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Review Article

Current understanding of electrochemical strain microscopy to visualize ion behavior on the nanoscale

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Abstract

Electrochemical Strain Microscopy (ESM) is a technique based on Atomic Force Microscopy and provides information about local ionic processes through electro-chemo-mechanical coupling. It is employed foremost in studying battery materials, from cathodes, and anodes to solid-state electrolytes. Based on this overlap we aim to connect the electrochemistry community further with those employing ESM, by providing the current understanding of ESM, starting with a thorough introduction to the technique. In the second section, typical applications and challenges identified in recent years are reviewed while in the third chapter new approaches to overcome these issues are presented. This includes the identification of various contributions to the ESM signal, the integration of ESM as part of a multi-modal characterization approach, and importantly, how to link local ESM results to the overall cell performance in batteries. Lastly, upcoming trends and new aspects are discussed, including the application of *in-situ* ESM directly in an electrochemical environment.

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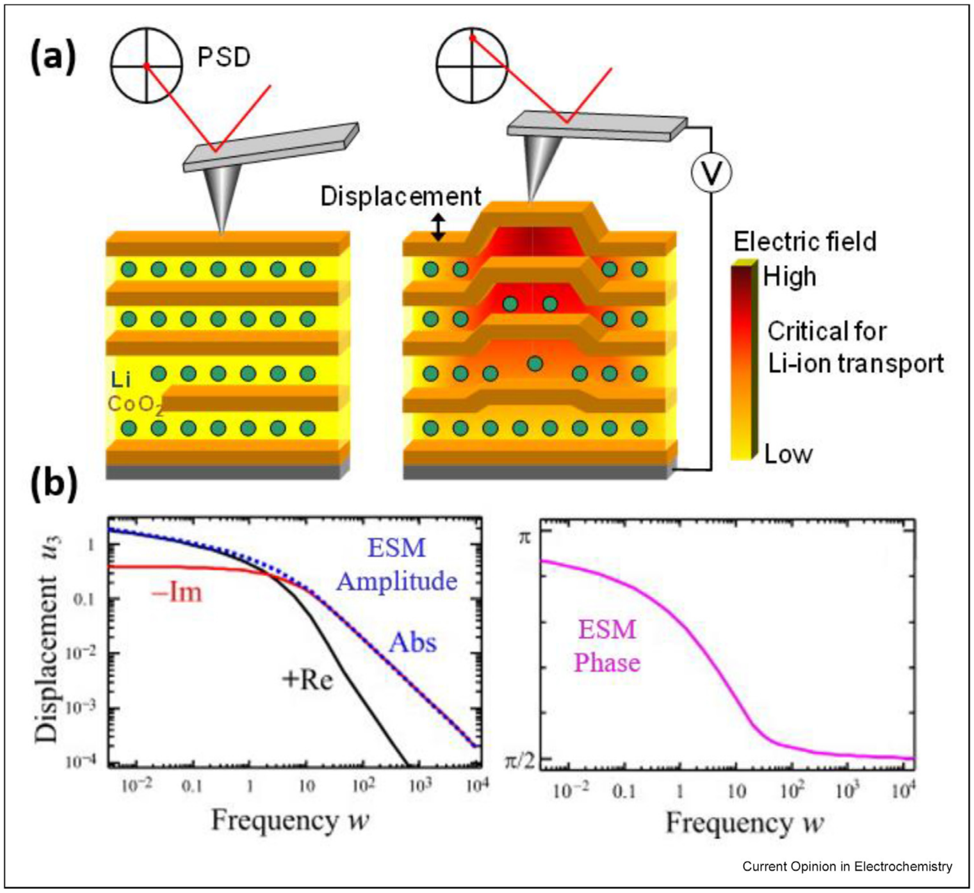
Keywords

Electrochemical Strain Microscopy (ESM), Ion mobility, Energy Materials, Batteries, Electro-Chemo-Mechanical coupling.

History and operating principle

Energy storage technologies, such as batteries or electrochemical capacitors, rely on ionic transport through the device across unit cells, grain boundaries, and interfaces. Accessing information about ionic transport on small-length scales is difficult with traditional electrochemical methods that measure electrical current due to limitations of electrode sizes. This challenge can be overcome when utilizing the electro-chemo-mechanical coupling between ion concentration and unit cell volume. Therefore, a closer scientific exchange between the electrochemistry community and those employing ESM in designing correlative investigations is envisioned to further develop the ESM technique. The change in ion concentration in materials produces a mechanical contraction or expansion of the material in order to accommodate the change in electron density or volume and mass of the inserting ion [1]. This mechanical response to ion intercalation is termed electrochemical strain or Vegard's strain and can be measured locally using Electrochemical Strain Microscopy (ESM). Similar to standard atomic force microscopy the achievable spatial resolution depends on various influences such as tip radius, surface morphology, scan speed, and dielectric properties of the material which determine the radial field drop. For ESM the probed volume by the applied electric field is typically tens of nanometres, slightly larger than the tip radius of about 20–50 nm. ESM utilizes a metallically coated probe that is scanned in contact over the sample surface. The probe can be used to apply localized electric fields to the sample resulting in a local redistribution of mobile ions. Typically, voltages are applied as sinusoidal waveforms to probe reversible ion transport. This induces cyclical volume changes that are detected by the ESM probe through a laser and a photodetector (Figure 1a) [1] and analyzed using lock-in techniques to extract the amplitude of the strain oscillation. The term ESM was first introduced in 2010 where ESM was demonstrated on $LiCoO_2$ thin films [2] and described theoretically [3]. The electrochemical strain is highly dependent on the frequency of the applied voltage (Figure 1b) [3]. At low frequencies, *i.e.*, below the characteristic diffusion time of the ions in the probed material volume, the expected amplitude of the varying electrochemical strain (ESM amplitude) is constant as all ions are fast enough to directly respond to the applied potential. However, when the frequency of the applied field is too high, the ions do not move at all anymore, resulting in a drop of the electrochemical strain amplitude and a time lag between the applied

Figure 1



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(**a**) The concept of ESM using a biased AFM probe for a layered material such as $LiCoO_2$. Adapted with permission from [1]. Green circles represent Li ions. (**b**) The absolute value and phase of normalized ESM amplitude (displacement u_3), vs dimensionless frequency for fixed ionic flux, where 1 is the characteristic diffusion time in the probed volume. Adapted with permission from [3]. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

field and the electrode's strain response, which is the ESM phase. The cross-over point between these two behaviors is the characteristic diffusion frequency τ which is proportional to the diffusion coefficient D. Therefore, ESM has the potential to directly image ionic diffusivity on local scales. However, the ESM signal is inherently coupled to the ion concentration itself. The diffusion coefficient depends on the overall ion concentration [4,5] which also affects the predicted ESM amplitude [6]. Therefore, the separation of diffusivity and ion concentration from ESM and the comparison of regions of different ion concentrations become difficult. To differentiate these influences from each other, ESM is used as part of a multimodal approach (c.f. section 3) or by fitting the ESM signal to theoretical models based on frequency-dependent measurements [7]. Moreover, the ESM signal itself will depend not only on the diffusion coefficients and concentration of the mobile ionic species and the frequency of the applied field, but also on other parameters such as the field amplitude, the tip radius, the dielectric constant of the material, and the electronic conductivity of the material [6].

Since electrochemical strain can be very small, most ESM work utilizes contact resonance enhancement of the ESM probe in contact with ionically conducting materials which acts as a harmonic oscillator. Multiple approaches have been used in ESM to measure the contact resonance enhancement including using a phase-locked loop (PLL) [8], dual AC resonance tracking (DART) [9], sequential excitation ESM (SE-ESM) [10] and band excitation (BE) techniques [2]. The different technical implementations affect accuracy of extracted ESM amplitude and phase, overall signal strength, and measurement time. In all cases, the contact resonance peak is fitted with a simple harmonic oscillator and the ESM amplitude and phase of the periodically varying electrochemical strain are extracted. Using the contact resonance enhancement to measure ESM results in a high signal-to-noise ratio and is easily implemented in commercially available atomic force microscopes. However, this approach limits ESM to the contact resonance frequency, typically several hundred kHz, which is well above the characteristic diffusion time. In this regime, the applied bias results in evanescent concentration waves with sub-nm ionic drift length but still measurable ESM response in the picometer regime [6]. Interestingly, the electronic conductivity was found to not affect the ESM signal in the high-frequency regime [6]. In the presence of electronic conductivity, the static Debye screening length becomes very small. However, the Debye screening length in response to the AC fields applied during ESM becomes frequency-dependent. In that case, the screening effectiveness is reduced at high frequencies, depending on the mobility of electronic charge carriers. Therefore, high-frequency ESM can be applied to mixed ionic electronic conducting materials.

In addition, low-frequency approaches to ESM that do not utilize the contact resonance enhancement have been implemented [7]. However, the applied frequencies were still in the kHz regime. To also probe ions with a slower reaction time than the applied AC voltage in the kHz regime, a DC voltage might be applied additionally. This allows the recording of different aspects, such as for imaging or tracking the ESM amplitude and phase as a function of DC voltage amplitude (so-called ESM hysteresis or ESM voltage spectroscopy) or following the relaxation process of the strain in the time domain (ESM relaxation) during and after DC voltage pulses at single points or spatial grids.

Applications and challenges

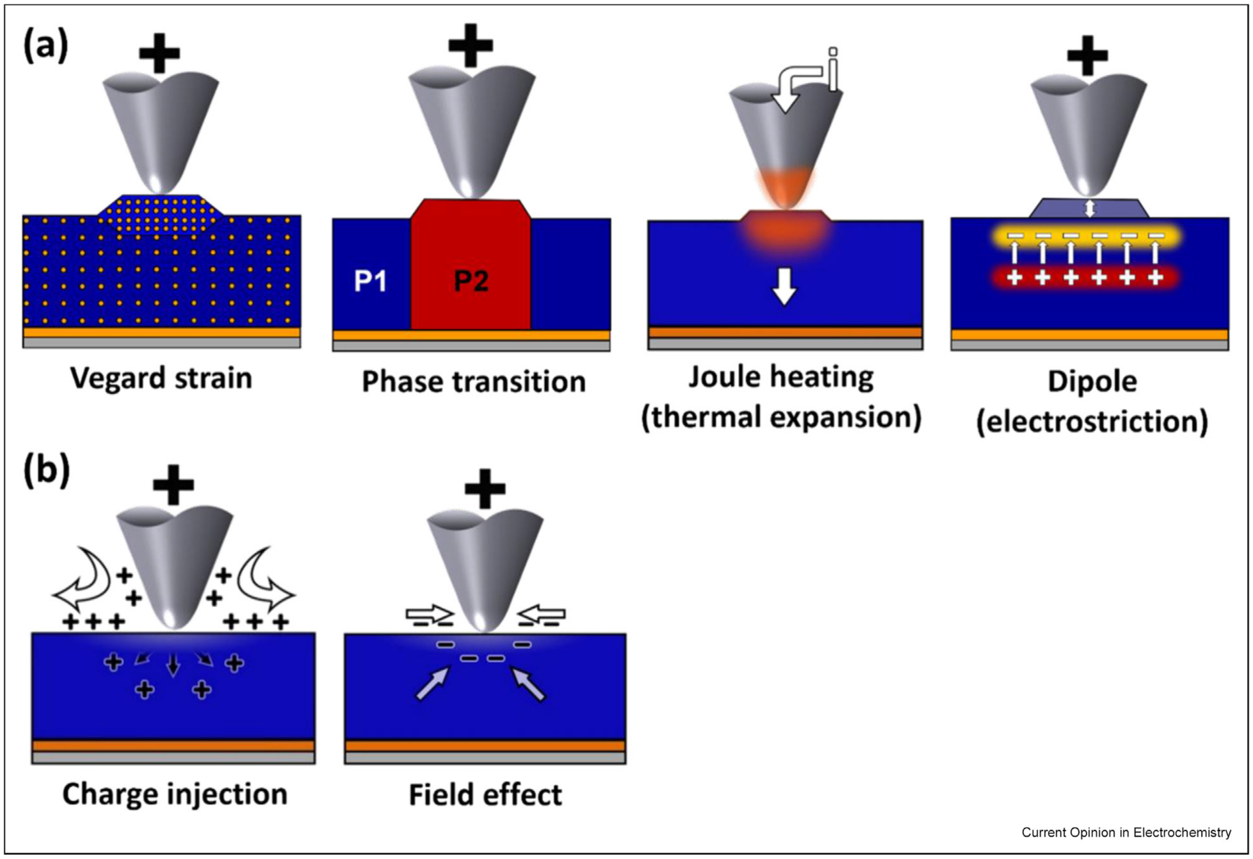
Since the early experimental ESM work on $LiCoO_2$ (LCO) [2], a typical cathode material for commercial Lithium-ion batteries, the technique has been applied to several energy storage materials and beyond. Recent reports of ESM include the analysis of ferroelectric properties [11], electrochemical transistors [12] and halide perovskites [13]. However, Li-ion battery materials remain the prioritized application for ESM reflecting the general trend in battery materials research: for cathode chemistries, ESM has been employed for materials like LCO [2] and $LiFePO_4$ [14], while more nickel- and manganese-containing materials such as $LiNi_{0\cdot6}Co_{0\cdot2}Mn_{0\cdot2}O_2$ (NCM) [15], $LiNi_{0\cdot885}Co_{0\cdot1}Al_{0.015}O_2$ (NCA) [16], or $LiMn_2O_4$ (LMO) [17] have been investigated in recent ESM experiments. In addition, other material classes have gained significant importance with polymer [18,19] and solid-state electrolytes in particular [20–22]. On the anode side, ESM is applied to graphite [23], silicon [24] or composite materials [25,26].

The most notable finding across the different materials is the locally large variation of the ESM signal, indicating a heterogeneous distribution in ion diffusivity [26] or concentration [7], the differentiation of local distribution of active material and binders [15], the detection of secondary phases, chemical distribution and grain orientation in ceramic materials for solid-state electrolytes [8,21,22], and even variations of the ESM signal within single active particles [15,17]. With the increased application of ESM, several challenges, however, have also been identified and addressed in the last few years. Three of the biggest challenges include the following aspects.

- Primary signal origin of ESM
- Direct quantification of ESM with respect to ion diffusivity or ion concentration
- Correlation of ESM with other microscopic and spectroscopic experiments as well as electrochemical performance

Figure 2a and 2b [27] illustrate the challenges for the interpretation of ESM signals as multiple effects can contribute to the measured ESM signal besides the Vegard strain that has been discussed for AFM-based techniques that utilize a biased AFM probe. This includes effects that cause an electrode volume change such as a bias-induced phase transition, thermal expansion when currents flow, and electrostriction (Figure 2a). Other effects can exert forces on the ESM probe, modifying the ESM amplitude, which includes electrostatic forces that vary in the presence of surface charges and depend on the dielectric properties of the material (Figure 2b). Importantly, only if the applied voltage induces Vegard strain, the applied method should be called ESM. Although in the case of zero-strain materials a contrast might be obtained, the term ESM should be avoided, and other terminology needs to be used. Currently, not all shown mechanisms are discussed in the context of ESM but are described in more detail for other AFM-based techniques that are comparable to ESM by Kalinin et al.[26] Furthermore, when contact resonance ESM is used, the ESM amplitude will be modulated by the mechanical properties of the electrode which can vary spatially and upon ion intercalation [19,28,29]. A change in mechanical material property effectively changes the contact stiffness between the tip and the sample which modulates the beam shape of the vibrating ESM probe [30]. Since ESM is measured using an optical beam deflection principle, the ESM amplitude will be very sensitive to beam shape changes. This effect is described for the related scanning probe technique named Piezoelectric Force Microscopy [30]. Hence, there is an understanding that the Vegard strain is only one out of various signal origins and the contribution of each mechanism to the overall signal will depend on the individual sample and its properties. This poses a grand challenge to the local quantification of ion diffusivity from ESM measurements.

Figure 2



(**a**) Possible signal origins contributing to an electrode volume change. (**b**) Electrostatic signal contributions to the ESM signal Adapted with permission from [27].

Besides ESM signal origin and quantification challenges, an important current drawback of ESM is that it cannot be readily compared to electrochemical measurements on the cell level. First, ESM is mostly applied to individual battery components and not to fully functional cells that include cathode, anode, and electrolyte. Second, the applied voltages during ESM are somewhat arbitrary in the absence of a reference electrode which makes comparison to electrochemical measurements challenging. Third, ESM measurements are often conducted at high frequencies only while electrochemical measurements often span multiple frequencies (or scan rates) at much lower frequencies. These items result in the question of how comparable ESM is to macroscopic measurement characterization approaches based on current that is the standard in energy storage research.

Overcoming challenges of ESM

The above-mentioned challenges need to be overcome to make ESM a quantitative and relevant characterization technique for energy storage research. This can be achieved if ESM is not a stand-alone approach but is coupled with theory and other characterization techniques across multiple length scales to guide the interpretation of ESM data. Currently, not all potentially parasitic mechanisms as illustrated in Figure 2 are discussed in the context of ESM which needs to be addressed. In addition, ESM measurements need to be adapted to closely align with traditional electrochemical techniques and relate to important parameters and considerations of the electrochemical community. In recent years, several works started to tackle the challenges of ESM. Great progress has been made in the advanced modeling of the ESM signal, the separation of signal contributions and reduction of electrostatics, the combination of ESM with other characterization techniques, as well as implementation of *ex-situ* and *in-situ* ESM modalities.

Identification of ESM signal origins

Non-Vegard signal contributions to ESM can be quite significant as shown by Schön et al. on the solid-state electrolyte $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (LATP) [22]. This aligns with early reports on solid-state electrolytes that excluded the effect of Vegard strain as the primary mechanism for ESM signal formation, based on ion dynamics calculations [20]. In addition, Badur et al. performed a more detailed analysis of the complex signal formation and found that even for a material with an exceptionally high diffusion coefficient, namely $Cu_2Mo_6S_8$, Vegard strains are only detected at sufficient temperatures and the suppression of electrostatic signals [31]. To avoid electrostatic signal contributions, ESM approaches that compensate frequency-independent electrostatic contributions were introduced [32]. If electrostatic contributions cannot be avoided, it will be important to separate them from the ESM signal which can be achieved by modeling the ESM signal under consideration of electrostatics. This requires a more accurate description of the ESM signal itself. Recent advances towards this goal have included ESM calculations of the solid-state oxide anion conductor CeO_2, considering the concentration-dependent Vegard strain and stress-dependent diffusivity [33]. Understanding ESM signal origins and improving theoretical signal descriptions will play an important part in extracting quantitative material properties, such as diffusivity, from ESM measurements.

ESM as part of a multi-modal characterization approach

In order to guide the interpretation of ESM measurements and identify the correlation between the local ionic transport and other material properties, such as structure, chemistry and mechanical properties, ESM needs to become a part of multi-modal characterization approaches. In recent years, ESM was predominantly combined with other methods to gain information about chemistry and electronic states. This included correlative energy dispersive X-ray spectroscopy (EDX) for LATP [8] and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) for a conductive Li ion glass ceramic [34]. In both cases, the authors directly correlated the ESM signal to Li-ion concentration and mobility, a strong step towards quantification of ESM. In addition, using Near Edge X-ray absorption fine spectroscopy (NEXFAS) on NCM622 particles, it was shown that the ESM signal relates to the electronic binding in the NCM particles and that the ESM signal correlated with the ion mobility rather than the concentration [15]. Another successful multi-modal characterization approach compared the heterogeneous ESM signal obtained on NCM622 particles with results from nanoindentation experiments on the same sample and found a close relationship between Hardness and reduced Young's modulus and the ESM signal [28]. Comparing ESM with complementary characterization approaches will allow to tie together information about structure, chemistry, and ionic transport in the future.

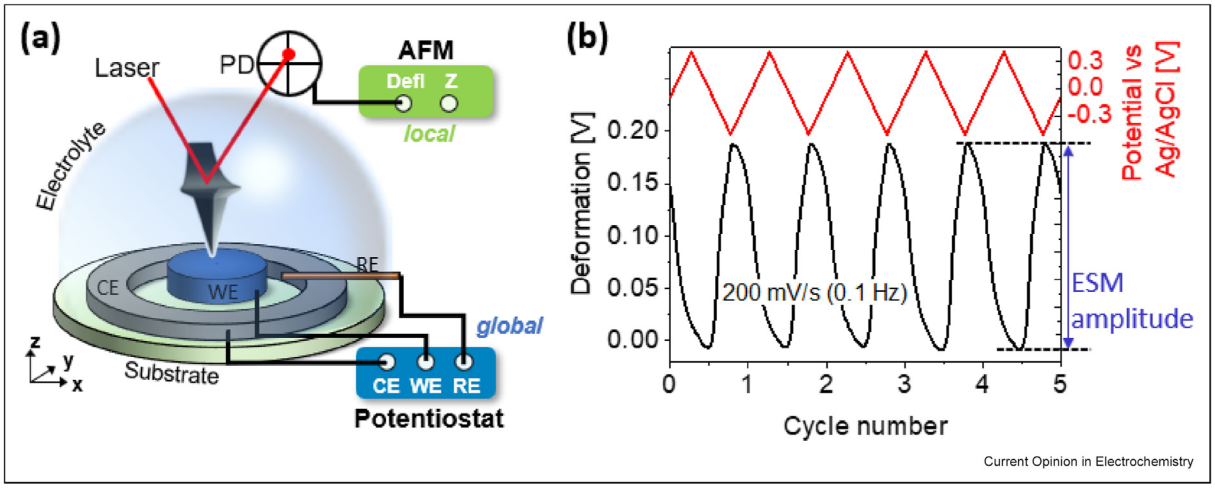
Linking local ESM information to cell-level electrochemistry

The link between the ESM signal and intrinsic electrochemical parameters that are defined on the cell-level, such as state of charge (SOC) and state of health (SOH) can contribute to a deeper understanding how nanoscale processes contribute to the overall performance indicators of batteries. Towards this goal, *ex-situ* ESM was performed on electrochemically cycled cells after they are disassembled. For LMO particles of different SOC, it was found that the ESM signal was larger for a sample with a higher Li content [17]. In addition, a reduced and more heterogeneous ESM was found for aged LMO, allowing for the proposal of lithiation/delithiation models. For NCM particles, a qualitative consistency between broader ESM amplitude distributions and a generally higher ESM amplitude for lower SOCs was reported [15]. Other important work compared ESM with classical macroscopic electrochemical impedance spectroscopy (EIS) [35]. An early comparison was made by Schön et al. who verified a major contribution to ionic conductivity by grains over grain boundaries in LATP [8], reported earlier on the same material by EIS [36]. Recently, Badur et al. compared the macroscopically determined activation energy of the chemical diffusion coefficient of Cu^{2+} in $Cu_2Mo_6S_8$ by EIS and found a very close agreement to those assessed by an Arrhenius plot of the local ESM data [31]. These results demonstrate the opportunity of ESM to unravel important features for optimizing the device level of energy materials. Further direct comparison between macroscopic analysis and ESM is strongly envisioned.

In-situ ESM

To improve on existing *ex-situ* ESM work, the development of *in-situ* ESM would be a strong asset. However, it is very challenging to bias the ESM probe in a highly conductive liquid [37]. A recent adaptation of ESM shows that the electrochemical strain can still be detected using a passive ESM probe. In that case, electric potentials are applied in a typical electrochemical three-electrode set-up providing meaningful electrochemical potentials (Figure 3a) [38]. The ESM probe is then simply used as a local strain detector while the electrochemical cell is cycled. The benefit of this variation of ESM is that volume changes are recorded and directly compared with the electrochemical current that is measured simultaneously, as demonstrated in Figure 3b. This approach differs from established scanning electrochemical microscopy (SECM) techniques as in SECM the tip is employed as the fourth electrode. Thereby, the potential at the tip can be controlled in relation to that of the sample to investigate electrochemical reactions locally. In addition, SECM measures current while ESM measures a material volume change which allows for a higher spatial resolution. The ESM approach allows for the recording of not only the ESM amplitude but also its time-dependence which is important to evaluate the nonlinearity of the measured signal. By *in-situ* ESM, ionic transport of ionic liquid into porous electrodes [39] as well as redox reactions in

Figure 3



(**a**) Schematic set-up to measure electrochemical strain *in-situ*. Adapted with permission from [38]. (**b**) Mechanical deformation of a WO_3 electrode for a scan rate of 200 mV/s, equivalent to 0.1 Hz.

Prussian Blue, birnessite MnO_2 and Ti_3C_2 MXene have been investigated [40–42]. Implementing *in-situ* ESM is a necessary step to compare ESM with cell-level performance.

Summary and outlook

With the ESM technique maturing in recent years, the general abilities are well demonstrated, especially for battery materials. Attempts are ongoing to overcome persisting difficulties such as clarifying individual signal contributions for different materials and quantification of the ESM signal. This includes a better theoretical understanding, as well as elucidating model samples and correlating ESM with other spectroscopic and microscopic techniques. Furthermore, advances in experimental capabilities such as the development of interferometric detection in AFM for eliminating the influence of electrostatic forces, will deepen our understanding of ESM and unravel insights into nanoscale behavior of energy materials for next-generation batteries and ion conduction materials. Furthermore, it will be of great importance to bridge the gap between isolated ESM experiments and cell-level electrochemistry, which is why we clearly see the need for the development of *in-situ* ESM.

Besides technical aspects, the material systems that are studied with ESM are expanding. A very important direction will be the application of ESM for polymer-based materials and polymer composites as these materials become more and more important in modern battery technology. The first experiments confirm the presence of a measurable ESM signal in polymer composite [18] materials as well as in organic electrochemical transistors by *in-situ* ESM [12]. However, critical questions like the influence of vastly different mechanical properties within the samples and its influence on the signal origin are still to be answered.

Lastly, from our perspective, the current hampering of a more widespread application of the ESM technique for investigating energy materials can be overcome with a closer connection between the electrochemical community and those applying ESM. A bright future for ESM is ahead and we encourage all scientists from both communities and interested in local ion dynamics to contribute to the growth of ESM in the next years.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

Acknowledgments

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