxides as Potential Candidates for Photovoltaic Applications. *Adv. Energy Mater.* **2023**, *13*, No. 2204337.
- (14) Gaining from mixing. *Nat. Mater.* **2023**, *22*, 401.
- (15) Dinic, F.; Voznyy, O. Unconstrained Machine Learning Screening for New Li-Ion Cathode Materials Enhanced by Class Balancing. *Adv. Theory Simul.* **2023**, *6*, No. 2300081.
- (16) Sendek, A. D.; Yang, Q.; Cubuk, E. D.; Duerloo, K. A. N.; Cui, Y.; Reed, E. J. Holistic computational structure screening of more than 12000 candidates for solid lithium-ion conductor materials. *Energy Environ. Sci.* **2017**, *10*, 306–320.
- (17) Kirklın, S.; Meredig, B.; Wolverton, C. High-throughput computational screening of new Li-ion battery anode materials. *Adv. Energy Mater.* **2013**, *3*, 252–262.
- (18) Jonderian, A.; Jia, S.; Yoon, G.; Cozea, V. T.; Galabi, N. Z.; Ma, S. B.; McCalla, E. Accelerated Development of High Voltage Li-Ion Cathodes. *Adv. Energy Mater.* **2022**, *12*, No. 2201704.
- (19) Szymanski, N. J.; Zeng, Y.; Huo, H.; Bartel, C. J.; Kim, H.; Ceder, G. Toward autonomous design and synthesis of novel inorganic materials. *Mater. Horiz.* **2021**, *8*, 2169–2198.
- (20) Biron, L. Meet the Autonomous Lab of the Future. <https://newscenter.lbl.gov/2023/04/17/meet-the-autonomous-lab-of-the-future/> (accessed on August 1, 2023).
- (21) High-Throughput Experimentation Accelerates Energy Storage Materials Discovery. <https://www.pnnl.gov/energy-storage-high-throughput-experimentation-system> (accessed on August 1, 2023).
- (22) Chen, J.; Cross, S. R.; Miara, L. J.; Cho, J. J.; Wang, Y.; Sun, W. Navigating phase diagram complexity to guide robotic inorganic materials synthesis. *arXiv*, submitted 3 April, 2023, DOI: 10.48550/arXiv.2304.00743 (accessed 2023–09–27).
- (23) Xiao, Y.; Zheng, P.; Yang, T.; Chakravarty, S. K.; Rodríguez-López, J.; Urban, A.; Li, Z. Integrated Combinatorial Synthesis, Characterization, and Test Platform for Lithium-Ion Battery Cathode Materials. *J. Electrochem. Soc.* **2023**, *170*, No. 050538.
- (24) Joress, H.; Green, M. L.; Takeuchi, I.; Hatrick-Simpers, J. Applications of high throughput (combinatorial) methodologies to electronic, magnetic, structural, and energy-related materials” from *Encyclopedia of Materials: Metals and Alloys*; Elsevier, 2022, pp 353–371.
- (25) Liu, P.; Guo, B.; An, T.; Fang, H.; Zhu, G.; Jiang, C.; Jiang, X. High throughput materials research and development for lithium ion batteries. *J. Materiomics* **2017**, *3*, 202–208.
- (26) Doble, M.; Kruthiventi, A. K. Chapter 10: combinatorial chemistry. In *Green Chemistry and Engineering*; Elsevier, 2007.
- (27) Martín-Yerga, D.; Milan, D. C.; Xu, X.; Fernández-Vidal, J.; Whalley, L.; Cowan, A. J.; Hardwick, L. J.; Unwin, P. R. Dynamics of Solid-Electrolyte Interphase Formation on Silicon Electrodes Revealed by Combinatorial Electrochemical Screening. *Angew. Chem., Int. Ed.* **2022**, *61*, No. e202207184.
- (28) Rehman, S.; Sieffert, J. M.; Lang, C. J.; McCalla, E. NbyW1-yOz and NbxTi1-xOz pseudobinaries as anodes for Li-ion batteries. *Electrochim. Acta* **2023**, *439*, No. 141665.
- (29) Kim, D.; Shim, H. C.; Yun, T. G.; Hyun, S.; Han, S. M. High throughput combinatorial analysis of mechanical and electrochemical properties of Li [NixCoyMnz] O2 cathode. *Extreme Mech. Lett.* **2016**, *9*, 439–448.
- (30) Jonderian, A.; Anderson, E.; Peng, R.; Xu, P.; Jia, S.; Cozea, V.; McCalla, E. Suite of high-throughput experiments for screening solid electrolytes for Li batteries. *J. Electrochem. Soc.* **2022**, *169*, No. 050504.
- (31) Matsuda, S.; Nishioka, K.; Nakanishi, S. High-throughput combinatorial screening of multi-component electrolyte additives to improve the performance of Li metal secondary batteries. *Sci. Rep.* **2019**, *9*, 6211.
- (32) Stein, H. S.; Sanin, A.; Rahmanian, F.; Zhang, B.; Vogler, M.; Flowers, J. K.; Fischer, L.; Fuchs, S.; Choudhary, N.; Schroeder, L. From materials discovery to system optimization by integrating combinatorial electrochemistry and data science. *Curr. Opin. Electrochem.* **2022**, *35*, No. 101053.
- (33) McGinn, P. J. Combinatorial electrochemistry—Processing and characterization for materials discovery. *Mater. Disc.* **2015**, *1*, 38–53.
- (34) Muster, T. H.; Trinchì, A.; Markley, T. A.; Lau, D.; Martin, P.; Bradbury, A.; Bendavid, A.; Dligatch, S. A review of high throughput and combinatorial electrochemistry. *Electrochim. Acta* **2011**, *56*, 9679–9699.
- (35) Fleischauer, M. D.; Topple, J. M.; Dahn, J. R. Combinatorial investigations of Si-M (M= Cr+ Ni, Fe, Mn) thin film negative electrode materials. *Electrochem. Solid-St. Lett.* **2005**, *8*, A137.
- (36) He, Y.; Jiang, L.; Chen, T.; Xu, Y.; Jia, H.; Yi, R.; Xue, D.; Song, M.; Genc, A.; Bouchet-Marquis, C.; Pullan, L.; Tessner, T.; Yoo, J.; Li, X.; Zhang, J.-G.; Zhang, S.; Wang, C. Progressive growth of the solid–electrolyte interphase towards the Si anode interior causes capacity fading. *Nat. Nanotechnol.* **2021**, *16*, 1113–1120.
- (37) Borhani-Haghighi, S.; Kieschnick, M.; Motemani, Y.; Savan, A.; Rogalla, D.; Becker, H. W.; Meijer, J.; Ludwig, A. High-throughput compositional and structural evaluation of a Li a (Ni x Mn y Co z) O r thin film battery materials library. *ACS Combi. Sci.* **2013**, *15*, 401–409.
- (38) McCalla, E.; Lowartz, C. M.; Brown, C. R.; Dahn, J. R. Formation of layered–layered composites in the Li–Co–Mn oxide pseudoternary system during slow cooling. *Chem. Mater.* **2013**, *25*, 912–918.
- (39) McCalla, E.; Rowe, A. W.; Shunmugasundaram, R.; Dahn, J. R. Structural study of the Li–Mn–Ni oxide pseudoternary system of interest for positive electrodes of Li-ion batteries. *Chem. Mater.* **2013**, *25*, 989–999.
- (40) Kumar, A.; Dutta, S.; Kim, S.; Kwon, T.; Patil, S. S.; Kumari, N.; Jeevanandham, S.; Lee, I. S. Solid-state reaction synthesis of nanoscale materials: Strategies and applications. *Chem. Rev.* **2022**, *122*, 12748–12863.
- (41) Wang, D.; Belharouak, I.; Koenig, G. M.; Zhou, G.; Amine, K. Growth mechanism of NiO. 3MnO. 7CO3 precursor for high capacity Li-ion battery cathodes. *J. Mater. Chem.* **2011**, *21*, 9290–9295.
- (42) Lipson, A. L.; Durham, J. L.; LeResche, M.; Abu-Baker, I.; Murphy, M. J.; Fister, T. T.; Wang, L.; Zhou, F.; Liu, L.; Kim, K.; Johnson, D. Improving the thermal stability of NMC 622 Li-ion battery cathodes through doping during coprecipitation. *ACS Appl. Mater. Interfaces* **2020**, *12*, 18512–18518.
- (43) Carey, G. H.; Dahn, J. R. Combinatorial synthesis of mixed transition metal oxides for lithium-ion batteries. *ACS Combi. Sci.* **2011**, *13*, 186–189.
- (44) Potts, K. P.; Grignon, E.; McCalla, E. Accelerated screening of high-energy lithium-ion battery cathodes. *ACS Appl. Energy Mater.* **2019**, *2*, 8388–8393.
- (45) Hebert, A.; David, C.; McCalla, E. Combinatorial Investigation of the Impact of Systematic Al Substitution into LiNi1–x–y Mn x Co y O2 Materials. *ACS Appl. Energy Mater.* **2023**, *6*, 4593–4603.
- (46) McCalla, E.; Parmaklis, M.; Rehman, S.; Anderson, E.; Jia, S.; Hebert, A.; Potts, K.; Jonderian, A.; Adhikari, T.; Adamič, M. Combinatorial methods in advanced battery materials design. *Can. J. Chem.* **2022**, *100*, 132–143.

- (47) Adhikari, T.; Hebert, A.; Adamic, M.; Yao, J.; Potts, K.; McCalla, E. Development of high-throughput methods for sodium-ion battery cathodes. *ACS Combi. Sci.* **2020**, *22* (6), 311–318.
- (48) Jonderian, A.; Peng, R.; Davies, D.; McCalla, E. Benefits and limitations of 226 substitutions into Li-La-Ti-O perovskites. *Chem. Mater.* **2023**, *35* (2023), 6227.
- (49) Bokov, D.; Turki Jalil, A.; Chupradit, S.; Suksatan, W.; Javed Ansari, M.; Shewael, I. H.; Valiev, G. H.; Kianfar, E. Nanomaterial by sol-gel method: synthesis and application. *Adv. Mater. Sci. Eng.* **2021**, *2021*, 1–21.
- (50) Jonderian, A.; Ting, M.; McCalla, E. Metastability in Li–La–Ti–O perovskite materials and its impact on ionic conductivity. *Chem. Mater.* **2021**, *33*, 4792–4804.
- (51) Murray, V.; Hall, D. S.; Dahn, J. R. A guide to full coin cell making for academic researchers. *J. Electrochem. Soc.* **2019**, *166*, A329–A333.
- (52) Cumyn, V. K.; Fleischauer, M. D.; Hatchard, T. D.; Dahn, J. R. Design and testing of a low-cost multichannel pseudopotentiostat for quantitative combinatorial electrochemical measurements on large electrode arrays. *Electrochem. Solid-St. Lett.* **2003**, *6*, No. E15.
- (53) Yik, J. T.; Zhang, L.; Sjölund, J.; Hou, X.; Svensson, P. H.; Edström, K.; Berg, E. J. Automated electrolyte formulation and coin cell assembly for high-throughput lithium-ion battery research. *Digit. Discovery* **2023**, *2*, 799–808.
- (54) Matsuda, S.; Nishioka, K.; Nakanishi, S. High-throughput combinatorial screening of multi-component electrolyte additives to improve the performance of Li metal secondary batteries. *Sci. Rep.* **2019**, *9* (1), 6211.
- (55) Konz, Z. M.; Wirtz, B. M.; Verma, A.; Huang, T. Y.; Bergstrom, H. K.; Crafton, M. J.; Brown, D. E.; McShane, E. J.; Colclasure, A. M.; McCloskey, B. D. High-throughput Li plating quantification for fast-charging battery design. *Nat. Energy* **2023**, *8*, 450–461.
- (56) Liu, M.; Zhang, S.; van Eck, E. R.; Wang, C.; Ganapathy, S.; Wagemaker, M. Improving Li-ion interfacial transport in hybrid solid electrolytes. *Nat. Nanotechnol.* **2022**, *17*, 959–967.
- (57) Bron, P.; Dehnen, S.; Roling, B. Li₁₀Si_{0.3}Sn_{0.7}P₂S₁₂—A low-cost and low-grain-boundary-resistance lithium superionic conductor. *J. Power Sources* **2016**, *329*, 530–535.
- (58) Han, F.; Westover, A. S.; Yue, J.; Fan, X.; Wang, F.; Chi, M.; Leonard, D. N.; Dudney, N. J.; Wang, H.; Wang, C. High electronic conductivity as the origin of lithium dendrite formation within solid electrolytes. *Nat. Energy* **2019**, *4*, 187–196.
- (59) Wu, F.; Fitzhugh, W.; Ye, L.; Ning, J.; Li, X. Advanced sulfide solid electrolyte by core-shell structural design. *Nature Commun.* **2018**, *9*, 4037.
- (60) Yada, C.; Lee, C. E.; Laughman, D.; Hannah, L.; Iba, H.; Hayden, B. E. A high-throughput approach developing lithium-niobium-tantalum oxides as electrolyte/cathode interlayers for high-voltage all-solid-state lithium batteries. *J. Electrochem. Soc.* **2015**, *162*, A722.
- (61) McCalla, E.; Carey, G. H.; Dahn, J. R. Lithium loss mechanisms during synthesis of layered Li_xNi₂–xO₂ for lithium ion batteries. *Solid State Ion.* **2012**, *219*, 11–19.
- (62) Minami, K.; Mizuno, F.; Hayashi, A.; Tatsumisago, M. Lithium ion conductivity of the Li₂S–P₂S₅ glass-based electrolytes prepared by the melt quenching method. *Solid State Ion.* **2007**, *178*, 837–841.
- (63) Chairunnisa, A. Synthesis of LiFePO₄ (Lithium Iron Phosphate) with Several Methods: A Review. *RHAZES: Green Appl. Chem.* **2020**, *10*, 49–81.
- (64) Degen, T.; Sadki, M.; Bron, E.; König, U.; Nénert, G. The highscore suite. *Powder diffraction* **2014**, *29*, S13–S18.
- (65) Jain, A.; Ong, S. P.; Hautier, G.; Chen, W.; Richards, W. D.; Dacek, S.; Cholia, S.; Gunter, D.; Skinner, D.; Ceder, G.; Persson, K. A. Commentary: The Materials Project: A materials genome approach to accelerating materials innovation. *APL Mater.* **2013**, *1*, No. 011002.
- (66) Ren, Z.; Ren, Z.; Zhang, Z.; Buonassisi, T.; Li, J. Autonomous experiments using active learning and AI. *Nat. Rev. Mater.* **2023**, *8*, 563–564.
- (67) JoVE Science Education Database. *Inorganic Chemistry. Single Crystal and Powder X-ray Diffraction*. JoVE, Cambridge, MA, 2023.