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Electrochemical/Mechanical Coupling in Ion-Conducting Soft Matter

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Abstract

Mechanical and electrochemical phenomena exhibit many interesting multidirectional couplings in ion-exchange soft matter due to their intrinsic material physio-chemical states and responses to environmental stressors. In this perspective, such coupling is explored in terms of recent studies with a focus on the degradation of polymer-electrolyte fuel-cell membranes. In addition, (electro)chemical-mechanical coupling of ion-conducting polymers in other applications is also introduced, as there is a research need to explore the interactions between these often wrongly assumed disparate fields in order to optimize, exploit, and discover new technologies and applications.

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Research activities and interests in electrochemical energy-storage and conversion devices (e.g., fuel cells, solar-fuel generators, batteries, *etc.*) have been continuously increasing as they offer a great potential for developing clean and renewable sustainable-energy technologies for stationary, transportation, and solid-state applications. Common among these technologies is the use of an ion-conducting polymer or ionomer that provides ionic transport between electrodes and hinders reactant and electron crossover. Ionomers are copolymers consisting of neutral and charged moieties. Typically, the neutral moiety is the polymer backbone and the charged moiety is comprised of pendant side chains containing tethered ionic groups that strongly interact with counter-ions and facilitate their transport through the ion-rich nanodomains, especially in the presence of polar solvents (e.g., water).¹ A key trademark of ionomers is that they are mechanically and chemically stable, yet provide sufficient transport properties; this is where the phase-separated structure becomes important. Furthermore, this phase separation is either engineered, for example, the long-heralded design motif of block copolymers, or occurs naturally. It has been shown that the phase separation is heavily dependent on a mechanical/chemical energy balance that allows for swelling and hydration of the polar moieties, yet maintains structural integrity due to the nonpolar regions.² This perspective explores the interactions of such chemical, electrochemical, and mechanical aspects in ion-conducting soft matter that occur at multiple scales.

The most common ionomer is Nafion[®], a perfluorosulfonic-acid (PFSA) material, which is composed of a hydrophobic polytetrafluoroethylene backbone with perfluorovinyl ether side chains that terminate in hydrophilic sulfonic-acid endgroups.³ This material serves as a key benchmark for exploring the coupling between different stressors and linkages of materials. One

aspect that has become more important recently is the coupling and synergistic effects between the electrochemical phenomena and mechanics, two disparate fields that typically are not investigated together. However, recent reports have shown that mechanical stressors can impact electrochemical response and vice versa. For example, there are related issues in shape-memory applications,⁴ electro-active polymers and bio-inspired ionomer-based actuators,⁵⁻⁷ and soft-active materials based on hydrogels exhibiting strong swelling-deformation coupling.⁸ Furthermore, electrochemical/mechanical interactions are tantamount in understanding failure of many electrochemical devices, seeing as device performance metrics are being met and now the research focus shifts more towards lifetime and durability issues. Examples of this include solid-state separators in Li-ion batteries to prevent mechanically the electrochemical growth of dendrites⁹⁻¹⁰ as well as fuel-cell membranes, as discussed below.

Overall, a grand challenge for solid-state electrolytes in electrochemical devices is to address simultaneously the performance and durability demands, *i.e.*, to reduce transport resistances without compromising mechanical stability. This requires an understanding of how they are interrelated as the ionomer's transport and mechanical properties are strongly correlated through the interactions between chemical structure, electrochemical state, solvent uptake, deformation, and morphology. A growing body of recent evidence on the synergistic chemical-mechanical interactions controlling the ionomer's performance and lifetime have provided clear evidence on the key role of the transport/stability interplay and morphology in optimizing ionomer functionalities in electrochemical devices.^{2, 11-16} Yet, it is neither fully understood nor satisfactorily explained, at a fundamental level, how chemical and mechanical stressors are

interrelated, and together control the ionomer's transport functionalities, especially in the presence of defects including dislocations, locally heterogeneous structures, *etc.*

This perspective aims to provide insights and identify needs in performance/durability correlations in electrochemical devices where the solid electrolytes are subjected to a combination of (electro)chemical and mechanical stimuli that interact synergistically. This exploration will be accomplished in terms of a case study of research work on fuel-cell ionomers, although additional application spaces and coupling phenomena will be mentioned.

Case study: fuel-cell membrane durability

An ionomer's response to electrochemical and mechanical stimuli in different environments (relative humidity, temperature, solvent, *etc.*) is key to understanding its performance and stability, which are strongly coupled through its morphology and transport properties. At a fundamental level, the energy balance between mechanical and chemical energies results in the phase-separated morphology that most ionomers adopt.² Due to this intimate relationship, electrochemical and mechanical phenomena are coupled and synergistically impact each other, especially in terms of durability. For example, any type of defect or discontinuity in the ionomer membrane (e.g., cracks, pinholes), and/or at the membrane/electrode interface (e.g., delamination) compromises the material functionalities and continuously deteriorates device performance over its operational lifetime, which also can concentrate the original degradation mechanism.¹⁶⁻¹⁹ Most of these defects could be formed in the presence of chemical and thermal stresses, and propagate due to mechanical stimuli and deformation generated in the

electrochemical device arising from device-assembly constraints, solvent uptake, temperature-humidity changes, and chemical reactions.

Figure 1 demonstrates various ionomer interactions in the presence of defects that must be accounted for in terms of the coupling between mechanical and chemical phenomena. Specifically shown is the representative case of a polymer-electrolyte fuel cell (PEFC), where the ionomer must operate under a variety of stressors. The complex interactions between the chemical and mechanical failure modes in a PEFC make it important, yet challenging, to understand the relationship between different stressors and failure modes and the dominating mechanisms that control membrane lifetime. PEFC operation occurs in an aggressive hygrothermal and electrochemical environment, often involving formation of highly reactive hydroxide radicals due to crossover of hydrogen to the high-potential air cathode. As the membrane chemically decomposes, depending on the operation, it could exhibit uniform thinning causing increased overall gas crossover and/or localized physical defects, or pinholes resulting in even higher rates of crossover therein.^{12, 15-17, 20-22} Thus, localized degradation and physical defects are critical aspects of failure in that they not only accelerate crossover, but also reduce mechanical stability and serve as potential failure initiation sites under mechanical stresses. These mechanical stresses are generated usually in compression mode due to the constraints in the PEFC architecture, which builds up additional stress as the constrained membrane swells with humidity.²³⁻²⁵

Figure 1. Illustrative description of various types of defects that can form in solid-electrolyte membranes or at its interfaces in electrochemical devices due to chemical and mechanical modes of degradation that often act synergistically. Some of the potential failure mechanism are also marked (circles: chemical stressors and squares: mechanical stressors).

When the ionomer with a pinhole is subjected to prolonged compressive stresses, this could cause creep and additional local deformation around the pinhole. In cases when the stress reaches the elastic limit (*i.e.*, yield strength), the ionomer undergoes plastic deformation, meaning permanent, irreversible changes occur in the membrane even after it deswells.²⁶⁻²⁷ In these cases, *i.e.*, when the ionomer is under tensile stress, a higher risk of failure occurs since the pinhole itself also acts as a stress-concentration site. Thus, there is an increase in the localized stresses around a geometric discontinuity that triggers defect-growth mechanisms.²⁶⁻²⁷ Furthermore,

variations in the ionomer's swelling and deswelling response due to operating conditions could induce cyclic fatigue stresses with a given stress-amplitude.^{23, 26, 28} In such a stress-state, the ionomer is more prone to failure under tensile (positive) stresses, which could trigger defect growth, whether it is a crack or a pinhole.^{26-27, 29} This concept is in agreement with data showing that PEFC mechanical failure commonly occurs in regions of high tensile stresses and/or low-compression.^{19, 30} Furthermore, it is also consistent with the increase in the number of crazing sites and/or crack density with increasing level of humidity amplitude or (cyclic) fatigue stress,^{29, 31} which arises from the tensile stress component as predicted by mechanistic models.^{26-27, 32} Recently, such a model was used to show that a membrane pinhole, assumed to be an idealized cylindrical void, grows under cyclic tensile stresses, which could be induced as residual stresses if a constrained membrane undergoes permanent plastic deformation as could be in the case of hygrothermal cycling.²⁶ The rate of pinhole growth under such mechanical swelling-deswelling cycles increases with increasing humidity change (dimensional change) from dry to wet state. Thus, the ion-transport functionality of an ionomer is indirectly related to the stresses it experiences as they both are controlled by the solvent uptake and dimensional change of the ionomer. Moreover, changes in mechanical properties, such as Young's modulus and yield strength, with solvent content results in a highly nonlinear material response.^{23-24, 26, 32}

Although an ionomer could form or grow defects even under hygrothermal cycling in the absence of any chemical effects, it is the combination of chemical/mechanical degradation that leads to accelerated crossover of reactant gases and increased power loss (Figure 2). Such effects are witnessed in accelerated-stress tests of membranes, where relative-humidity cycling without reactant gases exhibits stable crossover rates without any sign of failure, but when reactive gases

(e.g., oxygen and hydrogen) are introduced during the cycling, significant reductions in membrane and device lifetimes occur.³³ Such changes are correlated to real-world failure, thus emphasizing the need for understanding coupled and synergistic interactions. Recent studies exploring these interactions have demonstrated strong correlations between the gas crossover (permeability) and pinhole size.³⁴ More importantly, pinholes cause temperature spikes and local hotspots,^{17, 21} which could trigger thermal, chemical- and mechanical-decomposition mechanisms that feedback upon each other as shown in Figure 2. For example, chemical decomposition typically makes the ionomer more brittle by increasing its Young's modulus as well as decreasing its failure strain.^{20, 35} These changes make it less resistant to fracture failure, and provide another means through which (electro)chemical effects influence mechanical stresses.

Figure 2. Factors controlling the evolution of defects, represented here as a pinhole through the ionomer membrane, at various stages of degradation. Figure illustrates, in clockwise direction, (i) the crossover of reactant gases, (ii) initiation of defects due to chemical decomposition, (iii) resulting failure initiation sites that serves as stress-concentration points under mechanical loads, (iv) growth of defects under mechanical cyclical stresses leading to higher rates of gas crossover further accelerating all the subsequent processes (i $\rightarrow$ iv). When the chemical and mechanical degradation coexist, they affect each other and their synergistic interactions control the ultimate failure of the ionomer membrane.

To protect against the electrochemical/mechanical degradation, one can minimize the mechanical changes by, for example, adding a reinforcement matrix to the PFSA material such as expanded PTFE^{28, 36} or electrospun PVDF fibers.³⁷ These supported hybrid membranes could inhibit or slow down crack propagation by blunting the crack tip and also exhibit reduced in-plane swelling in favor of higher swelling into the thickness dimension; thus demonstrating significantly longer life under humidity cycling,³⁸ albeit at the increase in the inherent composite membrane transport resistance due to more tortuous pathways and possibly lower ionomer water uptake. Such changes exemplify further electrochemical/mechanical coupling as well as the tradeoff between performance and durability.

As shown in Figure 1, in addition to defect growth, interfacial delamination can occur in PEFCs. Such mechanical failure occurs via changes in the underlying mechanical/electrochemical interactions due to such phenomena as freeze/thaw cycling and cold start, where water is generated electrochemically and forms liquid that quickly freezes.^{30, 39} This ice can generate substantial pressures that cause the delamination. Such electrochemical compression occurs since it only requires a small voltage difference to increase pressure, a key and often overlooked issue in electrochemical devices. In fact, such compression is now being examined for use in flow batteries and may have possibilities for mechanically-driven devices such as pumps and pistons as well as water-treatment membranes, an area ripe for future exploration.

While the above highlights the importance of synergistic mechanical/electrochemical effects on the performance of a device, interactions occur at the nanoscale as well. For example, again using a PEFC membrane, recent studies demonstrated through an ex-situ Fenton's test that the chemical decomposition rate of a PFSA ionomer changes under tension⁴⁰ and compression⁴¹. It

was reported that the chemical decomposition of a PFSA ionomer increases with increasing levels of mechanical compression, which confirms and provides insight into the synergistic nature of chemical/mechanical degradation of ionomers.⁴¹ Compression and degradation of the membrane was also found to change its nanostructure, consistent with the changes in membrane's mechanical properties and chemical decomposition rate.⁴¹

Thus, it is possible that the deformation energy accumulated in an ionomer due to thermal and mechanical loads could accelerate the chemical reactions, whether they are the favorable electrochemical reactions, or unfavorable decomposition reactions. While the latter effect is important for improving material and device longevity by preventing undesired reactions, the former phenomenon provides an avenue for optimizing device performance by harnessing electrochemical-mechanical coupling. The relationship between mechanical stress/deformation and chemical reactions is a long-standing problem of interest, and sometimes termed *mechanochemistry*, that has been approached experimentally and theoretically,⁴²⁻⁴³ albeit not really applied to ion-conducting soft matter. The addition of a mechanical potential to a potential-energy surface was suggested to be conceptually similar to the addition of an electric potential in electrochemistry,⁴³ which, within the context of electrochemical devices, could shed light into the role of chemical-mechanical coupling in ionomer functionalities. To understand the origins of the role of mechanical stressors in chemical reactions, or vice versa, one must accurately describe the relationships between the macroscopic mechanical loads and the molecular deformations around polymer chains and ionic moieties, especially when they are rearranging at mesoscales in response to electrochemical stimuli (transport of neutral and charged species). It appears to be the case that the chemical-mechanical coupling is governed by

the competition between the energies of the material across the lengthscales, not just at molecular level, as the ionomer moieties are known to be responsive to the hydrogen-bonded water network and requires an approach that can bridge chemical-potentials and deformation energy. Such knowledge would be generally applicable, for example, self-healing ionomers would benefit from such investigations as their reaction kinetics in functional pores facilitate the healing process, i.e. activation of chemical reactions under controlled deformation and stress.

Summary and outlook

The above case study examined the multiscale electrochemical/mechanical coupling for a PEFC ionomer membrane, especially in terms of degradation. It was shown how a complete understanding of the synergistic electrochemical-mechanical coupling of ionomers warrants further investigation into how the chemical and mechanical energies control ionomer morphology while chemical reactions take place in the presence of mechanical stressors. However, there are further possibilities and future directions for electrochemical-mechanical coupling in terms of both devices and property examination.

One example is to exploit the coupling to interrogate intrinsic material and state properties that are hard to obtain with traditional techniques. Electroanalytical techniques are very precise in terms of coulomb counting, and thus the electrochemical potential can be readily related to intrinsic material property changes such as concentrations or partial molar volumes. In this fashion, one can use the electronic potential of an ionomer with a solvent gradient sandwiched between two electrodes to determine the partial molar volume,⁴⁴ which is a measure of its backbone compression and probably related to its modulus.²

In terms of applications, as mentioned, successful realization of solid-state batteries depends heavily on understanding and minimizing interfacial interactions, whether it is preventing dendrites or handling the mechanical stresses during intercalation.⁴⁵ However, modeling of dendrite growth and interfacial delamination requires mechanical characterization beyond the elastic regime, including fracture energy during lithiation, something that has not been brought to bear yet for these applications. Another important emerging field that benefits from such coupling is electroactive polymers, especially, ionic-polymer-metal composite (IPMC)-based soft actuators/sensors, which deform in response to an applied electrical stimulus (*actuating*), or generate a current due to deformation (*sensing*).^{5, 46} Ionomers are commonly used solid-electrolytes in IPMCs, where, under an applied potential, ions and accompanied water molecules transport towards the cathode thereby creating a swelling gradient, which results in bending towards the anode. Thus, in essence, an ionomer in an IPMC resembles that in a PEFC (see Fig. 1) as they both take advantage of some of the attractive properties of ionomers but operate on different principles. However, in actuators, unlike in PEFCs, the swelling-induced stress directly controls the deformation and thus the functionality of the device. As with most electrochemical devices, an ionomer-based active material requires optimization of functionalities. For example, one needs to balance having a fast response time and high conductivity while maintaining mechanical stability (to prevent a short circuit) or response (e.g., still exhibits adequate bending stiffness). Thus, optimization again provides an intriguing interplay between the transport and mechanical properties of the hydrated ionomer. Moreover, the counter-ions and ionomer chemistry (ion-exchange capacity) have been shown to influence the ionomer's behavior in actuators,^{7, 46} as they would in other electrochemical devices.

In addition, there are some experimental means that provide information on the linkages between electrochemical and mechanical phenomena. The most promising of these is broadband electric spectroscopy (BES), which has been shown to correlate the soft-matter transport and mechanical response across various timescales.⁴⁷ Although complex to interpret, such techniques have potential to provide information beyond traditional techniques probing only one of the phenomenon such as impedance (e.g., for ionic conductivity) or dynamic mechanical testing (for mechanical relaxation). There is a need to further exploit this information in carefully designed studies with model compounds, and validation of results with the complimentary techniques. Key is to probe simultaneously the various responses of a material using a variety of techniques to provide a holistic view of the governing phenomena. For example, investigation of the relaxation behavior that encompasses dielectric and ionic relaxation as well as mechanical (backbone) relaxation could shed light on the properties that are linked to both chemical and mechanical phenomena, as in the case of ionic moieties controlling electrostatic interactions as well as thermal-mechanical transition (temperatures). Such an approach needs to be balanced by systematic and controlled investigations to determine the primary factors controlling the material behavior with various counter-ions and solvent content and at different temperatures. In addition, one can take advantage of scattering techniques to probe the morphology *in-operando* at different time- and lengthscales, which allows investigation of material behavior within the context of (electro)chemical-mechanical phenomena. Studies on scattering of ionomers with x-rays and neutrons have provide numerous examples of such investigations, including, but not limited to, ionomer nanodomain alignment coupled with preferential diffusion under mechanical stretching,⁴⁸ the effect of compression on hydrated nanodomains and ion transport therein,⁴⁹ and

determination of the ionomer water profiles in an operating PEFC.⁵⁰ Although challenges remain to probe the dynamics of the phase-separated morphology under simultaneous mechanical and electrochemical loads, such investigations could (soon) potentially be undertaken with the continuing advances in scattering techniques and light sources.

Mechanical and electrochemical phenomena exhibit many interesting multidirectional couplings in ion-exchange soft matter due to their intrinsic material physio-chemical states and responses to environmental stressors. This field has become very relevant in both theoretical studies and practical devices as more emphasis is being given on processing and performance and durability issues. Understanding the origins of such chemical-mechanical interactions would have significant impact on technologies that exploit electrochemical-mechanical phenomena, from shape-memory applications, to electro-active polymers and bio-inspired ionomer-based materials, to solid-state batteries and electrochemical devices, to flexible electronics to soft-active materials. With the required understanding, one can tune the materials to be responsive to electrochemical potential, which could enable new morphologies to be obtained *in-operando* that reroute ionic pathways or adapt the structure/function relationship of the ionomer for specific conditions to control material behavior. Thus, there exists a fruitful area of research in terms of identifying the origins and impacts of electrochemical phenomena on mechano-chemistry that may allow one to exploit and control reactions as well as harness, optimize, and identify mechanical and electrochemical phenomena to be synergistically beyond what either can obtain on their own.

Ahmet Kusoglu holds B.S. and Ph.D. degrees in Mechanical Engineering, from ITU and University of Delaware, respectively. His research is focused on structure/function relationships and mechanics of soft matter for electrochemical devices including related transport and durability phenomena. He has published over 30 peer-reviewed articles on these topics.

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Notes

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QUOTES TO HIGHLIGHT

“A growing body of recent evidence on the synergistic chemical-mechanical interactions controlling the ionomer’s performance and lifetime have provided clear evidence on the key role of the transport/stability interplay...yet, it is neither fully understood nor satisfactorily explained, at a fundamental level, how chemical and mechanical stressors are interrelated...especially in the presence of defects including dislocations, locally heterogeneous structures, *etc.*”

“...there exists a fruitful area of research in terms of identifying the origins and impacts of electrochemical phenomena on mechanico-chemistry that may allow one to exploit and control reactions as well as harness, optimize, and identify mechanical and electrochemical phenomena to be synergistically beyond what either can obtain on their own.”

“A grand challenge for solid-state electrolytes in electrochemical devices is to address simultaneously the performance and durability demands, *i.e.*, to reduce transport resistances without compromising mechanical stability”

“...it is possible that the deformation energy accumulated in an ionomer due to thermal and mechanical loads could accelerate the chemical reactions, whether they are the favorable electrochemical reactions, or unfavorable decomposition reactions. While the latter effect is important for improving material and device longevity by preventing undesired reactions, the

former phenomenon provides an avenue for optimizing device performance by harnessing electrochemical-mechanical coupling.”