

Electroactuators: from understanding to micro-robotics and energy conversion: general discussion

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Andriy Yaroshchuk opened a general discussion of the paper by Tom Krupenkin: Where was the counter-electrode located in your “bubbler” device? If it was at the edge, is this not a problem for the upscaling?

Tom Krupenkin responded: The location of the counter electrode is mostly a design choice. Since the bubbler cavity is filled with a high conductivity liquid, most commonly a liquid metal, the exact counter electrode location is not really important, provided it is not far removed from the bubble array. One of the most obvious choices for the location is the plate at the top of the cavity, where the gas escape membrane is located.

Nikolay Brilliantov asked: In your analysis of the energy balance in the system you do not explicitly take into account dissipation losses, which may be significant at high frequencies. Have you made the according estimates of the viscous losses?

Tom Krupenkin answered: Viscous losses were analyzed as a part of the numerical investigation of the bubble growth and collapse process. It was discovered that for the liquids used in the experiment (mercury and Galinstan) the system dynamics were predominantly defined by the kinetic terms in the equation of motion. This holds true even at the higher range of frequencies between 1 kHz and 2 kHz. The influence of the viscous dissipation on the energy conversion efficiency is more difficult to address in general, as it depends strongly on the details of the device design including the number and the size of the gas supply channels, the substrate thickness, *etc.*

Alexei A. Kornyshev commented: This is a question related to your previous “bubbler”-based devices. If you have an electrolytic droplet in the polarized capacitor, why is it more profitable to have many droplets on patched surfaces instead of one droplet spreading/contracting continuously along the surfaces of the two electrodes?

Tom Krupenkin answered: The use of the droplet array provides an important flexibility in selecting a desired device response rate and a required displacement amplitude. The smaller the array droplets are, the faster the response and the smaller the required displacement are. This enables a high frequency operation which is virtually impossible in the case of a single large droplet.

Roland Bennowitz asked: What is the figure of merit for your harvesting devices? Is the ratio of electrical power over mechanical power the main selling point?

Tom Krupenkin replied: The ratio of the electrical power to the mechanical power characterizes the conversion efficiency. The conversion efficiency is usually not the most important metric in energy harvesting applications. The power density is often assumed to be a more important characteristic. This stems from the fact that in the majority of energy harvesting applications the amount of energy that the harvester actually absorbs from the energy source is assumed to be small in comparison with the total energy available from the source. Thus the total amount of energy produced by the harvester is mostly determined by its size and its power density.

Nikolay Brilliantov remarked: For practical implementations, the liquid should not have too small surface tension, otherwise very fast expansion of a droplet in the radial direction would lead to the formation of a hole in the droplet centre. Do you take this effect into account?

Tom Krupenkin responded: Indeed, it is desirable to use a high surface tension liquid in a bubbler device for a number of reasons. Stability of the bubbles is one of them. The other important reason is the ability to achieve the maximum power generation per unit area, which increases with the increase in the surface tension of the liquid. In our current set of experiments, liquid metals such as Mercury ($\sim 450 \text{ mN m}^{-1}$) and Indium–Gallium alloys ($\sim 600 \text{ mN m}^{-1}$) showed the best results.

Marco Balabajew opened a general discussion of the paper by Nina Balke: In the discussion of your paper you speculate on possible reasons for the improvement of Mg^{2+} intercalation after K^+ intercalation. You state that a possible reason could be that K^+ changes the interlayer spacing between MXene layers making it easier for bigger Mg^{2+} to intercalate. However, your dilatometry data (Fig. 3b) shows a contraction of approximately 5%. How should this help for the intercalation?

Additionally, you cite previous work (ref. 17) in which you show by XRD that the layer spacing does not change upon K^+ intercalation. How do you explain this discrepancy?

Nina Balke replied: The insertion of potassium results in relatively small volume changes. Depending on the sample batch, we have observed a range from -5% (like in the present paper) to $+1.5\%$.¹ I would consider this the error bar for the expansion/contraction behavior. So the X-ray results showing no change in lattice spacing fall into this range and it is hard to compare exact values within this range without measuring on the exact same sample batch. One also has to highlight that X-ray probes the interlayer spacing of the material whereas dilatometry probes the changes in the unit cell volume plus changes in intra-layer spacing between the flakes of MXene. In the paper, I listed possible explanations of why the contraction is reduced by approximately 30% when K^+ is pre-intercalated. Since we only measure a relative volume change, a pre-straining based on the K^+ intercalation could explain some but not all of it. In addition, the change is also affected by the change in overall Young's modulus E . With K^+ , E at the most negative potential is about 7 GPa. Without K^+ , we observe areas with around 5.5 GPa and 8.6 GPa (Fig. 4 and 5). It is hard to speculate which area contributes more to the macroscopically measured sample expansion since we cannot assume that the mechanical stresses are the same everywhere.

Irena Kratochvilova asked: How does your material compare to graphene/graphite? Is it typical for this type of 2D material to behave in the way shown in your paper?

Nina Balke answered: We have not tried a comparison with graphene/graphite. However, there is work about the actuation properties of MoS_2 during electrochemical cycling where they see noticeable volume changes. I do think it is a general behavior of 2D materials if ions can be inserted.

Elisabeth Smela commented: Can you clarify why the contraction occurs upon the insertion of cations; what is between the layers that holds them apart initially, before intercalation? Also, can you comment on the speed of this process?

Nina Balke responded: The layers of MXene are charged negatively determined by surface termination groups, such as OH^- , O^{2-} , and F^- . It is believed that the electrostatic interaction between the now negatively charged MXene layers determine the layer spacing. When cations are intercalated, they compensate for the negative charge effectively reducing the electrostatic repulsion leading to a more dense material. However, that is only true for small cations. If the inserted ion is larger than the original spacing, then we will see expansion. The effective size of the inserted ions is also determined by the solvation shell. A nice article showing the behavior for a large range of ions can be found here in ref. 1.

1 M. D. Levi, M. R. Lukatskaya, S. Sigalov, M. Beidaghi, N. Shpigel, L. Daikhin, D. Aurbach, M. W. Barsoum and Y. Gogotsi, *Adv. Energy Mater.*, 2015, 5, 1400815.

George Schatz said: Certain series of behaviour are expected based on ionic conductors, with the soft ion K^+ being a better conductor than Mg^{2+} . Could you try other ions to see if these trends continue for ions like Na^+ ?

Nina Balke responded: The role of electrolyte conductivity is an interesting aspect. We will check some other ions such as Na^+ and also perform a series of one electrolyte with increasing molarity.

Alexei A. Kornyshev asked: You actuate based on the principle that when you impregnated the gaps with potassium or other cations, the gap with negatively charged walls will shrink. Can you extend that principle to provide a bending type of action, rather than simply shrinking? Of course, the latter could be converted into any other deformation, but that would be a less direct acting device.

Nina Balke answered: Depending on the charge and size of the inserted ion, we can achieve a large spectrum of shrinkage and expansion which can reach up to 20%. The expansion comes into play if the inserted ions become larger than the gap between layers but also different types of synthesis methods resulting in different surface terminations can affect the sign of the volume change. The benefit of this system is that with a simple electrolyte exchange, one can change from one actuation behavior to another making a tunable device which could also be used for sensing purposes. We have not focused, so far, on making active actuation elements but bending behavior could be achieved through a bi-layer type design as it is often employed for bending actuators.

Martin Bazant remarked: When ions intercalate into layered materials, there are often thermodynamically preferred configurations or stable phases at specific concentrations, such as the stages of lithium in graphite, which influence the patterns that form during intercalation.¹ Is there any evidence of staging phenomena in MXenes with these ions? Moreover, in these and other battery or capacitor materials, the patterns of ion concentrations are strongly affected by long-range elastic coherency strain.² What is the role of coherency strain in determining the voltage-dependent patterns observed here? Could you explain the wavelength and structure of the patterns? Does the pre-intercalation of K^+ affect mechanical properties such as the misfit strain tensor or the effective elastic constants of the host material?

1 Y. Guo, R. B. Smith, Z. Yu, D. K. Efetov, J. Wang, P. Kim, M. Z. Bazant and L. E. Brus, *J. Phys. Chem. Lett.*, 2016, 7, 2151–2156.

2 D. A. Cogswell and M. Z. Bazant, *ACS Nano*, 2012, 6, 2215–2225.

Nina Balke answered: The analogy to staging is interesting; right now we cannot answer this question. In order to test this, we can repeat the material with much more voltage steps to see if we have a continuous change in patterns or if they propagate in a step-like behavior which would indicate staging. I do expect for coherent strain to play a role in ionic transport. The difficulty here is to measure this strain locally to make the connection to ion intercalation. Right now, we do not have the means to measure this property. More experiments would be necessary to extract statistically meaningful values for the wavelength and structure of the patterns.

The question is if the behavior is dominated by the electrode surface morphology or if it is an intrinsic material behavior. Measurements on single

flakes or provide many access points to the electrode with holes or similar structures could be used to investigate this.

When we measure the nanoscale Young's modulus we do not see any changes when we intercalate K^+ . That is in agreement with the fact that there are only very small volume changes close to zero. Therefore, we conclude that K^+ by itself does not change the elastic constants of the material, at least not the direction we are probing with SPM.

Frieder Mugele asked: I am a bit confused about the origin of the patterns that we observe. If I consider that the MXene paper consists of many small flakes that are somehow stacked together in an irregular fashion, I would expect that intercalation of the ions always starts from the edges of the flakes. This should be the location where it is easiest for the ions to penetrate. Therefore, my question is do the structures/patterns that we see in the AFM contact resonance images somehow correlate with structural features of the paper, in particular with the edges of flakes? Or alternatively, would you say that this is not the case? The latter would in some sense be more exciting. Then fancy intrinsic instabilities like the one discussed by Dr Bazant could play a role. But, it should first be clarified whether much simpler and (admittedly) more boring structural aspects are responsible.

Nina Balke replied: The SEM images of MXene fabricated as free standing paper for electrochemical measurements show a very rough surface with many parts sticking up (Fig. 1). When we image in contact mode to perform our measurements, we will flatten it down for sure. Also, during scanning over hours

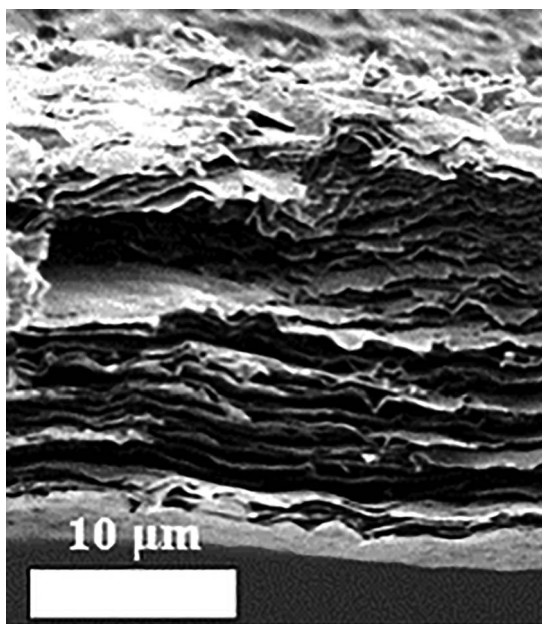


Fig. 1 Scanning electron microscopy image of the cross-section of a prepared MXene film for electrochemical studies.

during charge and discharge and the volume changes, local areas can change due to drift and/or delamination. Therefore, tracking one particle throughout the entire experiment is rather challenging and we cannot give a definitive answer whether the pattern is just a result of edge effects. More well defined samples would be needed to achieve this. However, if it is an edge effect, I would expect it to be there even in the case of K^+ pre-intercalation.

Elisabeth Smela commented: It is interesting to compare the intercalation in this material with that occurring in other layered structures, including graphene and PPy(DBS).

Nina Balke replied: It would be very interesting if multi-layer samples can be produced. We thought about trying single flake studies as well but then we don't get enough current for the electrochemistry and we won't be able to tell if no ions go in or if the ion intercalation does not affect the mechanical properties.

Andy Mount communicated: Fig. 3(a) in your paper seems to indicate the (slight) development of redox peaks centred around -0.4 V in addition to the (super)capacitive response for the CV data in blue (Mg^{2+} after K^+). When combined with Fig. 4(a), this might suggest regions of the surface with different structures and mechanisms for the intercalation of Mg^{2+} into $Ti_3C_2T_x$. We have seen a similar effect in our previous work with progressive cation insertion into poly(indole-5-carboxylic acid) films¹ and showed that in such a situation, where different electrode reactions may be occurring in parallel, impedance measurements and equivalent circuit analysis give insight into, and potential deconvolution of, the combined response. Have you made such measurements and, if so, do they provide this insight?

1 A. R. Mount and M. T. Robertson, *Phys. Chem. Chem. Phys.*, 1999, **1**, 5169–5177.

Nina Balke responded: No, we have not combined our measurements with impedance analysis but we are set up to do so. We think it would add valuable information and we will add this measurement in future studies.

Nikolay Brilliantov opened a general discussion of the paper by Hyacinthe Randriamahazaka: As I can see from your slides the energy of your system contained two components, one associated with the elastic part and the other with the electrostatic part; however, it lacked the part associated with the kinetic energy of the moving material. How large is the latter part and is it justified to neglect it at high frequencies?

Hyacinthe Randriamahazaka replied: In our case, the model describes the electromechanical properties of the actuators at a low frequency range. Indeed, the mechanical response is related to the electrochemical stress due to the intercalation process. The intercalation in solid state electrochemistry exhibits slow kinetics. Then, the kinetic energy is not included in the current model.

Alpha Lee remarked: In your model of electroactuation, you have accounted for the strain due to electrode expansion but it seems that you have neglected the

electrostatic interactions between the ions and the deformation of the electrical double layer. We have developed models of electroactuation of ionomeric polymer metal composites,¹ and a more rigorous model has been derived,² which account for electrostatic interactions between the ions and the deformation of the double layer, but neglected electrode expansion. Perhaps it would be interesting to combine the two modelling approaches.

1 A. A. Lee, R. H. Colby and A. A. Kornyshev, *Soft Matter*, 2013, **9**, 3767.

2 Y. Cha and M. Porfiri, *J. Mech. Phys. Solids*, 2014, **71**, 156.

Hycinthe Randriamahazaka responded: Thank you, this is a very interesting remark. In order to improve the current model, we will include the electrostatic interactions between the ions and the deformation of the double layer.

Irena Kratochvilova asked: Regarding the relaxation model used, were oscillators useful? What is a typical model to use for your material? How does it work?

Hycinthe Randriamahazaka answered: I am not sure that an oscillator is useful. Herein, we use bucky gel based on carbon nanotubes and ionic liquids as active materials for the flexible electrode in this kind of two-terminal device. The basic mechanism is the asymmetric volume change of the electrode due to the ionic intercalation (de-intercalation) when a voltage is applied. The intercalation (de-intercalation) process induces an increase in the volume of one electrode concomitant with the decrease in the volume of other electrode. These electrochemical processes lead to a bending of the actuator.

Nikolay Brilliantov asked: All of your curves demonstrate monotonic dependence on frequency, while your system seems to have intrinsic time scales. Does a lack of resonance imply that these are well separated from the frequency range you have used?

Hycinthe Randriamahazaka replied: You are right, the frequency range that we have used is lower than the resonance frequency.

Frieder Mugele commented: Dr Randriamahazaka, at the beginning of this session, we heard from Dr Krupenkin about how he can very efficiently harvest energy by reversing the electrowetting process. In principle, the idea of operating an electromechanical transducer in reverse to harvest energy from mechanical motion is rather general and should be applicable to your polymer actuators as well. Do you think that this would work and where would you see a limitation, *e.g.* regarding speed of recovery, reversibility, degradation?

Hycinthe Randriamahazaka replied: I agree with your comment. We plan to investigate this point.

Elisabeth Smela asked: Electrochemical polymer actuators have been studied for over 2 decades. What are the remaining big questions in the field, and if they are answered are there commercial applications that will be enabled?

Hyacinthe Randriamahazaka answered: In my opinion, we will go beyond electrochemical polymer actuators. It will be of interest to develop multifunctional flexible devices for specific applications such as soft robotics, nanomedicine, and bio-ionic systems. From a scientific point of view, a multidisciplinary approach is necessary to resolve some major questions related to the materials, the electrochemical properties, the modelling, and the fabrication technology. To be competitive, the electrochemical polymer actuator field should find specific applications.

George Schatz opened a general discussion of the paper by Martin Bazant: The theory provides a generalization of Glansdorff–Prigogine theory to include such problems as chemical kinetics. If the inverted regime in Marcus theory is also included, does this give multiple stationary points? Concerning photodriven systems, let me suggest to the author that he consider the work in ref. 1.

1 A. Nitzan and J. Ross, *J. Chem. Phys.*, 1973, **59**, 241–250.

Martin Bazant replied: The analysis here only considers the linear stability of a given base state in a chemically reactive mixture, which could be time-dependent and non-uniform, to perturbations in the concentration profiles. The nonlinear dynamics, including possible stationary points under external driving, are not considered explicitly, but are obviously related. This work considers, apparently for the first time, the thermodynamic stability of a driven chemical reaction with "negative differential resistance", as illustrated by the inverted region of Marcus kinetics for electron transfer reactions, and shows that this unusual property tends to invert the stability of the system, making an otherwise thermodynamically stable state unstable, and *vice versa*. We may expect that this phenomenon could also lead to new fixed points of the nonlinear dynamics. For example, a phase separating mixture could be arrested in a given (possibly moving or time-periodic) pattern by a reaction that switches from autocatalytic to auto-inhibitory as the overpotential is varied. In particular, the inverted region of electron transfer could lead to new phenomena in pattern formation on semiconductor or low-dimensional (*e.g.* carbon nanotube or graphene) electrodes. This possibility is discussed in the Outlook section, including possible applications to thermopower waves¹ and photo-electrochemical devices.² On that note, the reference to the work of Nitzan and Ross is appreciated, which clearly represents another class of driven open systems, in which only selected chemical species in a reaction network adsorb photon energy throughout the bulk mixture.

1 R. Ihly, K. S. Mistry, A. J. Ferguson, T. T. Clikeman, B. W. Larson, O. Reid, O. V. Boltalina, S. H. Strauss, G. Rumbles and J. L. Blackburn, *Nat. Chem.*, 2016, **8**, 603.

2 A. T. Liu, Y. Kunai, P. Liu, A. Kaplan, A. L. Cottrill, J. S. Smith-Dell and M. S. Strano, *Adv. Mat.*, 2016, **28**, 9752–9757.

Marco Balabajew asked: For the intercalation of lithium in lithium iron phosphate you have shown the formation of a pattern of stripes of the two different phases which was observed experimentally and predicted by your theory. The reason for the formation of these stripes is strain in the material due to the

phase transition. What kind of patterns would you expect in the case of a zero strain material such as lithium titanate?

Martin Bazant answered: Lithium titanate is considered a "zero strain material" and indeed this would eliminate the striped phase patterns predicted¹ and observed² in LiFePO_4 . The latter are in fact due to the strange "mixed" mechanical response of FePO_4 to lithium intercalation, which involves expansions along two crystal directions, and contraction in the third direction. This leads to "tilted" phase boundaries along certain directions (111) that lead to interfaces causing zero net elastic strain in an infinite system.¹ In finite particles, boundary conditions of zero traction and "surface wetting" by the two solid phases conspire to produce intricate patterns of stripes in large particles, and a size-dependent nucleation barrier,³ which results from the competition of elastic strain (scaling with volume) and intercalation of the stable phase at surfaces (scaling with area).²

1 D. A. Cogswell and M. Z. Bazant, *ACS Nano*, 2012, 6, 2215–2225.

2 J. Lim, Y. Li, D. H. Alsem, H. So, S. C. Lee, P. Bai, D. A. Cogswell, X. Liu, N. Jin, Y.-S. Yu, N. J. Salmon, D. A. Shapiro, M. Z. Bazant, T. Tylliszczak and W. C. Chueh, *Science*, 2016, 353, 566–571.

3 D. A. Cogswell and M. Z. Bazant, *Nano Lett.*, 2013, 13, 3036–3041.

Robert Hillman commented: Your simulations show the nucleation of a new phase as lithium ions are inserted into the structure, but the scale of the simulation (involving a single nucleus) does not indicate the nature of this process for a larger sample of material. Specifically, there is no information on whether nucleation is instantaneous or progressive or whether it subsequently proceeds by growth in one-, two- or three-dimensions. There is also the question of whether growth (irrespective of dimensionality) is controlled by kinetics or transport (diffusional) processes. Are you able to expand on this issue?

Martin Bazant responded: The analysis presented here is only for linear stability to infinitesimal perturbations of the concentration profile in a reactive mixture, in the case of isothermal spinodal decomposition coupled to externally driven reactions. Nucleation, which is an inherently nonlinear phenomenon of large perturbations, is not considered. In some simulations, as confirmed in the experiments of Fig. 7, we also consider heterogeneous nucleation at surfaces, which are preferentially "wetted" by the new phase of a binary solid,¹ although we do not consider nucleation by random fluctuations on the surface or in the bulk. In the case of surface-wetting nucleation, the system can bypass the driven spinodal decomposition, but some general features of the control of phase separation remain, when the interior of the particle is relatively unaffected by surface nucleation and may still fill uniformly as "quasi-solid solution".² At low rates and during lithium extraction (electro-autocatalytic reactions), nucleation and growth is predicted and observed in LiFePO_4 nanoparticles and would certainly depend on dimensionality and the shape of the particles and diffusion. For typical nanoparticles limited by reactions, above the critical discharge current (electro-auto-inhibitory reactions), phase separation is suppressed even in the presence of surface nucleation. However, you correctly point out that this discussion is only for single particles. For collections of bi-stable particles, size-dependent

nucleation plays a critical role in determining the order and spatial profile of transforming discrete particles *via* the "mosaic instability" at low rates.³ The situation is not described by classical KJMA nucleation and growth statistics, but rather (in the simplest case of fast transport between particles) by Markov-chain population dynamics models, which predict different non-monotonic transient profiles of transforming particles.⁴

1 D. A. Cogswell and M. Z. Bazant, *Nano Lett.*, 2013, **13**, 3036–3041.

2 P. Bai, D. A. Cogswell and M. Z. Bazant, *Nano Lett.*, 2011, **11**, 4890–4896.

3 T. R. Ferguson and M. Z. Bazant, *Electrochim. Acta*, 2014, **146**, 89–97.

4 P. Bai and G. Tian, *Electrochim. Acta*, 2013, **89**, 644–651.

Robert Hillman commented: Although a galvanostatic control function is widely used in battery research, potentiostatic control is a more common approach in mechanistic electrochemical studies at large. Your simulations therefore offer a slightly different perspective on redox properties of materials on electrode surfaces. In particular, the implicit variation of potential in a galvanostatic experiment means that the rates of any potential-driven elementary steps may vary, with the consequent possibility that there may be changes in the rate limiting step, *e.g.* between electron transfer and ion diffusion or between instantaneous and progressive nucleation. Are you able to comment on this? Additionally, I recall a paper¹ in which analogous experimental studies on films of the redox polymer polyvinylferrocene showed divergent types of behaviour when made to undergo redox switching (and consequent ion insertion) in different media. Specifically, there were unusual phase and activity effects in aqueous media, but not organic solvent media. Can you comment on the parallels here?

1 P. Daum and R. W. Murray, *J. Phys. Chem.*, 1981, **85**, 369.

Martin Bazant replied: Indeed, there can be redox switching phenomena, or more generally changes in the rate limiting step and reaction mechanism, predicted by the present theory, depending on the type of driving applied to the system. Even in the simple example of this paper for driven ion insertion, the Damkohler number, which controls the relative importance of reactions to diffusion, varies strongly with concentration and thus also with time at constant current. At constant potential, these effects can indeed be enhanced, since there is no externally imposed time scale, such as the time to fill a particle at constant current. The connection with redox polymer polyvinylferrocene is an excellent one, which I will make in the proof corrections of the article, but with a different, more recent reference:¹ "Nanostructured redox-polymer electrodes for super capacitors have been made by simultaneous electropolymerization of pyrrole and electro-precipitation of polyvinylferrocene,¹ and the microstructure depends on the applied current and electrolyte composition." The observed patterns could be explained in principle by the present theory, based on electro-autocatalytic competing reactions on the evolving surface. Similar comments apply to corrosion problems, such as the formation of nanostructure gold by selective electro-dissolution of silver from a binary alloy, where simulations accounting for phase separation on the evolving surface could only reproduce the observed microstructure for certain choices of the exchange current in a Tafel kinetics model.² The control of pattern formation in lithium peroxide deposition

discussed in the paper is another related example.³ The general feature in all of these cases is the control of phase separation patterns by solo-autocatalytic deposition or dissolution reactions.

- 1 W. Tian, X. Mao, P. Brown, G. C. Rutledge and T. A. Hatton, *Adv. Funct. Mater.*, 2015, **25**, 4803–4813.
- 2 J. Erlebacher, M. J. Aziz, A. Karma, N. Dimitrov and K. Sieradzki, *Nature*, 2001, **410**, 450–453.
- 3 B. Horstmann, B. Gallant, R. Mitchell, W. G. Bessler, Y. Shao-Horn and M. Z. Bazant, *J. Phys. Chem. Lett.*, 2013, **4**, 4217–4222.

Nikolay Brilliantov asked: I would expect that non-equilibrium free energy of a system may be introduced, as a practical tool of theoretical analysis, only for the case when the system is in a steady state. Otherwise the free energy would depend on a specific evolution route. Do you agree?

Martin Bazant responded: This is a reasonable intuition, which is essentially correct. A nonequilibrium free energy can be defined consistently for non-steady states, only if the system is driven by a particular evolution route, such as a constant external current, since the current must enter the definition and control the deviation from the equilibrium free energy. This is clearly illustrated in the paper. In section 2 for the simple example of driven adsorption at constant total flux, where the base state is not stationary and represents a spatially uniform concentration increasing in time, I explicitly construct a non-equilibrium free energy, whose curvature controls linear stability. Later in the paper (eqn (64)), it is shown that this is a special case of a more general nonequilibrium free energy functional, defined by its second variation (eqn (60)). In the case of driven adsorption without diffusion, this expression can be integrated to obtain a path independent nonequilibrium free energy function (eqn (6)), whose variational concentration derivative is the chemical potential of the external reservoir, which acts as a "chemostat" driving the system out of equilibrium. The second variation of a nonequilibrium free energy can always be defined at a given moment in time in terms of the linear stability growth matrix around any base state, but this expression often cannot be twice integrated to obtain a consistent nonequilibrium free energy functional since the integration will be path dependent. In general, there is no way to define nonequilibrium thermodynamic "state functions" that are local in time and space and control thermodynamic stability, but the linear stability matrix is well defined for any nonequilibrium state for any thermodynamic consistent dynamical model, such as linear irreversible thermodynamics for mass and energy transport and nonlinear thermodynamics for reactions, as defined in the paper.

Ranabir Dey remarked: Can the stability analysis presented in your paper be applied to purely elastic systems (like polymer–polymer or polymer–gel systems)? Will the assumption of linear elasticity be essential for such an analysis?

Martin Bazant answered: The variational stability analysis considers the most general system of thermodynamic reaction–diffusion equations, in which the local chemical potential of each species is determined by the functional derivative of the total free energy functional with respect to concentration perturbations. It

is possible to include elastic coherency strain in solids, or other mechanical effects in the free energy, in which case the theory propagates their effects into the general stability criterion. This has already been done for (linear) elastic coherency strain effects in binary solids driven by intercalation reactions,¹ and the resulting correction, first derived by Cahn in the absence of reactions,² also appears in the present analysis for electro-autocatalytic ion intercalation. This model has also been extended for (isotropic) nonlinear elasticity and plastic deformation in simulations of battery nanoparticles,³ albeit without performing linear stability analysis. In general, nonlinear mechanical effects in multiphase solids or polymer systems can be included in the full model and will affect the "base state", but the linear stability analysis will always neglect any nonlinear effects on the growth of perturbations around the base state.

1 D. A. Cogswell and M. Z. Bazant, *ACS Nano*, 2012, **6**, 2215–2225.

2 J. W. Cahn, *Acta Metall.*, 1962, **10**, 179–183.

3 C. V. Di Leo, E. Rejovitsky, and L. Anand, *J. Mech. Phys. Solids*, 2014, **70**, 1019.

Astrid S. de Wijn said: The effect you are describing is essentially the result of two competing time scales, given by the reaction rate and the mass transport. If one or both of the phases involved are solid, they will have extremely slow mass transport when compared to, for example, liquids. How will this affect the usefulness/applicability of the theory?

Martin Bazant responded: The control of phase separation by (electro)autocatalysis is a phenomenon of nonequilibrium thermodynamics, which is affected by competing time scales for diffusion and reactions, but which also exists in the absence of diffusion. Driven reactions fundamentally alter the thermodynamic stability of the system, by effectively altering the curvature of a nonequilibrium free energy landscape, which includes the rate-dependent and concentration-dependent over-potential required to maintain the applied current, or more generally, the prescribed exchange of matter and energy with external reservoirs. This is the "driving work" missing from the classical Prigogine analysis. The canonical example of driven adsorption on a phase-separating surface in section 2 illustrates how a single driven solo-autocatalytic reaction can alter stability (set here by the derivative of external chemical with concentration), without any diffusion of the adsorbate. As such, this phenomenon is particularly relevant for solids, as shown by the experimental evidence in Fig. 7 for LiFePO₄ nanoparticles, which have negligible solid diffusion in the lateral direction. It is simply the variable rate of reaction during ion insertion, which stabilizes a uniform "quasi-solid solution" concentration profile of an otherwise phase-separating material, as described by the so-called "Allen–Cahn Reaction model".¹ Diffusion plays a secondary role in this phenomenon. By itself, diffusion cannot alter thermodynamic stability (Duhem–Jougeot Theorem), but in cooperation with solo-autocatalytic reactions (as defined in the paper), diffusion can influence linear stability. In the example of driven adsorption, this can indeed be understood *via* an effective Damkohler number, Da , which is a ratio of diffusion to reaction time scales. For slow diffusion (as in many solids), $Da > 1$, the critical current to suppress phase separation is independent of the diffusivity and completely

determined by the reaction kinetics and free energy landscape. For fast diffusion, $Da < 1$, the critical current increases and diverges for $Da \gg 1$, as "un-driven" classical thermodynamic phase separation by backward diffusion (e.g. described by the Cahn–Hilliard equation without reactions) becomes increasingly favored, and the control of phase separation by the driven reaction is eliminated. Recent experiments, building on those in Fig. 7, have verified these predictions for LiFePO_4 nanoparticles, by determining the effect of surface diffusion on the critical current to suppress phase separation.²

1 M. Z. Bazant, *Acc. Chem. Res.*, 2013, **46**, 1144–1160.

2 Y. Li, H. Chen, K. Lim, J. Lim, D. Fraggadakis, P. M. Attia, S. C. Lee, N. Jin, Z. Guan, J. Hong, Y. S. Yu, M. S. Islam, M. Z. Bazant and W. C. Chueh, Fluid-enhanced Surface Diffusion Controls Intra-particle Phase Transformations, 2017, submitted.

Frieder Mugele opened a general discussion of Tom's, Nina's, Hyacinthe's and Martin's papers: Dr Bazant explained in an impressive manner the role of instabilities in driven electrochemical systems far from equilibrium. The energy harvesting concept based on reverse electrowetting with a massive array of parallel microbubbles that are supposed to grow and collapse in a periodic manner to increase power generation is obviously also far from equilibrium and could give rise to non-linear coupling between adjacent bubbles. Most likely, this would compromise the performance of the proposed system. At very high frequencies, this can give rise to acoustic coupling between adjacent liquid menisci.¹ At the present much lower frequencies, the problem would probably resemble more the situation of membrane emulsification, where also care has to be taken to prevent a few of the many parallel nozzles to attract all the activity and leave the others more or less inactive. Do you have any ideas how this could be suppressed?

1 H. Rathgen, K. Sugiyama, C.-D. Ohl, D. Lohse and F. Mugele, *Phys. Rev. Lett.*, 2007, **99**, 214501.

Martin Bazant responded: Energy harvesting by reverse electrowetting in arrays of microbubbles will be governed by similar principles as described in my paper, and the nonlinear interactions mentioned by Prof. Mugele will be very important in determining the stability of the system. The growth of a single micro bubble will typically exhibit bi-stability, which is familiar by analogy with a balloon being filled with air. At first the filling of a small bubble is resisted by surface tension, until the air becomes so compressed that a larger stable state is suddenly reached after air expansion. This can be understood as a phenomenon of phase separation under increasing chemical potential, going past the spinodal instability point. The same kind of phenomenon occurs as lithium intercalates with increasing voltage into a two-phase nanoparticle of a material such as lithium iron phosphate.

In all of these cases (bubbles, balloon, battery nanoparticles), a collection of many bi-stable elements will undergo "mosaic instabilities" in which a uniformly filling state suddenly breaks into many discrete phase transformations, even in the absence of interactions between particles (such as dynamical acoustic coupling of micro bubbles) other than the shared, externally controlled chemical potential. Mosaic instability has been studied extensively in Li-ion battery porous

electrodes,^{1–3} and the surprisingly relevant analogy with balloon arrays has been made, *via* theory and experiment.⁴ An array of balloons attached to nozzles on a single, thick air tube filling at nearly constant applied pressure will inevitably break into discrete balloon-filling events.

The same mosaic instability is potentially a fatal flaw for the concept of energy harvesting with a micro bubble array. As noted by Prof. Mugele, gas flux will not be equally shared between the bubbles, leading to electro-mechanical instabilities that may reduce the efficiency and lifetime of the energy conversion device. However, I could suggest some strategies that could help to control the mosaic instability: (1) Motivated by my paper on driven thermodynamic stability, design a confining geometry in which the pressure–flux relationship for each growing bubble is "auto inhibitory", *i.e.* slowing the growth with increasing gas volume at the same pressure or flow rate. This could be accomplished with diverging confinement channels. (2) Attempt to mechanically isolate the microbubbles from each other, so that gas back flow and acoustic waves are suppressed.

- 1 W. Dreyer, J. Jamnik, C. Guhlke, R. Huth, J. Moškon and M. Gaberšček, *Nat. Mater.*, 2010, **9**, 448–453.
- 2 Y. Li, F. El Gabaly, T. R. Ferguson, R. B. Smith, N. C. Bartelt, J. D. Sugar, K. R. Fenton, D. A. Cogswell, A. L. D. Kilcoyne, T. Tylliszczak, M. Z. Bazant and W. C. Chueh, *Nat. Mater.*, 2014, **13**, 1149–1156.
- 3 T. R. Ferguson and M. Z. Bazant, *Electrochim. Acta*, 2014, **146**, 89–97.
- 4 W. Dreyer, C. Guhlke and R. Huth, *Phys. D (Amsterdam, Neth.)*, 2011, **240**, 1008–1019.

Tom Krupenkin responded: Indeed, the conceptual outline of the arrayed bubbler device as presented begs a question about a possibility of undesirable interference between the neighboring bubbles. From a practical standpoint this might be not a significant problem, however, as a number of design modifications can be readily utilized to reduce or even completely eliminate the bubble interference. As already mentioned in the comments, one of the most obvious solutions is to separate the bubbles in the array by some sort of partition walls, effectively confining each bubble to its own individual cell. This might somewhat reduce the array density, but not to the extent that would noticeably compromise the device performance.

George Schatz opened a general discussion of the paper by Elisabeth Smela: Is it possible that the force arises from the gradient of electric field, as it does in dielectrophoresis? This has the advantage that no charged species are required. This also shows that molecules with a larger polarizability will show larger effects.

Elisabeth Smela answered: We have used DEP in prior devices for particle manipulation.^{1–3} Typically AC voltages are used, although DC DEP has been reported. DEP forces on particles scale as R^3 , so they are vanishingly small for molecules.

- 1 M. Urdaneta and E. Smela, Multiple frequency dielectrophoresis, *Electrophoresis*, 2007, **28**(18), 3145–3155.
- 2 M. Urdaneta and E. Smela, The design of dielectrophoretic flow-through sorters using a figure of merit, *J. Micromech. Microeng.*, 2008, **18**(1), 015001.
- 3 M. Urdaneta and E. Smela, Parasitic trap cancellation using multiple frequency dielectrophoresis, demonstrated by loading cells into cages, *Lab Chip*, 2008, **8**(4), 550–556.

Andriy Yaroshchuk remarked: If the charge carriers are produced in the process the electroosmosis can be expected to be a non-linear function of voltage. Was this the case?

Elisabeth Smela responded: The flow rate is linear with voltage, as is the membrane deflection in sealed devices. In microchannels, the flow rate (Fig. 4 of ref. 12 in the paper) and deflection (Fig. 7 and 8 in ref. 11 of the paper) curves have an intercept at the origin. In the mm-scale tubes, there can be a turn-on voltage before flow occurs (3 kV for a 2 cm electrode separation).

David Schiffrin commented: The experiment that you described in your presentation, showing two metal needles inserted in a polyethylene tube connected to a reservoir at one end and to a pipette on the other containing propylene carbonate (PC) and to which a high voltage was applied is very interesting. Clear flow of PC was observed in the pipette when applying potential between the two needles.¹ The surface of polyethylene in aqueous solution carries a negative charge above pH ~ 2 ,² which has been attributed to the dissociation of carboxylic groups formed during its manufacturing process.³ The zeta potential in aqueous solution ranges from ~ 0 to approximately 63 mV between pH 2 and 10. Electroosmotic flow is, however, unlikely since no additional electrolyte was present in the organic solvent employed.

If the observed flow were due to an electroosmotic effect, the flow direction would be reversed by changing the polarity of the applied potential. Did you observe this change in flow direction?

Another way to analyse the electrostatic problem is to consider the symmetry of the field. If the electric field between the two needle electrodes was strictly symmetrical, electrostriction of the propylene carbonate fluid in the field would not provide any directional force for fluid movement. However, a different situation would prevail if the field created by the two needles was asymmetric. The energy density (U) in a dielectric is given by:

$$U = \frac{1}{2} \epsilon_0 \epsilon_r E^2$$

where ϵ_0 is the permittivity of free space, ϵ_r is the relative permittivity of the fluid and E is the electric field in the fluid. U has also units of pressure. Thus, if the field is asymmetric and the fluid is not bound, the difference in energy in different regions, for instance around your needle electrodes, provides the driving force for fluid movement. This electrostatic pumping mechanism, also called the Maxwell pressure gradient, has been demonstrated for dibutyl decanedioate, linalyl acetate and dibutyl adipate as test fluids.⁴

A demonstration that the mechanism above discussed is valid is to investigate the measured flow rate as a function of the square of the applied potential. Have you done this?

1. D. Sritharan, A. Simpson Chen, P. Aluthgama, B. Naved and E. Smela, *Electrophoresis* 2015, **36**, 2622–2629.
2. W. Schutzner and E. Kenndler, *Anal. Chem.*, 1992, **64**, 1991–1995.
3. P. Benes and M. Paulenova, *Colloid Polym. Sci.*, 1973, **251**, 766–771.
4. R. V. Raghavana, J. Qina, L. Y. Yeoa, J. R. Friend, K. Takemura, S. Yokota and K. Edamura, *Sens. Actuators, B*, 2009, **140**, 287–294.

Elisabeth Smela replied: The flow rate appears to be linear with the potential between 3 and 7 kV, based on the preliminary data from these large-diameter tubes. Thank you for the suggestion to look at this more carefully, since there are definitely multiple phenomena occurring under different experimental conditions.

David Schiffrin said: As we discussed in the previous session on electro-tunable wetting, when a liquid surface (or interface) becomes charged by applying an electric field, the surface (interfacial) tension decreases. As discussed above, for an asymmetric geometry, the gradients of interfacial tension can give rise to Marangoni convective flows and hence, a net movement of liquid. If the flow is caused by electroosmosis due to fixed charges on the PE tube surface containing the high tension needles, the flow should be reversed when reversing the polarity but remain the same if the Marangoni effect is operative. Can you tell us what happens in your experiment with PE tubing when the field was reversed?

Elisabeth Smela replied: The flow reverses when the voltage is reversed. This is an effect we can watch closely in upcoming experiments on large diameter tubes, since in those there are two opposing flows seen under different conditions (changing electrode diameter, changing voltage). In micro-scale tubes, the flow is only ever in the direction expected for EO.

Konstantin Kornev remarked: Firstly, all of the examples presented in the introductory notes to this paper are helpful for understanding the proposed principles of actuation and are quite illustrative for formulating the challenges associated with the physics of fluid pumping. It would be nice to add some illustrative material to this volume of Faraday Discussions.

Secondly, the experiments with the moving meniscus appear quite informative and helpful for understanding the pumping physics. Can you please comment on any systematic data on the position of meniscus *versus* time at the given voltage? If the meniscus velocity is constant, how does it depend on the tube diameter?

Elisabeth Smela answered: In response to your first question, the experimental results were all previously published in detail (references 11, 12 in the paper and the associated electronic supporting information). With regards to your second question, we have not yet carefully studied the meniscus position as a function of time. That is an excellent suggestion.

Andy Mount remarked: The flow induced by the application of voltage between the two electrodes in propylene carbonate seems from the discussion to potentially arise from several processes. Have you considered making impedance measurements to try and resolve the relative contributions of these processes? This should be highly informative, as each process should have a characteristic frequency range in which the effect would make a (or the) significant contribution to the response. Fitting the response as a function of frequency to an appropriate equivalent circuit should then enable physicochemical insight, and potentially quantification in terms of parameters such as ion concentration, diffusion coefficients, double layer capacitance, *etc.*

Elisabeth Smela replied: This is a good suggestion, and I hope to be able to get some data on that question in the near future.

Hubert Girault commented: To follow up on the comments of Prof. David Schiffrin, it would be interesting to study the influence of the electrode reactions on the PE tube itself to see if the surface property of the PE is altered thereby generating a gradient of surface tension and generating a Marangoni flow.

Elisabeth Smela responded: This is a good suggestion, thank you.

David Schiffrin asked: Does the rigidity and material of the tubing containing the high tension needle contacts influence the flow rate results?

Elisabeth Smela replied: Not that we have observed. We have used glass, PDMS-coated glass, and PE tubes. However, this is something that can be monitored in future work.

David Schiffrin asked: Can you comment on the different configurations for electrokinetic fluid pumping (series, parallel) from the point of view of force achieved and modularity of construction?

Elisabeth Smela replied: To achieve high force, one needs to use a pumping medium with small channels, since the force is expected to scale as $1/d^2$, where d is the smallest channel diameter. Paper, porous monoliths, and packed beads are good choices, with paper having advantages in terms of fabrication. Stages can be placed in series to increase the pressure. The flow rate and pressure are both linear with the field, so to lower the voltage the electrodes in each stage should be close together. For high flow rate, the more channels in parallel the better, since that scales with the total cross-sectional area.

Oliver Robotham asked: You mentioned that the rate of field-induced flow through the tube was observed to be independent of the size of the tube. Have you considered investigating the system response at weaker fields?

Elisabeth Smela replied: Yes, this was true for tubes between 3 and 7 mm (it was not the case for the microchannels). In the large tubes, it typically took at least 3 kV to produce flow, and in some cases flow reversed when the voltage was increased to 7 kV (in microchannels, flow was proportional to the field and never reversed direction). The flow in larger tubes requires further study to understand the various competing effects.

Roland Bennowitz asked: Your specifications require a certain power density to be realized in a finite size robot. I would expect that independent of the specific technology, any actuation based on electroactive materials needs a corresponding surface density across the device. Can a single membrane pump really achieve the required power?

Elisabeth Smela responded: This is a good point. Since the force scales as $1/d^2$ where d is the smallest dimension of the channel, smaller channels are critical to

producing significant work. We have shown that going from large microchannels¹ to paper as the pumping medium² increases the work, as well as the speed. The required power depends on the application, but in a soft robot (as in biology) one would likely be using a combination of contractile fibers.

1 D. Sritharan, A. S. Chen, P. Aluthgama, B. Naved, and E. Smela, *Electrophoresis*, 2015, **36**, 2622–2629.

2 D. Sritharan and E. Smela, *Polymers*, 2016, **8**, 400.

Alexei A. Kornyshev opened a general discussion of the paper by Nikolai Brilliantov: Both in your paper and in the slides you show dependence on electric field. But there is no such quantity in your system as the electric field in the gap will be varying in space. All that you can know would be the electrode potential measured relative to the reference electrode. What is the meaning of the graphs showing as a function of “electric field”?

Nikolay Brilliantov replied: In our article and in the slides, we use the external field E , which is associated with the surface charge of the bottom and upper electrodes. Certainly, the presence of the salt ions, charged polyelectrolyte and the counterions will result in the space-dependent total field. In the article, we calculate all quantities that determine the actual field that varies in space, that is, we have the complete information about the total field and it is straightforward to obtain the potential difference between the electrodes. In this way, we have one-to-one correspondence between the external field E and the potential difference U . In other words, for each U we have the according value of E . The analysis, however, is more simple and transparent, when the variable E is used instead of U .

Carlos Drummond asked: Shouldn't the adhesion (and adhesion hysteresis) between the particle and the plane be included in the model to better evaluate the feasibility of the proposed nano-device?

Nikolay Brilliantov answered: For the present model of the nano-device, the adhesion may be simply taken into account by including this into the normal force, that is, the normal force will be composed of the elastic and the adhesive parts, as in the Johnson, Kendall, and Roberts (JKR) model. We have also shown¹ that this approach is valid for nano-particles. Hence the adhesion will enhance the clenching coefficient. On the other hand, the adhesion hysteresis may be unfavorable for the unclenching of a particle, hence, at least one of the planes of the nano-vices should have as small an adhesion hysteresis as possible.

1 K. Saitoh, A. Bodrova, H. Hayakawa and N. V. Brilliantov, *Phys. Rev. Lett.*, 2010, **105**, 238001.

Astrid S. de Wijn addressed Alexei A. Kornyshev and Nikolay Brilliantov: This comment is in response to Alexei Kornyshev's question and Nikolay Brilliantov's response to it. You do not have a flat surface. If you are at zero temperature and apply a force, an elastic surface will bend. Moreover, even atomically flat surfaces still have atomic-scale corrugation. This leads to static friction, as well as non-viscous contributions to the dynamic friction, except in some special cases that are not relevant for these applications. For a recent review on our understanding of friction on atomic scales, see, for example ref 1.

1 A. Vanossi, N. Manini, M. Urbakh, S. Zapperi, and E. T. Colloquium, *Rev. Mod. Phys.*, 2013, 85, 529.

Nikolay Brilliantov responded: We consider two limiting models: one for the rough surface when the thermal fluctuations of the surface, modulating its height are negligible compared to the size of the surface asperities and the other model of a molecular smooth surface, when the height of the surface is determined by the surface phonons with the vibration direction normal to the surface. At zero temperature, when the amplitude of the phonons vanishes, the local form of the surface will be determined by the elastic deformation due to interaction with the nano-particle. In our study, we use Hertz's contact theory, where the deformation (bending) of the surface, as well as the deformation of the particle itself are both taken into account. (Note however, that the Young's modulus of nano-particles is usually very small, see ref. 24 of our article). In the limiting model of molecular smooth surface, we indeed neglect the atomic scale corrugation, which entails static friction. As far as we know, there exists no model that quantifies the amplitude of the corrugation potential as a function of the normal load, which is crucial to obtain the clenching coefficient. Hence our limiting model of molecular smooth surfaces provides an estimate for the low boundary of the solid friction force due to thermal fluctuations only.

Andriy Yaroshchuk opened a general discussion of the paper by Kelsey Hatzell: This topic is a nexus of electrochemistry, colloid science, rheology, energy storage and so on; it is really interesting. My understanding is that the X-ray tomography is carried out under static conditions. However, the real system is dynamic where contacts between the particles are permanently established and broken. The coagulation dynamics could play an important role. Could you comment on this?

Kelsey Hatzell answered: The imaging was done under static conditions and the results demonstrate the equilibrium percolation pathways. We expect these percolation pathways to be disrupted during flow, and future work intends to examine how this disruption decreases ion removal capacity and the loss mechanism (self-discharge). The system has a relatively high salt content, unlike terms of a traditional colloidal system (100 mM or greater), so the system is strongly aggregated and stable.

Andriy Yaroshchuk commented: Given the complexity of the process, wouldn't it be useful to simplify, at least, the system geometry and use model, for example, spherical mono-disperse electronically-conducting particles? Have there been any attempts of this kind?

Kelsey Hatzell replied: We did not formally investigate electroosmosis effects, but this is an important phenomena to investigate. Generally, flow-electrodes demonstrate similar phenomena to film electrodes where the charge efficiency/current efficiency (which measures the energy to remove an ion) decreases with decreasing desalination voltage.

Robert Dryfe asked: My question is possibly naïve. Stability of colloidal suspensions is often charge based; if you are reducing the electrolyte

concentration of carbon-containing suspensions using capacitive de-ionisation, does the induced reduction in electrolyte concentration cause aggregation of the particles?

Kelsey Hatzell responded: We are working with relatively high concentrations (>100 mM) of salts in comparison to traditional colloidal systems so we don't observe significant aggregation during experiments. In traditional CDI systems, we target low concentration water sources (brackish water) so during desalting the actual salt content entering the flow electrode is sometimes small in comparison to the overall volume. In the experiments in this study we cannot image suspensions without salt because of rapid sedimentation and Brownian motion. Thus, at least in this system, we benefit in terms of stability by adding a salt and increasing repulsion between particles to some extent. It would be interesting to see if we can induce aggregation when desalinating at high concentrations, but we have not explored those conditions as of yet.

Roland Bennewitz asked: Percolation is an important parameter in your flow electrodes; is it more important for the electrochemical surface processes, or is it mostly important for the overall conductivity?

Kelsey Hatzell replied: Electrochemical percolation is important for effective ion electroadsorption. It is believed that the loss of electrical percolation during flow (shear processes) decreases the capacity to remove ions in ion removal processes. We believe that percolation is more important because the conductivity can change during flow operation; however, more work is needed to make clear conclusions.

Alexei A. Kornyshev opened a general discussion of Elisabeth's, Nikolay's and Kelsey's papers: I have one philosophical question. Bending electroactuators is easier, the softer the bending elastic modulus is. For instance, the induced curvature of the polymer–electrolyte composite based electroactuator was larger, when the beam is softer.¹ But if the thing is very soft, it will not be able to do any work, because the work is what we do against resistance. In short, the electroactuator's deformation will not sustain such resistance. But if you, alternatively, make the beam very stiff, it will not acquire any curvature. How is this problem usually resolved? Does it depend on the target application or is it just an engineering problem (such as arranging one hundred rabbits to replace a horse to move a carriage, like what takes place in a human muscle)? Could you educate us on this front?

1 A. Lee, R. Colby, A. A. Kornyshev, *Soft Matter*, 2013, **9**, 3767–3776.

Elisabeth Smela replied: Yes, there is an inherent trade-off between strain and stress. In general you want to maximize their product to produce the most work. Speed is the third critical metric, so that you can deliver enough power. It has proven challenging to achieve reasonable values for all three. After reaching those targets, which vary by application, then efficiency, lifetime, creep, form factor, integratability, scalability, cost, and other considerations also come into play.

Regarding the question of stacking actuators, yes, this is one solution that can be employed to increase force. (For example, this has been used for DEAs, which are high strain, low force actuators.) In other cases, one can use mechanical linkages to amplify the strain. (This has been used with conjugated polymer actuators, which are high force but low strain.) However, "just engineering" does not do justice to the challenges of getting electroactive materials to perform useful work, since the additional complexity, weight, and volume can doom the final device. This is one of the reasons that artificial muscles are still not in widespread use.

Nikolay Brilliantov commented: I believe that polyelectrolytes are very promising materials for future electro-actuators for two reasons: firstly, they have a very large expansion range, varying from an expanded to collapsed state. Secondly, these materials have a short relaxation time, associated with the time of a conformational change of a polyelectrolyte. The latter is determined by the time needed for counterions to travel a molecular-scale distance.

Elisabeth Smela replied: Force and speed need to be given as much emphasis as expansion. For mass-transporting EAPs, the challenge is creating a molecular structure that allows ion and/or solvent ingress and egress at a fast enough rate, while the structure is also stiff enough to produce significant force but not so stiff that the strain is negligible. It would be even more preferable if ionic liquids could be used, so that the actuators can work in air. Other considerations include efficiency, integration with electrodes, packaging, *etc.*