The operation of batteries, fuel cells, and other energy storage and conversion devices is underpinned by the intricate synergy of ion transport, phase transformations, and electrochemical reactions. While electrochemical processes in well-defined molecular systems are amenable to classical chemical techniques including in situ optical spectroscopies and nuclear magnetic resonance (NMR), phase transformations and reactivity in solids and at solid interfaces remain largely an enigma. The presence of multiple types of structural defects and imperfections, competing electron and ion transport pathways, and multiple possible surface reconstruction types, combined with the directionality of ion flows and state of charge transformation fronts render these phenomena inaccessible to macroscopic interrogation techniques. At the same time, knowledge of the individual mechanisms involved in electrochemical reactivity of solids at the level of individual, atomic size structural elements is required for understanding the fundamental mechanisms of energy storage, factors controlling charge/discharge rates, degradation and failure processes, and ultimately knowledge-driven prediction and optimization of energy materials.1,3

In the last 15 years, a number of remarkable breakthroughs in aberration correction in the transmission electron microscope (TEM) and scanning transmission electron microscope (STEM) have opened possibilities for sub-angstrom characterization of materials, both from structural and chemical points of view (see schematic of a STEM in the center of Fig 1). With achievable resolution as low as 0.5 Å4 imaging single atoms became routine, and it became possible to identify a single atom both from imaging5 and from spectroscopic signals.5,7 For crystals, collection of two-dimensional, atomic resolution chemical maps became feasible,8,9 and imaging of light element columns such as lithium10,11 and even hydrogen12 has been reported.

Alongside these developments in the world of ultra-high resolution, there has been remarkable development in a variety of in situ techniques and platforms enabling observation of dynamic processes under a variety of external stimuli inside an electron microscope. The progress made is evident, and is manifested in the advances in in situ mechanical testing of micro- and nanoscale objects,13-15 in studies of heterogeneous catalysts at elevated temperatures and in gaseous atmosphere while preserving high resolution,16-18 and in imaging of processes occurring in liquids19. Another growth area within the in situ electron microscopy field involves the application of bias inside the microscope. A variety of approaches have been reported, from uniform biasing of specially fabricated specimens20 to using a setup with a moveable tip to apply the bias locally.21,22 While most of the results reported thus far deal with ferroelectric switching, materials such as oxygen conductors23 and resistive memories24 can also be characterized using in situ biasing. An especially interesting variation involves the use of vacuum-compatible ionic liquids.25

In this article, we present the possibilities that STEM and electron energy loss spectroscopy (EELS) offer in terms of probing fundamental aspects of electrochemical systems by combining electron microscopy with in situ control of local electrochemical potentials by tuning the atmosphere, by biasing, or using a liquid environment. A graphical summary of the available methods is given in Fig 1, with several examples below. The examples discussed herein will follow Fig. 1 clockwise from the upper right, starting with high resolution investigations in static or ex situ conditions and ending with in situ electrochemical liquid cell studies.

One of the beneficial consequences of the higher resolution of the aberration-corrected microscopes has been a marked improvement in signal to noise ratio of the images, enabling detection of structural distortions down to the single picometers level. This capability was most extensively utilized to probe ferroelectric materials, where off-center displacements of metal cations in the unit cell are directly related to ferroelectric polarization.26-30 However, the same capability can be utilized for atomic-level studies of the oxygen conducting oxides used in solid oxide fuel cells based on their chemical expansivity behavior. Chemical expansivity refers to the expansion of some oxygen conducting materials in a reducing atmosphere and is well known in the field of solid state electrochemistry.31 Their expansion scales linearly with the log of oxygen partial pressure and can be detected dilatometrically.31-32 In Ref. [33], Kim and coworkers have demonstrated that the concept of chemical expansivity can be extended all the way to atomic level, showing that local lattice spacings measured from high-angle annular dark-field (HAADF) STEM images are linearly related to the local oxygen content. They studied La$_{1.5}$Sr$_{0.5}$CoO$_3$ (LSCO) thin films on lanthanum strontium aluminum tantalate (LSAT) and neodymium gallate (NGO) substrates. Both films demonstrated lattice parameter modulations; EELS studies were used to show that the modulation was associated with oxygen vacancy ordering, with larger local lattice spacing corresponding to an oxygen-depleted layer (Fig. 2a). The LSCO/NGO film was identified as brownmillerite La$_{2.9}$Sr$_{0.9}$CoO$_{3+δ}$ via a detailed structural study, while the observed chemical expansion in LSCO/LSAT film was lower. First principles calculations were

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then used to demonstrate that local lattice spacing changes increased linearly with the number of oxygen vacancies. The results of the calculations, which matched very well with experimental measurements of layer spacings in $La_{0.5}Sr_{0.5}CoO_{2.5}$, were then used as a calibration curve to recalculate lattice spacings into a local oxygen content (Fig. 2b, c). From this interpretation, the average composition of the LSCO/LSAT thin film was determined to be $La_{0.5}Sr_{0.5}CoO_{2.75}$. This film showed considerable local inhomogeneity, highlighting the capabilities of the method to detect both global composition and local variations.

Distribution of oxygen vacancies and the emergence of vacancy ordering are of critical importance to ionic conductivity, and changes in the vacancy distribution under a given operating condition can have a profound effect on the longevity of the material. While the fine structural analysis used by Kim et al. is not yet feasible under bias or other realistic conditions, ex situ studies, when materials are being investigated before and after external stimuli are applied, can provide initial insights. Recently, Leonard et al. used Electrochemical Strain Microscopy (ESM) to subject different areas of the $La_{0.8}Sr_{0.2}CoO_{3-δ}$ (LSCO) thin film on yttria stabilized zirconia to bias cycling with different amplitudes. The deformation hysteresis loops resulting from the cycling were recorded. Additionally, bias cycling produced visible and irreversible deformation of the surface, the extent of which varied with the amplitude of the bias applied (see AFM image in Fig. 2d).

To examine the nature of the structural changes, a focused ion beam was used to make a STEM specimen with individually addressable windows for each applied bias value (Fig. 2e). Most of the visible deformation was attributed to surface amorphization and the formation of voids; however, changes to the crystalline structure as a function of bias were also detected. Fig. 2f shows a HAADF STEM image of LSCO crystal lattice showing some lattice modulation, using the same approach as Kim et al. The spacing map derived from the area in the red square shows that the ordering is not homogeneous. Leonard et al. collected a sampling of such maps for regions for each value of bias amplitude. Using the average difference between high and low lattice spacings as a measure of the degree of order,
they showed that the degree of order increased after bias cycling, however the increase was independent of the bias amplitude (Fig. 2g). This finding suggests that vacancy ordering is thermodynamically favorable, however kinetically hindered under the growth conditions. Bias cycling effectively “anneals” vacancies to the favorable ordered state.

Of equal interest are the atomic-scale investigations of structural and electronic structures of materials for lithium-ion batteries (LIB). The presence of mobile (at room temperature) ions in these materials renders them extremely sensitive to the electron beam. Recently it has been demonstrated that the combination of Z-contrast imaging and EELS is an ideal technique for studying cycling or degradation mechanisms of LIB electrode materials, especially for cathodes based on transition metal intercalation oxides. These materials consist of a largely unchangeable host with specific sites wherein Li ions intercalate. While charging, Li ions are extracted from the cathode host and solvate into and move through the non-aqueous electrolytes. The charge balance during Li extraction is retained by the oxidation of transition metal(s) in the material. During discharge, lithium ions are expected to insert back to the lattice frame fully while the transition metal(s) is/are reduced to their original states. The structural and chemical stabilities of the material at the atomic/ionic scale upon electrochemical cycling thus heavily affects its reversible capacity and operating voltage, which directly determines the energy density and longevity of the LIB.

Recent electron microscopy studies have revealed unexpected structural and chemical evolutions at atomic-scale, which can rarely be detected by other characterization techniques. As an example of such work, Fig. 3a-d (continued on next page)

**Fig. 3.** (a, b) Atomic resolution Z-contrast images of pristine (a) and after 10 cycles (2-4.8V) (b) of Li-rich layered Li[Ni$_{1/3}$Li$_{1/3}$Mn$_{1/3}$]O$_2$ grains along the [100] zone axis. The surface structural transformation due to TM ions migration to lithium sites after cycling partially blocks the Li transport pathway, as schematically shown by dashed arrows; small orange arrows show observed TM migration in grain bulk (less pronounced than at the surface). (c) EELS fine structures of O-K and Mn-L edges proves the surface structural transformation. (d) Li-K edge spectra show significant Li loss at the surface of cycled particles. EELS spectra of MnO$_2$, LiF and NiO used for MLLS fitting are also displayed for reference. (e) The schematic of low-noise, high-stability biasing stage developed for in situ atomic resolution imaging and spectroscopy upon electrochemical cycling in all-solid-batteries. (f) TEM image of the e-beam transparent window before cycling (g), and elemental maps of each component after one charge-discharge cycle inside an electron microscope between 1.5-3.6V (panels a-d adapted from Ref.37).
We recently developed an *in situ* biasing stage based on direct connection of an all-solid nanobattery to two fixed contacts, providing a relatively robust design for *in situ* TEM observations at atomic resolution. The schematic of the design is shown in Fig. 3e. Such design allows the combination of *in situ* analysis with a complete suite of advanced electron microscopy techniques such as atomic-resolution imaging, EELS analysis and diffraction, which are difficult to achieve with other existing *in situ* TEM setups. This configuration is believed to enable direct observation of Li diffusion, transition metal valence alteration, and compositional/structural evolution over a wide length scale, from μm to Å, under electrochemical bias.

This approach was demonstrated via *in situ* studies of an active battery structure as illustrated in Fig. 3f-g, depicting elemental maps of each component in the nanobattery after one charge-discharge cycle inside an electron microscope between 1.5-3.6 V. This nanobattery was composed of A12O3 (substrate), Au (current collector), LiCoO2 (cathode), LIPON (lithium phosphorus oxynitride, electrolyte), Si (anode), Pt (current collector), and W (FIB protective layer). EELS spectrum-imaging was performed to monitor lithium migration and transition metal oxidizing/reducing characteristics during cycling. Detailed dynamic electronic structural evolution of each component can be investigated using such a configuration. For example, as shown in Fig. 3g, the lithium in LIPON can be differentiated from that in LiCoO2 by selecting their characteristic fingerprints in the EELS fine structure. It is important to point out that further improvements of such *in situ* stages (in terms of stage tilting flexibility, stability, and the incorporation of cooling and vacuum-transfer systems) are needed for atomic-resolution studies in battery research.

A variety of *in situ* TEM characterization platforms have been developed and recently utilized to probe electrochemical processes in real time and with high spatial resolution in terms of structural and chemical changes as a result of electrical stimuli. These electrochemical measurement platforms can be subdivided into two categories: an open cell electrical biasing platform and a closed electrochemical cell platform. In the open cell configuration, an *in situ* TEM biasing system is used to apply a potential difference between electrodes to induce structural and chemical changes. Specific to Li-ion battery research, structural changes in SnO2 nanowire electrodes have been studied during Li intercalation in experiments facilitated by the use of TEM vacuum-compatible, ionic liquid-based electrolytes as a medium for Li-ion transport.49,50 Organic and aqueous based electrolytes have a high vapor pressure and would readily evaporate when placed in the high vacuum environment of the electron microscope; therefore, an alternative method has been developed.

In *in situ* liquid cell microscopy is a rapidly emerging *in situ* S/TEM based characterization technique that allows for the direct imaging and analysis of liquid phase phenomena at high spatial and temporal resolution.51 This method utilizes microfabricated silicon microchip devices to encapsulate thin layers of liquid electrolyte between electron transparent silicon nitride membranes. The entire assembly is contained within vacuum-tight *in situ* TEM holders. The silicon nitride membranes provide an electron transparent media through which evolving chemical processes within a liquid environment can be directly imaged and analyzed. Modification of the liquid cell microchip platform with microelectrodes has opened a new pathway to investigate electrochemical processes in a technique termed *in situ* electrochemical S/TEM (*In situ* ec-S/TEM). Here the “on-chip” microelectrodes are interfaced with electrical biasing contacts that are embedded within the tip of the vacuum-tight *in situ* TEM holders, which are in turn interfaced with a potentiostat for electroanalytical studies. The electrochemical microchip devices along with the *in situ* TEM holder can be seen in Fig. 4 a-d.

With this system, the reactions kinetics and mechanisms of electrochemical processes have been explored. For example, Unocic *et al.*52 have applied several electroanalytical techniques (cyclic voltammetry, chronamperometry, and electrochemical impedance spectroscopy) to demonstrate how quantitative electrochemical measurements can be performed using these microfluidic electrochemical cells with microfabricated microelectrodes using a ferri-ferrocyanide redox reaction couple. They also showed that the results could be quantitatively analyzed and compared with well-established theories in electrochemistry. Additional electrochemical studies using this approach have elucidated dynamics of metal nanoparticle nucleation and growth under galvanostatic electrodeposition conditions, which were then compared with electrochemical nucleation rate theory.52,53 Similar studies have been used to investigate the electrodeposition of Ni films from an aqueous NiCl2 electrolyte and Pb dendrites from an aqueous Pb(NO3)2 electrolyte under constant potential.54,55 Related to lithium ion battery research, this technique has recently been used to visualize the lithiation and delithiation of silicon nanowires,56 to track ionic transport in LiFePO4,57 and to investigate the nucleation and growth mechanisms of the solid electrolyte interphase (SEI) layer in lithium ion batteries49 using organic battery electrolytes as shown in Fig. 4e.

This article summarizes some recent advances in electron microscopy based studies of electrochemical processes in solids and at solid-liquid and solid-gas interfaces. STEM/EELS directly probes a broad range of parameters related to the electrochemical state of the system, including local atomic configurations, bond length and angles,
behavior into the functionality of a given material under study, and using this information to develop and refine predictive theories. Overall, the combination of STEM/EELS with dynamic electrochemical probing promises to provide an outstanding tool for the exploration of electrochemical systems at hitherto unreachable levels of magnification and resolution.

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