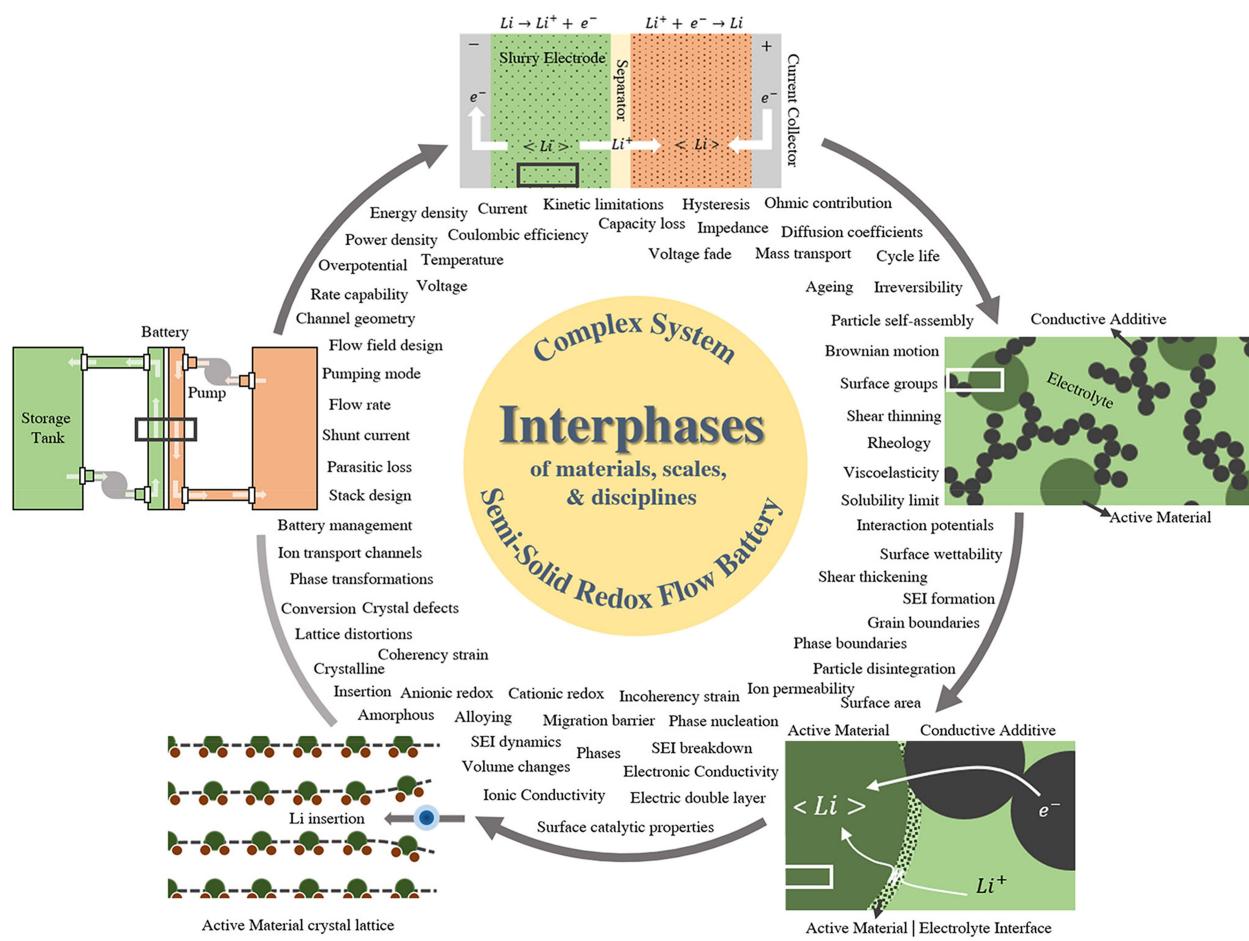




Interphases in Electroactive Suspension Systems: Where Chemistry Meets Mesoscale Physics

Garima Shukla^[a] and Alejandro A. Franco*^[a]

Semi-solid redox flow batteries (SSRFBs) consist of electrochemically active particle suspensions as electrodes and can potentially be applied to large scale energy storage. Invented just a decade ago, these batteries already face dwindling commercial value as they can be too complex to study systematically. This review illustrates the depth and width of the state of the art of knowledge that needs to be taken into account. Additionally, this work shows how SSRFBs are an embodiment of complex systems. Conventional theoretical paradigms, experimental

tools, and modeling methods generally reduce the size of the problem to solve it. However, this is nearly impossible for highly complex systems with interdependent parameter relationships. This review shows how rheology plays a very significant role in impacting electrochemistry. It concludes that the fastest way to optimize SSRFBs is by obtaining as many experimentally observable parameters as possible using advanced simultaneous techniques, followed by incorporation of this multidisciplinary data into a unified theoretical framework.

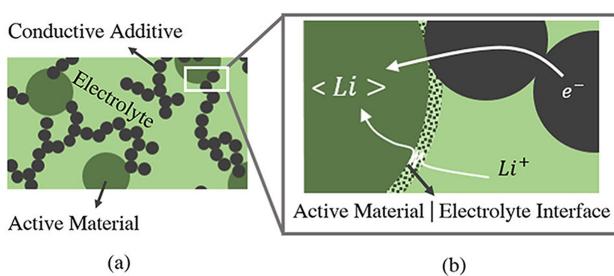
1. Introduction

The individual industrial successes of lithium-ion batteries (LiBs)^[1] and redox flow batteries (RFBs)^[2] over the last decades led to the advent of the semi-solid redox flow battery (SSRFB) in 2009,^[3] essentially a flowable lithium-ion battery. RFBs consist of ionic solutions as electrodes which can be stored in external tanks, enabling grid scale energy storage. LiBs have solid electrodes soaked in electrolyte and are typically used for portable applications, additionally, numerous battery units can be employed for stationary applications of various scales and purposes. The novelty of SSRFBs is the new type of multiphase electrode wherein an ionically conducting electrolyte is used as a suspension medium for two types of solid particles: (i) an electron conductive additive, and (ii) active material responsible for storing energy. (Scheme 1).^[4] When compared to ion solutions in RFBs, a higher concentration of active material can be dissolved in the same electrode volume for slurry electrodes, resulting in potentially 5–20 times greater volumetric energy density.^[4] The first publication on SSRFBs in 2011 was born out of a patent by Chiang et al. and contains sufficiently generalized observations from an industrial point of view.^[3,4] Active materials like LiCoO_2 , LiFePO_4 , $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, and graphite, with carbon-based conductive additives like Ketjen Black (KB) were used in this study to make slurries in electrolytes composed of different alkyl carbonate solvents and LiPF_6 salt. The electrochemical tendencies of these slurry electrodes have much in common with LiB electrodes fabricated with the same materials. Electronic conductivity of the conductive additive was shown to be a limiting factor. Further rheological investigation showed presence of shear thinning behavior and this suggested that electronic conductivity arises from networks of conductive additive particles and could be tailored. Additionally, different flow conditions like continuous and intermittent i.e. stop-discharge-and-go, were studied. Intermittent flow showed less parasitic losses and it was suggested that round trip efficiencies can be improved by tuning flow rates.^[4]

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An invited contribution to a Special Issue on SEI and Interphases at Electrodes

The concept of SSRFBs opened doors for a bounty of design possibilities at the level of redox chemistry, multiphase electrode, and cell architecture. This subject has been addressed in reviews^[5–7] and the last ten years show an explosion of diverging possibilities like flow capacitors,^[8–17] water desalination,^[8,18–20] incorporation of redox mediators,^[21–29] carbon-free suspensions,^[30,31] polysulfide or metal-ion based carbon suspensions,^[32–42] and semi-solid metal-air flow batteries.^[43–45] In the interest of brevity, this review is specifically focused on how the state of art of LiBs and particle suspensions impact SSRFBs. However, the generalized point of view on complex systems developed in this review is applicable to the aforementioned systems. Research relevant to SSRFBs itself is spread out over many different kinds of studies and approaches. For instance, in a very recent study, an electrode capable of switching between flow and static modes *in-operando* has been proposed, offering greater technical and operational flexibility.^[46] Transition velocities required to switch between modes are shown to be strongly influenced by aggregation and interaction forces between particles.^[46] Another study illustrates the deleterious impact of solid electrolyte interface (SEI).^[47] The SEI is an electronically isolating thin film formed when the active material is electroactive outside the window of stability of the electrolyte. When the SEI deposits on the entire surface area of the suspended active material particles, it can result in complete electrical isolation of said particle and a consequent loss of capacity.^[47] Evidently, as the SEI modifies the surface of active material particles, it may potentially impact aggregation and flow behavior as well.



Scheme 1. a) Mesoscopic picture of particle suspension and particle self-assembly where electronically conducting additive particles wire active material to the current collector. b) Insertion of lithium into active material during battery functioning.

In conjunction to experimental studies, the first continuum models came out after 2012; they involve a combination of Newman's porous electrode model and power law based hydrodynamic flow to capture non-Newtonian behavior of the suspension.^[48–51] The main conclusions of these studies are that: (i) spatial uniformity of current extraction and stoichiometric flow depend on the voltage profile;^[48] (ii) intermittent or plug flow mode is beneficial for extracting maximum capacity from the slurry electrode;^[4,49] (iii) extended electroactive zones can exist, i.e. electrochemical activity can be observed in pipes just outside the cell, and their impact can be minimized through appropriate design and operating conditions.^[50] In order to distinguish between flow batteries and flow capacitors, capacitive Damköhler number has been introduced.^[51] This number is essentially a ratio between exchange current density and Peclet number which in turn is the ratio of advection to diffusion. Based on the assumption that infinitely fast pulses during intermittent flow can help isolate electrochemical phenomena from fluid flow phenomena, the use of a discretized model using finite volume method is possible.^[49] Even without considering an explicit correlation between fluid and electrochemical behavior, this study shows that electrochemical efficiency can be improved through better flow volume control, tailored suspension rheology, and resistance to flow can be reduced by enhancing slip.

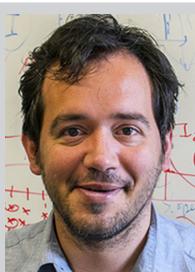
SSRFBs based on different material systems were demonstrated in subsequent studies by various research groups: (i) a full-cell based on carbon coated LiTi₂(PO₄)₃ and LiFePO₄ with KB in aqueous electrolyte;^[52] (ii) a half-cell with LiFePO₄ with KB in commercial LP30 (EC:DMC) electrolyte;^[53] (iii) a half-cell with silicon with KB in LP30^[54] and EC:DEC,^[55] and (iv) a full-cell with P2-type Na_xNi_{0.22}Co_{0.11}Mn_{0.66}O₂ and NaTi₂(PO₄)₃ in EC:DMC:NaPF₆ (0.5 M).^[56] These studies are proof of the great potential SSRFBs have in terms of utilizing a variety of active materials, conductive additives, and electrolytes. However, these studies also demonstrate that traditional electrochemical techniques used to study LiBs fail to provide quantitative explanations of trends observed for SSRFBs. The added challenge is that rather than forming a clearer picture of underlying mechanisms, these studies appear to provide phenomenological explanations based on conflicting assumptions. For instance, silicon and

carbon based slurries are shown to maintain both good and bad inter-particle contact under cycling.^[54,55] The contribution of interface between current collector and slurry towards electrical resistance is shown to be both significant and insignificant.^[9,57] Two schools of thought explain the mechanism of electrical conductivity in slurries; one wherein particle networks are known to dominate and another wherein electron tunneling dominates such that distribution and size of particle clusters is more important.^[58–61] The zeta potential of conductive carbon suspensions in organic electrolyte also cannot be generalized to either always positive or always negative; furthermore, the size of the cation used in the electrolyte is shown to be significant.^[58,62] The impact of channel depth on electrical conductivity of slurry is shown to vary with multiple simultaneous parameters like flow rate, active material concentration, and C-rate.^[9,63] At this juncture, it is evident that standard experiments and models developed to study either LiBs or RFBs are an insufficient means to achieve commercialization. Consequently, two main approaches and their combinations can be found in literature: (i) the use of more sophisticated experimental tools to enhance fundamental understanding of mechanisms and (ii) studying the response of SSRFBs to modifications induced by additives and different material combinations.

Given the lack of concrete and generalized quantitative understanding, it can be concluded with certainty that SSRFBs are complex systems. Non-linearity and non-intuitiveness are hallmarks of complexity and any emergent behavior is merely the appearance of unanticipated phenomena that tends to confound and polarize the scientific community. So how does one obtain a quantitative description of all the important and sensitive parameters that impact SSRFB performance? A recent review by Gandomi et al. on diagnostic and characterization tools for RFBs provides a comprehensive picture of important research goals.^[5] At the material chemistry level it is essential to decrease material cost while simultaneously improve power and energy density so that consequently system cost falls. For SSRFBs, this implies the added goal of optimizing material performance and reversibility specifically for multiphase electrodes. To ensure battery durability, capacity decay and parasitic losses need to be mitigated with appropriate system design.



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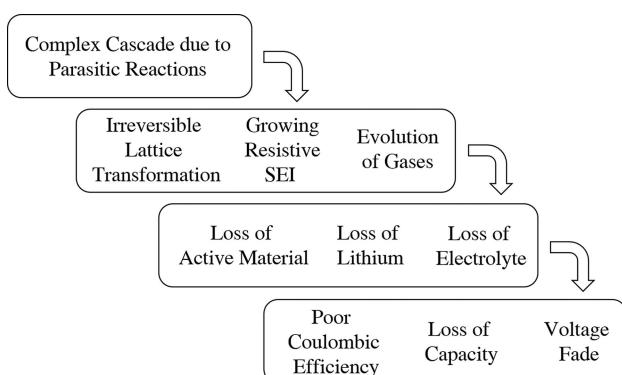
Furthermore, implementation of battery management systems on commercialization requires the development of rigorous mathematical models. In their review, Gandomi et al. show that optimized battery architecture is chemistry dependent and that loss mechanisms can only be dealt with when the complexity of electron and charge transfer on the surface and electrode reaction mechanisms are fully understood.^[5]

The potential of this new field is evident but the lack of concentrated effort on a specific SSRFB and the lack of an industry-ready prototype suggests that more mysteries remain to be unraveled. The following sections are designed to illustrate the various facets of an SSRFB that make it a complex system. Understanding these aspects is essential to create systematic methods to achieve device optimization and eventually, a bankable prototype.

2. Origin of Complexity in SSRFBs

2.1. Interphases in Lithium-Ion Battery Materials

According to Aurbach et al., the short lifetime of post-LiB systems lies in: (i) instability of crystallographic phase transition of active materials and (ii) uncontrollable reactions at solid-liquid interface leading to unstable SEIs.^[64] Additionally, material optimization is specific to commercialization of a battery technology; this means that the same material would have a tendency to behave poorly in a new type of battery. The general term, battery performance, is known to be influenced by mass transport limitations, kinetic limitations arising from electrochemical charge transfer, and ohmic or resistive contributions within the battery. Here, overpotential, quasi-static hysteresis, and rate capability limitations also play a role.^[65] Ageing of a battery is captured as the progressive capacity loss and increase in internal resistance, eventually leading to voltage fade and power loss.^[66,67] To construct an overarching understanding, all these phenomena can be generalized under one umbrella, i.e. important aspects frequently encountered when studying new battery materials or systems.



Scheme 2. A simplified representation of cascading effects of side reactions in a battery across time and scale. Numerous feedback loops can exist between these phenomena.

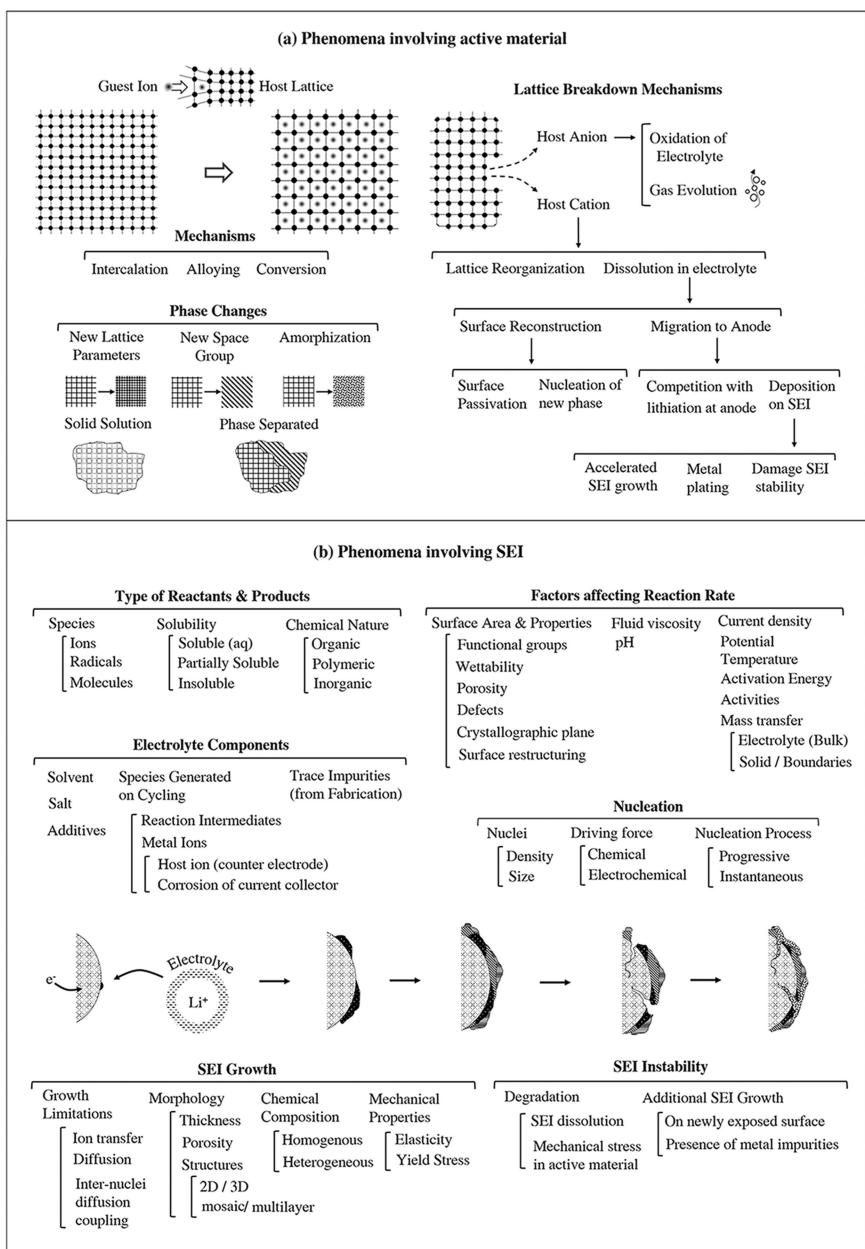
From a phenomenological point of view, it becomes convoluted to assign specific mechanisms to every performance metric because of cascade effects that can impact the entire battery (Scheme 2).^[66] For instance, parasitic reactions on either electrode can manifest as increased thickness of SEI which leads to increased resistance, consumption of useful electrons and ions, impact on coulombic efficiency, loss of lithium or even host site, and consequently loss of capacity.^[67–71] If the active material host lattice irreversibly transforms along cycling, lithium transport and lithium storage can be impacted, contributing to thermodynamic changes that may appear as hysteresis or voltage fade; furthermore, mechanical disintegration of particles can lead to capacity loss.^[1,65,71–77] The existence of these specific pathways is nearly impossible to isolate and prove experimentally even in highly optimized and commercialized LiBs;^[67,69] this inadvertently reveals the complexity of the battery system.

While it may seem reasonable to reduce the scale of a problem by eliminating insignificant mechanisms, this may not be possible in such interdependent systems. For instance, the presence of anionic redox activity was never established in conventional layered cathode materials and remained a source of confusion because numerous explanations were provided for side reactions involving host anions.^[72] However, when lithium rich cathodes showed a dominating presence of anionic redox activity, this phenomenon was systematically studied and controversies were put to rest across oxide based layered material families.^[78] Another instance is nucleation of a new phase which is said to be determined by the surface to volume ratio of a particle, however, literature of phase changes on ion insertion is also quite complex.^[79] The model cathode material, LiFePO₄, was initially touted as a material with low rate capability because of kinetic barriers to lithium diffusion originating from phase boundaries.^[80] It was soon demonstrated that decreasing the particle size had a more significant impact on the electrode resistance than introducing a carbon coating.^[81] Interfacial energy, surface energy, coherency strains, free energy of mixing, solubility limits of lithium, lithium transport in bulk and on the surface, and lithium insertion kinetics were shown to impact the miscibility gap; determining whether solid solution or phase separation mechanism take place, and induce complex multi-particle effects like the domino cascade effect.^[80,82,83] Given the importance of surface transport mechanisms in phase changes, SEI and its evolving nature along cycling could also play a role. Many physical aspects influence SEI formation, such as, surface catalytic sites, nucleation and growth mechanisms, disintegration, and regeneration.^[66,68,84–87] The nature of SEI and how particles interact with each other and with the solvent is expected to have a direct impact on rheological properties of the suspension which will further be illustrated in the following section. Grain boundaries are another subject of complexity; they are known to possess higher crystallographic disorder and their ion migration barrier can either be low^[77] or high.^[88] Even in the absence of grain boundaries, two way diffusion processes on cycling have shown evidence of lithium trapping in alloying electrodes and current collectors.^[89] Evidently, grain boundaries

can significantly influence resistance regardless of whether they are present in polycrystalline active materials or within the SEI.^[77,85] A collection of some parameters and phenomena linked to phase transitions and SEI are presented in Scheme 3; viewing the phenomenological landscape as a collection of all mechanisms can help identify conditions when otherwise masked mechanisms begin to dominate. Organizing and summarizing this vast number of phenomena in literature is especially challenging with regard to nomenclature and significant effort has gone into providing an exhaustive yet generalized picture

2.2. Interphases of Scales and Disciplines

The presence of inhomogeneity at nanoscale and mesoscale in batteries is known to impact lithium-ion transport.^[119] Thermodynamic studies on insertion materials show that voltage hysteresis also originates from many-body effects or collective behavior.^[90] A domino cascade effect where particles are shown to sequentially undergo charging and discharging has been experimentally proven.^[83] Battery models that treat electrodes as effective media where discharge occurs simultaneously in all particles cannot capture this effect; thus promoting interest in 2-D or 3-D models that consider multi-particle interactions. This



Scheme 3. Schematic showing a selection of generalized aspects that introduce complexity in batteries with reference to a) active material and b) SEI on the surface of active material. Feedback loops between categories shown here are difficult to visually demonstrate but are intended implicitly.^[1,17,66–74,76–87,90–92,93,93–118]

may typically be carried out by models originally developed for microscale and parallelized for efficiency such as Molecular Dynamics, Dissipative Particle Dynamics, Brownian Dynamics, or Stokesian Dynamics.^[120–125] However explicitly considering dynamic parameters like state of charge, particle volume, surface area, or surface functional groups that are inherent to electrochemical systems, would require simulation methods designed specifically to handle such complex phenomena at mesoscale. Mechanistic models like those based on kinetic Monte Carlo provide a suitable framework for such purposes.^[65,126–136] However application of such models is challenging because they necessitate elucidation of parameters that have not yet been measured or fully understood, and improving algorithmic efficiency through parallelization may not be straightforward if the physics to be captured by the model is to be left open to modifications.

The consequences of many body interactions are especially exacerbated in SSRFBs. Here, since high concentrations of solid particles are in suspension, simple electrostatic repulsion may or may not maintain a stable colloidal suspension. The particle size distribution of active material and conductive carbon generally lies within nanometric range for maximizing electrochemical performance. The combined effect of high solid fraction and small particle size, in the absence of steric hindrance, can encourage particles to aggregate.^[137] Attractive colloidal forces can manifest at two levels; formation of clusters and arrested mesoscopic particle networks.^[138] While particle contact is necessary for electronic conduction in the multiphase electrode, too much aggregation can result in sedimentation or flocculation and can render SSRFBs inactive. Flocculation of particles is probable if the liquid medium consists of ionic species which are usually present in high concentrations in battery electrolytes. DLVO theory for colloidal stability is typically used to capture particle interactions and their tendency to aggregate by considering van der Waals forces of attraction and electrostatic repulsive forces of double layers.^[137,139–141] It has shown to provide useful qualitative explanations of the effect of ionic strength on particle behavior of slurry electrodes.^[46] However, to rigorously use DLVO for SSRFBs, one may need to consider on-the-fly coupling with undergoing electrochemical dynamics that potentially impact particle surfaces.

An additional aspect is Brownian motion; it can be significant because the size of particles relevant for battery applications may satisfy the condition of a Brownian particle. In this case, parameters like solid concentration, slurry viscosity, temperature, diffusion coefficient of particle, Peclet number or Reynold's number can impact the degree of Brownian motion of the particles.^[120] However, even suspensions containing non-Brownian particles show a variety of highly complex phenomena due to non-Newtonian and viscoelastic behavior. For instance, shear thinning behavior exists and is a result of disintegration of pre-existing particle networks such that the suspension flows more easily. This, however, can mask a shear thickening regime, wherein the suspension starts forming new particle networks and inhibits flow which would impact operation of SSRFBs. The shear thickening regime can be briefly

revealed under a certain range of shear rate based on parameters like particle size distribution, particle aspect ratio, inter-particle interactions, and even electric or magnetic fields for systems susceptible to these forces.^[142,143] On increasing solid volume fraction, the suspension can also enter a jammed regime where the particle assembly leads to complete arrest; this would be highly disadvantageous for flowing electrodes.^[142] Regimes of shear thickening and jammed clusters have only recently been unraveled in SSRFBs.^[58,59] If the mesoscopic intricacies of such electrochemically evolving suspensions are better understood, mechanical pumping losses associated with SSRFBs would be minimized and particle connectivity could be enhanced.

The importance of dynamic viscosity makes rheological studies essential, however, these are scarcely performed in conjunction to batteries. The use of the Herschel Bulkley model is common; it consists of only a few parameters, namely, yield stress, consistency coefficient, degree of non-Newtonian behavior, and experimentally measured shear strain.^[144] While it provides a sufficiently rich description of rheology, it does not help identify specific phenomena or their mechanistic details. Previous research on viscosity or interaction potentials that can explain colloidal stability has been driven by the search for a unique equation. For instance, in line with Einstein's relation wherein viscosity is a function of volume fraction of solid in suspension, several expressions with different coefficients were proposed for different ranges of solid fractions.^[145] However, further studies showed the importance of considering additional aspects like maximum solid fraction within the fluidity limit, particle diameter, particle shape, particle size distribution, viscosity of medium, and shear rate.^[146] Interactions between particles or electro-viscous effects, Brownian motion, energy dissipation in gaps between particles, and local fluid flow around anisotropic particles were also identified as relevant phenomena and there are numerous diverging theories, none of which are able to universally capture viscosity.^[144] Theoretical approaches based on Kirkwood's molecular theory and molecular dynamics all show large deviations from measured viscosity data.^[145] Soon afterwards, it became clear that such empirical relations are oversimplified and cannot provide a generalized equation with wide applicability.^[146] This observation, however, is not to subdue the importance of empirical equations, insofar as the assumptions and conditions behind their validity are taken into consideration, such equations are very reliable.

The theory of viscosity or any theory that describes interaction forces in a colloidal suspension, like DLVO, are known to only implicitly capture the vast underlying material complexity. A brief historical account of interaction potentials demonstrates how theory took into account more explicit details in order to evolve. By 1784, Newton's gravitational law and Coulomb's law of electrostatics had triggered a race to find a new fundamental force that governs material properties.^[147] Laplace postulated the first inverse power law in 1806.^[148] Decades later, in 1873, the van der Waals force was proposed and its two main assumptions were the presence of attractive forces between particles and that particle volume could not be neglected.^[149] Many of the physical phenomena which were

being studied in the preceding century, like capillarity, sublimation, and adsorption, could be explained with this theory. Research naturally turned towards predicting the attraction term theoretically along the lines of Laplace's inverse power law. Sutherland generalized attraction to r^{-n} in 1887 and Gustave Mie, for the first time, included a repulsive term in addition to the attractive van der Waals term; both of which were described generically as r^{-m} and r^{-n} , respectively.^[147,150] In the following years, many scientists tried to find a unique exponent for the repulsive term. In 1925, Lennard Jones found that at shorter distances, ions similar to Ar and Ne repelled with inverse power laws of r^{-9} and r^{-11} respectively, while at a larger distance, a better approximation was given by r^{-15} .^[151] This line of research appeared to provide scope for endless claims, none of which were proven to be universally applicable. Quantum mechanics, which was getting popularized in 1920s, offered a more rigorous treatment for the origin of the repulsive term. In 1921, Debye gave a very exact description of molecular forces and showed that the energy of a molecule resulted from the existence two simultaneous forces, that of attraction and repulsion.^[152] In 1925, Pauli stated that two electrons can only exist in the same volume element of space if they have sufficiently different velocity. Thus, repulsion between atoms depended on the electron spin. For cases like unsaturated molecules where electrons can easily change their spin to overlap electron clouds, repulsions exist only for short distances, while for atoms which require very high energy to change their electron spins, repulsions are much stronger.^[153] Hence, repulsive forces depend on rather subtle details of the charge distribution of the molecules and it is consequently nearly impossible to connect them with simple constants of molecules, quite unlike attractive terms. Interaction potentials were hereafter expressed as a sum of a variety of attractive and repulsive terms of electrostatic origin, as described by London.^[154] Evidently, the search for a unique force was abandoned and replaced by an approach that takes into account as many complex details as possible. Today, the Lennard Jones potential is often used in simulations when the objective is to model a general class of effects and the only requirement is to have a physically reasonable potential; thereby it is no longer material specific.

Recent theoretical developments relevant for SSRFBs also lean towards taking greater phenomenological intricacies into account. Advancement in theory for electrochemical impedance spectroscopy for in-situ characterization has been proposed by Hoyt et al. and it takes into account current induced by convection of surface charge on particles under flow.^[155] An impedance element that accounts for oscillatory behavior of surface charge boundary layers is added in series with contact resistance in the equivalent circuit. This study, performed in context to flow capacitors, provides a quantitative means to capture electronic diffusivity, slurry conductivity, and contact resistance as a function of flow rate.^[155] Another study addresses how diffusion is hindered in confined spaces and while this effect is significant in some fields, like zeolites^[156] or drug delivery,^[157] it has only recently been applied to electrochemical particle systems.^[158] The theoretical framework pro-

posed by Chan et al., incorporates Nernst-Planck equation to capture mass transport by diffusion and migration, the Gouy-Chapman model for electrode-electrolyte interface, and a hindered diffusion model^[159] that takes into account modification of Brownian motion due to presence of the interface. Migration and hindered diffusion are shown to compete with one another and this competition determines the tendency of particles to accumulate at the interface; thus providing a means to tune mass transport.^[160] Electronic percolation, vital for the functioning of SSRFBs, has also been elaborated theoretically. A recent study by Golovnev et al. proposes an analytical probabilistic framework,^[161] for particles with high aspect ratio which are expected to provide higher conductivity and better flowability at lower solid concentrations.^[60] It predicts percolation threshold more accurately than excluded volume theory and can provide a detailed mesoscale picture of particle networks above the threshold; thus creating a basis for structure-property relationships. This generalized framework offers more opportunities like implicitly accounting for interaction potentials, influence of solid interfaces, and particle alignment due to electrolyte flow.^[161] A recent modeling approach by Lohaus et al. reports coupling of Butler Volmer based electrochemical dynamics with Computational Fluid Dynamics (CFD) and colloidal physics based on Discrete Element Method (DEM).^[162] This approach studies the dynamics of percolation networks as a function of solid volume fraction. Fluctuations in current density are coherent with the discrete nature of DEM, here the magnitude of current density and 3D visualization of state of charge of particles are used to ascertain extent of percolation.^[162] By expanding the number of phenomena taken into consideration, such studies can potentially unearth a multitude of emergent phenomena, making SSRFBs more intuitive to study.

However, there is still a need to address the complex nature of SSRFBs more rigorously, suggesting that a new scientific paradigm is needed at this junction. Studying hypothetical aspects of theory has known to provide fundamental breakthroughs that can help both experiment and modeling cross critical hurdles. For instance, between, 1905 and 1908, the theory of Brownian motion was treated theoretically by Einstein, Smoluchowski, and Langevin since experimentalists did not know what to measure.^[163] Our approach to handle complexity incorporates tools developed for systems theory, adaptive dynamic systems, Bayesian networks, and structural equation modeling. Graph theory and model specification have been used to create a causal flow diagram. This captures parameters influencing mesoscopic phenomena and their interdependencies, which can be further analyzed by parameter sensitivity analysis. The objective is to create a skeletal mind map with maximum possible freedom for parameter correlation.^[126] Based on this framework, a grey box kinetic Monte Carlo model was developed,^[127] which essentially hybridizes first principles and statistical mechanics methods. This allows creation of a pseudo-topological ordering in the causal flow diagram, which is typically cyclic for complex systems.^[126] It was proven through these studies that understanding the dynamics of competing phenomena is equally, if not more important

than studying and quantifying a specific phenomenon in isolation. Challenges that lie ahead include processing high dimensional data, wherein simultaneously, multiple parameters are varied to study their impact on battery performance and quantify the degree of parameter interdependence within a complex system.

Evidently, since any advancement of SSRFBs requires capturing more types of phenomena, in-situ and in-operando studies that gather experimental information across multiple scales simultaneously, become vital.^[164] However, new diagnostic tools need to be standardized by studying complex systems which are still poorly understood. Also, the massive amount of data collected from in-operando studies can be difficult to handle with conventional methods.^[164] Due to this conundrum, it can take years for researchers to filter away phenomena originating from anomalies of measurement techniques and identify the phenomena that need to be studied. For instance, in-situ liquid cell transmission electron microscopy studies which can be useful to observe slurry electrodes, face several hurdles due to beam effects. Unexpected particle behavior like bouncing may be observed^[165] and such anomalous behavior may suppress phenomena under study like Brownian motion of particles.^[166] Solid samples to study behavior of lithium metal or sensitive interfaces like SEI provide more information under in-situ cryogenic electron microscopy rather than room temperature techniques since the beam damage is minimized.^[166,167] While the most significant advancements have been made with in-situ TEM and in-situ X-ray tomography, in-situ research is gaining momentum.^[164] Recent tools, for instance, include simultaneous in-situ electrochemical impedance spectroscopy and operando electrochemical quartz crystal microbalance with dissipation monitoring. This offers an ability to track SEI formation from a mechanical and electrochemical perspective while providing information on local viscosity changes in the electrolyte.^[168]

3. Studying Semi-Solid Redox Flow Batteries with Advanced Experimental Techniques

Simultaneous rheo-electrical studies by Lestriez et al. provide a much needed window into the complexity of SSRFBs.^[58] Slurries with conductive additives C45 and KB in organic electrolyte propylene carbonate (PC) show that on increasing the concentration of the additive, three distinct regimes emerge: weak rheological gel, strong rheological gel, and electrical percolation. The viscoelastic nature of the suspension reveals a transition from shear thinning to a brief shear thickening regime followed by shear thinning again. While electronic conductivity is shown to depend on existence of particle networks, this is true only below percolation threshold. Above the threshold, it is suggested that conductivity follows a bell-shaped curve. Initially, on increasing shear rate, conductivity decreases because three dimensional networks break down, but afterwards, conductivity increases due to probable electron tunneling mechanisms between particle aggregates. In terms of

conductivity and viscosity, KB is shown to be superior to C45, owing to significantly higher surface area.^[58] Parameter sensitivity analysis with multiple parameters are reported for studies based on Li₄Ti₅O₁₂ (LTO) and KB in PC; such as the impact of channel depth, active material concentration, and C-rate on discharge capacity.^[63] Interestingly, increasing LTO negatively influences both rheology and conductivity of the slurry in this study.^[63] When comparing suspensions of carbon black in aqueous and organic media, despite a higher percolation threshold seen in the former, its plateau modulus is lower and electrical conductivity is higher.^[169] Another study shows that the addition of non-ionic surfactant to slurries of LTO and KB in PC works to increase the inter-particle repulsion. This possibly stabilizes the slurry to promote good electronic connectivity even at large channel depths which would otherwise show poorer capacity.^[170] Carbon nanofibers (CNFs) as additives to suspensions containing carbon black have shown to provide additional elasticity and rigidity to the particle networks while maintaining conductivity.^[171] A significant step towards tailoring interactions between particles has been the creation of biphasic electrodes that show high energy density and fast charge transport at low-dissipation flow.^[172] The interactions between LFP based active material particles and those between KB-LFP are made repulsive by addition of non-ionic dispersant to maintain good dispersion. On the other hand, interactions between KB particles are attractive to enable formation of percolation network. From shear viscosimetry and oscillatory measurements, it is evident that the addition of dispersant lowers stiffness of the percolating network, thereby offering a means to tune flow behavior, thus greatly reducing time-average pumping rate.^[172] The use of Arabic gum as emulsifier and alginate as Newtonian viscosifier has been reported to delay sedimentation by increasing viscosity of carbon suspensions in water; the impact of which has been studied with Zeta potential and XPS measurements.^[60] The same study reports a comparison between three types of carbons, namely compressed carbon acetylene black, ENSACO, and KB. These suspensions show good electronic conductivity even under flow conditions and this observation is attributed to formation of networks below percolation threshold.^[60]

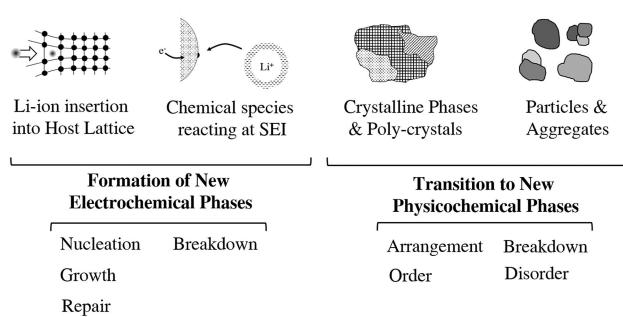
Rheo-impedance studies by M.H.G. Duits et al., on suspensions of LTO and KB in LP30 suggest that electronic resistance and yield stress are a function of lithiation.^[57] A mechanistic picture based on temporally evolving SEI is provided to explain the changing nature of KB particle interactions that impact rheology. This is in context to other studies that suggest that at higher voltages, SEI layer is sparse, less insulating, prone to dissolution, and predominantly organic; while SEI at lower potentials is thicker, denser, less soluble, more insulating, and comprised of inorganic compounds.^[57] To simplify the SSRFB system, the absence of SEI or any dynamically changing particle surface is recommended. Another study by the same group shows low frequency real impedance and viscosity responses to change in shear rate.^[173] The mechanistic description proposed explains that a fast or immediate response arises from open agglomeration and that a slow response arises from densification of aggregates. The fast response exists under low shear

rates and provides higher electronic conductivity and higher viscosity. The slow response emerges at high shear rates, resulting in lower hydrodynamic volume fraction, reduced viscosity, and also reduced electronic conductivity due to lesser available pathways. These observations have been verified by a model based on Krieger-Dougherty equation to capture the hydrodynamic volume and Potanin model to capture a relationship between agglomerate radius and fractal dimension.^[173]

In a recent study, the combined use of small angle neutron scattering (SANS), ultra-small angle neutron scattering (USANS), dynamic light scattering (DLS), oscillatory rheology, and impedance spectroscopy offers the most elaborate synergistic experimental effort to connect structural, mechanical, and electrical behavior of carbon black suspensions. The most significant finding of this study is that electron hopping is seen to be the dominant charge transport mechanism both below and above gel transitions rather than particle networks or stress bearing chains that are generally regarded as the reason for electronic conductivity. It is shown that gelation does not arise from strong attractive forces between primary aggregates, but rather, a clustered fluid phase is created that forms system-spanning particle network when further concentrated. The means through which shear impacts electronic conductivity is not by breaking up particle networks but rather by impacting cluster size that consequently affects the dominant hopping mechanism.^[59] This study clearly demonstrates how preconceived notions of the correlation between electronic conductivity and spatial arrangement of particles, as adopted from LiB field, led to the belief that particle networks are an important qualitative explanation of trends observed in SSRFBs. Such multipronged experimental studies are expected to provide groundbreaking discoveries of hidden mechanisms that govern electrochemical systems and may transform the black box of batteries into a system that can be tailored and optimized more effectively.

4. Conclusions

With the goal to adopt the best of both LiBs and RFBs, SSRFBs face a multidisciplinary and multiscale challenge. LiBs and particle suspensions are complex systems themselves and are only predictable under specific conditions that have been



Scheme 4. Classification of phenomena discussed in this review and suggestions on how to categorize their dynamics.

arrived at by empirical optimization. Therefore, the SSRFB is not only complex but also notoriously difficult to optimize and generalize for different material systems. This review provides a platform to connect knowledge scattered across disciplines based on the principles of complex systems. The objective is to generate a comprehensive understanding of SSRFBs to provide a collection of various aspects that need to be kept in mind for scientists who encounter non-intuitive results in experiments. Scheme 4 summarizes some of the relevant phenomena that exist at different scales and have been discussed in this review.

We believe that the behavior of a system is difficult to predict only when the understanding of its important parts is either poor or missing. Any system and the dynamics of its interacting parts can be described in terms of state descriptors. These descriptors can either be experimentally observable or unobservable. Both these types of parameters can possess varying degrees of quantification (Scheme 5 (a)). Through the

Parameters		
Measurement		Quantity Measured
Type	Quality	Dynamics & Evolution State Descriptors
Observable	Quantitative	
Unobservable	Qualitative	

Interphases relevant for SSRFBs		
Material	Scale	Discipline
Solid-Solid	Multiscale Ripples	Electrochemistry
Solid-Liquid	Many-body Problem	Fluid Dynamics Rheology Crystallography Mechanics

Scheme 5. a) Unifying classification of parameters that can be helpful to reduce complexity. b) Interphases of materials, disciplines, and scales that impact battery performance while simultaneously introducing complexity.

development of new experimental characterization tools, especially in-situ and in-operando measurements, more parameters can be experimentally measured. The rest of the experimentally unobservable parameters constitute the reason behind the complex nature of a system. These parameters can be implicitly inferred through hypothetical consideration of experimental evidence. This review explores how these important but often ignored unobservable parameters lie at the interphases of matter or in the gaps between disciplines (Scheme 5 (b)).

Such aspects that bring tremendous difficulties to experiments can remain invisible until scientists question the assumptions behind state of the art of fundamental knowledge. Evidently, SSRFBs offer an excellent study for complex system dynamics in the field of materials for energy storage. The creation of a single unified understanding of all phenomena in SSRFBs is urgent and can also help related disciplines such as LiBs, electro-rheology, and devices based on slurry electrodes.

This will not only provide context and verification for cross-disciplinary experimental data, it can greatly enhance accuracy for estimation of parameters that are difficult to measure experimentally. Even advanced modeling tools like machine learning typically need accurate, reproducible, and coherent data as a starting point. But as seen in this review, the required quality and quantity of data, is yet to be achieved for SSRFBs. Therefore, while human intuition based trial-and-error experimentation may be unavoidable for the near future, we hope that such efforts can help form more accurate assumptions, aid human intuition, and prevent appearance of conflicting observations, thereby accelerating system optimization.

Acknowledgements

The authors deeply acknowledge the Région Hauts de France and Fonds européen de développement régional (FEDER) for the financial support through the project "WONDERFUL". A. A. Franco gratefully acknowledges Institut Universitaire de France for support. Discussions at Laboratoire de Réactivité et Chimie des Solides with Dr. Charles Delacourt, Dr. Gregory Gachot, Emiliano Primo, Ulas Kudu, and Theodosios Famprikis for the schematic on complexity in lithium-ion batteries, are deeply appreciated.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: complex system · interphases · multidisciplinary · multiscale · semi solid redox flow battery

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Manuscript received: December 22, 2018

Revised manuscript received: March 27, 2019

Version of record online: April 24, 2019