

ABSTRACT

Title of Dissertation: INTERFACES IN THIN-FILM SOLID-STATE BATTERIES

Victoria Castagna Ferrari, Doctor of Philosophy,
2024

Dissertation directed by: Prof. Gary W. Rubloff, and Department of
Materials Science and Engineering

The lack of a diagnostics approach to monitor interface kinetics in solid-state batteries (SSBs) results in an incomplete knowledge of the mechanisms affecting device performance. In this study, a new protocol for process control of SSB interface formation and their evolution during operation is presented. Thin-film SSBs and diagnostic test devices that are composed by a permutation of isolated layers were simultaneously fabricated using sequential sputtering deposition and in-situ patterning using shadow masks. Physics-based electric circuit models were designed for deconvolution of impedance profiles, which enabled an evaluation of bulk properties and space-charge layers at interfaces individually and during operation under different states-of-charge. Relative permittivity values of fundamental battery components (cathode, electrolyte and anode) were calculated as a function of the frequency and the applied voltage. Interfacial impedances, as well as space-charge layers formed at heterojunctions during charge and discharge processes, were successfully deconvoluted using the diagnostic test devices and electric circuit modeling. The cathode-electrolyte interphase was kinetically stable under a

voltage window of 0 – 3.6 V vs Cu, and it had an estimated ionic conductivity of the order of 10^{-9} S/cm, hence it is a localized limiting factor for Li^+ transfer. The anode-electrolyte interphase was thermodynamically stable upon completion of the fabrication process, but it became kinetically unstable during charge and discharge cycles. Hence, the proposed diagnostics protocol enlightened the necessity of implementing interfacial engineering on these interphases in the future for improvement of cyclability and stability of SSBs and ionic devices.

INTERFACES IN THIN-FILM SOLID-STATE BATTERIES

by

Victoria Castagna Ferrari

Dissertation submitted to the Faculty of the Graduate School of the
University of Maryland, College Park, in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy
2024

Advisory Committee:

Professor Gary W. Rubloff, Chair

Professor Sang Bok Lee

Dr. David M. Stewart

Professor A. Alec Talin

Professor Chunsheng Wang

© Copyright by
Victoria Castagna Ferrari
2024

Dedication

To my beloved grandmothers, Iolanda and Belia

Acknowledgements

I would first like to thank Prof. Gary Rubloff for giving me the opportunity to work in the greatest research laboratory that has ever existed. His patience with me and his generosity in sharing his scientific perceptions allowed me to become a better scientist.

I also would like to thank Dr. David Stewart for the day-to-day mentoring since I have started my doctoral degree. He is a role model to me with respect to dealing with students with different backgrounds, and his knowledge in thin-film technology and energy storage systems is so vast that I am glad I could learn many different fundamental science questions from him. Our scientific discussions have resulted in incredible ideas for current and future projects, so I will always be thankful for those moments.

Thanks to the former ANSLab members (Prof. Alex Kozen, Dr. Zoey Warecki, Dr. Haotian Wang, Dr. Blake Nuwayhid, Dr. Kunal Ahuja, Sam Klueter) for being my lab buddies and for teaching me the practical skills needed to conduct my research in the laboratory. Thanks to the current colleagues in our research group for the innumerable scientific discussions and the good moments during happy hours and Fall Guys parties: Daniela Fontecha, Stefan Theodoru, John Hoerauf, Leo Tapia-Aracayo and Dr. Keith Gregorczyk.

Thanks to the FabLab staff, especially Dr. Nam Soo Kim and Jon Hummel, for training me on experimental tools that were essential for completion of my projects, and for the many discussions that we had about weird (or sometimes great) depositions.

Thanks to my collaborators from the Chemistry department at UMD that are part of Prof. Sang Bok Lee's research group, for the fruitful collaborations: Osma Gomez, Dr. Yang Wang and Dr Nam Soo Kim (once again).

Thanks to my external collaborators that have provided me with the ability to work on different projects: Dr. Alec Talin (Sandia National Laboratories), Prof. Chuan-Fu Lin (Catholic University of America – CUA), Binh Hoang (CUA), Roya Damirchelli (CUA), and Prof. Leonard Brillson (Ohio State University).

My doctoral work could not have been done without the support and love of my partner, Thiago Assumpção, who has been an inspiration to me as a scientist since the first day I met him back in 2011. I am very thankful for all of your care in these years and your ability to tell new jokes every time that I ask you about it. I would also like to thank the love of my family back in Brazil: my parents Rosana and Rene, and my sister Mariana.

Lastly, I would like to acknowledge my funding sources over the course of my doctoral degree. This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Grant DE-SC0021070. I also acknowledge the support of the Maryland NanoCenter and its FabLab, and the support from the UMD Graduate School through the Flagship Fellowship and the Ann G. Wylie Dissertation Fellowship.

Table of Contents

Dedication.....	ii
Acknowledgements.....	iii
Table of Contents.....	v
List of Figures.....	vii
Chapter 1: Introduction.....	1
1.1. Solid-State Batteries.....	1
1.1.1. Device Mechanism, Materials and Properties	1
1.1.2. Thin-Film Batteries.....	6
1.2. Complexity of Device Architectures and Performance	7
1.2.1. Planar Batteries	7
1.2.2. 3D Solid-State Batteries.....	8
1.3. Types of Interfaces in Solid-State Batteries.....	10
1.3.1. Thermodynamically Stable Interfaces	10
1.3.2. Kinetically Stable Interfaces	11
1.3.3. Kinetically Unstable Interfaces.....	12
1.4. Strategies for Stabilization of Interfaces.....	13
Chapter 2: The Multibattery Prototype.....	15
2.1. Consequences of Fabrication Process on Interface/Interphase Formation .	16
2.2. Summary of the Chapter	17
Chapter 3: Methodology: Electric Circuit Modeling of Solid-State Batteries.....	18
3.1. Fundamentals on Electrochemical Impedance Spectroscopy	18
3.2. A Physical Approach to Decouple Interfacial and Bulk Properties.....	23
3.2.1. Ambiguities Arising from Unrealistic Electric Circuit Models.....	23
3.2.2. Physics-Based Electric Circuit Model: the Huggins Approach.....	24
3.3. Summary of the Chapter	31
Chapter 4: Design of a Platform to Decouple Interfacial and Bulk Properties of a Thin-Film Solid-State Battery.....	33
4.1. The Concept of Diagnostic Test Devices.....	33
4.2. Prototype Fabrication Using Simple Materials.....	35
4.3. Properties of Interfaces and Interphases	37
4.4. Summary of the Chapter	39
Chapter 5: Electric Circuit Modeling Implementation on the Platform for Thin-Film Solid-State Battery Diagnostics	40
5.1. Full-Cell Electric Circuit Model Built from Component EIS Signatures...	41
5.1.1. Electrolyte-Only Diagnostic Test Device	41
5.1.2. Cathode-Only and Anode-Only Diagnostic Test Devices	44
5.1.3. Electrolyte-Cathode (Anode-Free) Diagnostic Device.....	47
5.1.4. Anode-Electrolyte (Cathode-Free) Diagnostic Device.....	51
5.2. Describing the EIS of the Thin-Film SSB Full Cell	53
5.2.1. Building an Electric Circuit Model for a Full Cell from Impedance Signatures of Diagnostic Devices	53
5.2.2. Cathode Interfaces During Cycling	56
5.2.3. Anode Interfaces During Cycling.....	57

5.3.	Performance of the Full Thin-Film SSB	59
5.4.	Prognosis.....	62
5.5.	Summary of the Chapter	65
Chapter 6: Conclusions and Perspectives		68
6.1.	Contributions to Scientific Publications During the Doctoral Degree.....	69
Appendix.....		72
	Error propagation of derived parameters from electric circuit modeling	72
Bibliography		75

List of Figures

Figure 1.1. Simplified schematics of a solid-state battery.	2
Figure 1.2. Planar versus 3D thin-film solid-state batteries. Reproduced from Pearse et al. ⁶⁸	9
Figure 2.1. Cross section of a representation of a multibattery, which leverages thin film processing to stack multiple layers of anode, electrolyte, and cathode in a manner which magnifies the energy storage for a given device footprint. Such batteries may be made in arbitrary shapes and intimately integrated into micro-electronics devices. The total number of battery layers depicted is small, but would scale depending on the desired performance. Reproduced from Ferrari et al. ⁹¹	15
Figure 2.2. A three-layer multibattery prototype. a) Top-view of 9 identical devices, fabricated by in-situ patterning of sputtering depositions; b) expected layered structure of a multibattery. Gold and copper served as the cathode and anode current collectors, respectively; c) cross-sectional SEM image of a multibattery.	16
Figure 3.1. An Illustration of Potentiostatic Electrochemical Impedance Spectroscopy technique.	20
Figure 3.2. An illustration of a Staircase Potentiostatic Electrochemical Impedance Spectroscopy.	20
Figure 3.3. Nyquist plots of a resistor and a capacitor under different associations.	22
Figure 3.4. Two different electric circuit models fitting the same SSB data.	23
Figure 3.5. Metal-Electrolyte-Metal electric circuit model based on physical properties of charge transport.	29
Figure 3.6. Metal-electrode-metal electric circuit model based on physical properties of charge transport.	31
Figure 4.1. Description of methodology used for impedance analysis.	34
Figure 4.2. New methodology for fabrication of thin-film SSBs and diagnostic test devices. Illustration of shadow masks used for in-situ patterning of devices, and an image of a real batch of devices. In this case, 16 SSBs and auxiliary devices were fabricated simultaneously in a 3-inch silicon wafer. Materials: Copper as anode current collector, amorphous silicon (a-Si) as anode, lithium phosphorus oxynitride (LiPON) as electrolyte, lithium vanadium oxide (LVO) as cathode, and aluminum as cathode current collector.	35
Figure 5.1. Impedance profile of LiPON-only device. a) Impedance spectrum of LiPON-only diagnostic test device at OCV with the representation of the electric circuit model for data analysis; b) LiPON ionic conductivity on different applied voltages; c) relative permittivity of LiPON on different frequencies at OCV; inset: Bode diagram of device at OCV, in which the blue line corresponds to the phase of the total impedance, and the black line is the log of the total impedance modulus; d) computed SCL width at the Electrolyte-Metal Interface (EMI) under different applied voltages calculated at the lowest frequency measurement (250 mHz).	42
Figure 5.2. Impedance profile of LVO-only and Si-only devices. a) Electric circuit model for the LVO-only test device and impedance spectrum at OCV. b) Impedance spectrum of Si-only diagnostic device at OCV and the electric circuit model that represents this device.	45

Figure 5.3. <i>Impedance profile of LVO-LiPON device.</i> Impedance spectra of LiPON-LVO diagnostic test device when a) increasing the voltage, and b) decreasing the voltage gradient; c) schematics of the device and the electrically modeled interfaces (and interphase). The values of circuit parameters in blue were taken from the LiPON-only device, and the same applies for circuit parameters in red, taken from the LVO-only device. Circuit parameters in orange are representing the CEI; d) cyclic voltammogram of LiPON-LVO device; e) LVO ionic conductivity and f) LVO electronic conductivity as a function of applied bias.	47
Figure 5.4. Interface kinetics of the LVO-LiPON diagnostic test device. Evolution of a) Cathode-Electrolyte Interphase (CEI) resistance; b) Space-Charge Layer (SCL) formed at the CEI; c) SCL at Electrolyte-Metal Interface (EMI); d) SCL at the Cathode-Metal Interface (CMI) of the LiPON-LVO diagnostic test device.	50
Figure 5.5. Impedance spectrum of Si-LiPON diagnostic device (green curve), and the electric circuit model that was built for data analysis. Values of the electric circuit parameters in green were extracted from the Si-only test device, and the blue ones were taken from the LiPON-only test device. The impedance data of LiPON-only device is shown in blue for visual comparison.	52
Figure 5.6. Electric circuit model and impedance profile of a full thin-film SSB. a) Description of the proposed electric circuit model for interpretation of the thin-film SSB impedance analysis; b) Impedance spectra of every auxiliary device at OCV, including the impedance profile of the SSB stack as-deposited; Impedance of the SSB after several galvanostatic charge/discharge cycles at 8C recorded at different biases during c) charge; and d) discharge half cycles. A discrepancy in the impedance curves at 3.6 V when applying the bias in reverse directions possibly occurred due to relaxation between the charge and discharge measurements.	54
Figure 5.7. SSB cathode interfaces after cycling. a) SCL at the LVO-Al interface; b) resistance of LVO-LiPON interphase; c) SCL at the LVO-LiPON interphase.	56
Figure 5.8. SSB anode interfaces after cycling. a) SCL at the Si-Cu interface; b) resistance of Si-LiPON interphase; c) SCL of Si-LiPON interphase.	57
Figure 5.9. Charge-discharge cycles of thin-film SSB and cross-sectional SEM images. a) Cyclic voltammogram of a thin-film SSB, right after deposition. Under the 2-electrode configuration, the copper contact was used both as reference and as a counter electrode. Increasing the total cell voltage refers to charging; b) discharge capacity under different constant current densities (so different C-rates) for 45 cycles in a fresh, yet uncycled SSB. Inset: capacity fading at fast charging/discharging for 500 cycles at 8.5 C (50 $\mu\text{A}/\text{cm}^2$) after cycling 45 times under variable C-rates; cross-sectional SEM images of the thin-film SSB atop the SiO_2 substrate c) before any electrochemical cycling; and d) after 545 cycles at 8.5 C at a charging state.	59
Figure 7.1. Electric circuit models for diagnostic devices and SSB.	68

Chapter 1: Introduction

1.1. Solid-State Batteries

1.1.1. Device Mechanism, Materials and Properties

Lithium-ion batteries (LIBs) enabled a technological revolution in portable devices, hybrid and electric vehicles, and smart devices. However, the majority of commercially available LIBs employ flammable liquid electrolytes, which increase the risk of excessive heating and possible internal short circuits.^{1,2} For this reason and more, solid-state batteries (SSBs) are anticipated as the next energy storage technology to replace present-day LIBs.³

Figure 1.1 presents a simplified description of the main components in a SSB. During a charging process, an external applied bias induces an electric field between the terminals of the battery. In this case, electrons located in the **cathode** layer will move to the **cathode current collector** (positive terminal) so the electronic current feeds the **anode current collector** (negative terminal) with electrons through the external wiring. At this point, the electrons are still under the electric field until they reach the **anode** layer. This net of negative charges simultaneously drives positive ionic species (lithium ions in the case of LIBs) from the cathode layer to the anode, passing through the **electrolyte** in between them to promote charge neutrality. During the discharging process, both positive ions and electrons will move on the reverse direction

due to an internal electric field driving these charges, so electricity can be provided for appliances as a DC current.

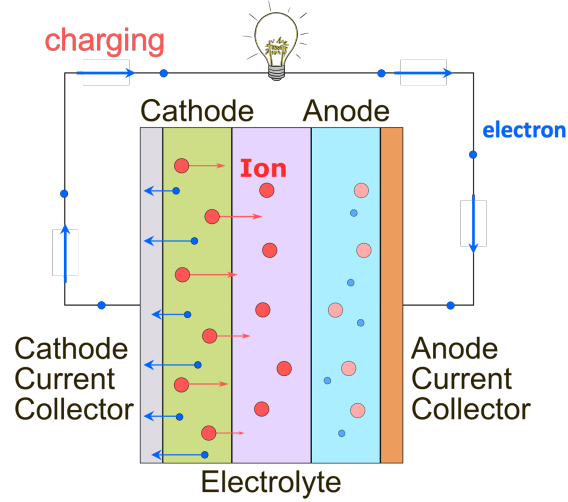


Figure 1.1. Simplified schematics of a solid-state battery.

The electrochemical reactions occurring inside the cathode and anode layers will determine the total amount of charges that can be stored in them. The **capacity (Q)** is then defined as the number of Coulombs that a cathode/anode can utilize for charge and discharge processes, in which its theoretical value is given by the following equation, normalized by the mass:

$$Q = \frac{nzF}{M} \quad (1.1)$$

Where n accounts for the number of active species participating in the electrochemical reaction, z corresponds to the charge of the active species (1 for Li^+), F represents the Faraday's constant ($\sim 96,500 \text{ C/mol}$) and M is the molar mass of the anode/cathode in g/mol . Frequently, the capacity is reported in units of mAh/g as a result of direct measurements of the time taken to fully charge/discharge a battery when a constant current is applied.

The total energy that a battery can provide is then calculated based on the capacity and the voltage during cell operation ($E = \Delta Q \cdot \Delta V$). Therefore, ways to optimize batteries^{4,5} to increase their energy are directly related to the **intrinsic properties of materials (Q) and their combination in a form of a device (ΔV)**. In this sense, there are many challenges⁶⁻⁸ in the design and operation of SSBs that can effectively make this technology suitable for a variety of applications.

The first challenge arises from the electrical properties of the SSB components. Current collectors should be excellent conductors while acting as ion-blocking materials to avoid side reactions that would consume active charges used in the charge/discharge processes. Usual choices are metals, in which noble ones are preferred, but are more expensive. Anode and cathode components are mixed conductors, in which different mechanisms of charge insertion/extraction may occur, such as intercalation, conversion or alloying reactions.

For materials where intercalation/deintercalation takes place, an imbalance of electronic and ionic conductivities may result in poor kinetics and decomposition of compounds, leading to smaller capacities and battery ageing.^{6,9-11} Transition-metal oxides with layered or spinel structures are commonly studied as possible materials to be used for intercalation of charges¹²⁻¹⁷ due to the ability of transition metal atoms to easily change their valence states. Materials that undergo alloying reactions usually have higher theoretical capacity values like silicon,¹⁸⁻²⁵ but they suffer from large volume expansions during cycling²⁶⁻²⁸, which can drastically compromise the battery operation. Materials where conversion reactions are expected to happen have been less studied than the other ones. Conversion electrodes suffer from the possibility of

emerging irreversible phase transformations that can lead to low diffusivities of active species, and a lack of reversibility and low capacities when cycling the SSBs.^{29–35}

Solid electrolytes, on the other hand, are expected to be ion-conducting dielectrics. This is, in fact, a great advantage of SSBs *versus* LIBs because the solid electrolyte, at the same time, act as a mechanical separator between the cathode and the anode, and sustains ionic conduction.³ However, the solid electrolytes developed so far that effectively prevent lithium dendrite growth have low ionic conductivities ($10^{-7} - 10^{-5}$ S/cm),^{29,36–39} and the ones that have achieved decent ionic conductivity values ($10^{-4} - 10^{-2}$ S/cm) suffer from available paths for electronic conduction in their structure and/or have presented low chemical and electrochemical stability against lithium metal, for example,^{13,40–44} which leads to the second challenge encountered in engineering SSBs.

The electrochemical compatibility of materials in a SSB is essential to ensure that the voltage window of the full device is maximized under safety conditions to avoid side reaction that might lead to internal short circuits. The cell voltage (V) of a SSB determines the voltage window of its operation, which can be defined as the electrochemical potential difference between the cathode and the anode:^{45,46}

$$V = - \frac{(\tilde{\mu}_{Li}^{cathode} - \tilde{\mu}_{Li}^{anode})}{nzF} \quad (1.2)$$

In which $\tilde{\mu}_{Li}$ corresponds to the electrochemical potential of lithium (in kJ/mol) in a certain material (whether a cathode or an anode), and it is a sum of the chemical potential (μ_{Li}) and the electrostatic potential of Li^+ (ϕ) within a material:

$$\tilde{\mu}_{Li} = \mu_{Li} + nzF\phi \quad (1.3)$$

And therefore equation (1.2) can be rewritten in terms of the open-circuit voltage (OCV),^{47,48} which is the chemical potential difference across the SSB, and the difference in electrostatic potential ($\Delta\phi$) due to the movement of Li^+ and electrons under an electric field:

$$V = -\frac{(\mu_{Li}^{cathode} - \mu_{Li}^{anode})}{nzF} - (\phi^{cathode} - \phi^{anode}) = OCV - \Delta\phi \quad (1.4)$$

The voltage window is usually determined by the stability of the chosen solid electrolyte in terms of the chemical potential values.^{2,45,49} The stability must, ideally, occur in both anode and cathode sides, so deciding which materials to be used together in a SSB is crucial. The cell voltage can be maximized by increasing the OCV, i.e., having a suitable cathode (anode) in which its chemical potential is high (low), and finding a solid electrolyte that will be stable within this range. In practice, many solid electrolytes are electrochemically stable either at low or high voltages, but not simultaneously on both, which can lead to their decomposition at the interface with the electrode.^{8,13}

Lastly, the multiscale ion transport in a SSB is negatively affected from a combination of charge transfer, microstructure, and interfaces, at different length scales. In particular, SSBs based on particulate materials have their performance compromised due to tortuosity effects^{50,51}, besides the need of using inactive materials. Uneven particle size distribution, dead-end pores, and inefficient ionic pathways all contribute to a decrease in cell capacity, since less charges will be participating in the

electrochemical reactions inside the electrodes.^{6,46} In addition, additives such as binders and carbon black particles add an extra mass to the SSB, decreasing the overall cell capacity.^{5-7,31,50}

Furthermore, many **interfaces** are created in different locations across the SSB as a consequence of the microstructure, in which the energy barriers to allow conduction of charges can vary depending on the choices of materials, electrochemical stabilities, morphology, and their electrical properties.^{13,46,47,49,52} In general, these interfaces may or may not significantly increase the impedance (and hence, ohmic losses) of SSBs.⁵² Therefore, it is crucial for material scientists and engineers to find strategies to stabilize those interfaces, and to reduce their total amount in a single device. Dense films, such as the ones in thin-film SSBs, eliminate the use of particulates, so less interfaces are present, besides several other advantages and applications that will be discussed further on.

1.1.2. Thin-Film Batteries

For certain applications in biomedical devices and electronics, thin-film SSBs are an important alternative, compatible with many well-established micro-fabrication processes for electronics integration. Borrowing techniques from the micro-electronics industry, important factors regarding scalability, processing cost, and flexibility in shape and size are generally applicable to thin-film SSBs⁵³⁻⁵⁵.

Among the benefits of using thin-film SSBs, the well-defined surface area obtained from physical vapor deposition (PVD) techniques allows excellent characterization of electrochemical and electrical properties for further development of

individual constituent layers^{54,56}. More practically, the diffusion lengths needed for electrons and lithium ions are smaller in thinner films and, according to the relationship between the charge transport length (L) and relaxation time (t)⁵², where D corresponds to the effective chemical diffusivity of a charge carrier at a specific material:

$$L \propto \sqrt{Dt} \quad (1.5)$$

the time taken to transfer charges in a thin-film SSB layer to another device component is reduced, which increases the power density of thin-film SSBs in comparison to particulate-based SSBs.^{2,4,57–59} Therefore, the design of advanced SSBs that can increase **both the power and energy densities** is essential to make such devices realistically and commercially competitive to the conventional lithium-ion batteries.^{40,60–65}

1.2. Complexity of Device Architectures and Performance

1.2.1. Planar Batteries

As indicated in **Figure 1.1**, the simplest way to arrange a thin-film SSB consists of a multilayered stack, where the battery's constituents are deposited on a substrate. Because of the simplified geometry of planar (2D) thin-film SSBs, different shapes are easily patterned by photolithography processes or by shadow masking^{59,66,67}, and calculation of important parameters such as conductivity are straightforward.

As it was previously mentioned, thin-film SSBs can achieve high power densities due to the smaller time that charges take to diffuse because of the dimension of the battery components. Usually, thin films for planar batteries range from the

nanometer to the micrometer scale. For the case of solid electrolytes, having smaller thicknesses is very beneficial for this transport of charges between the cathode and the anode. However, the use of thin cathode layers in a planar SSB leads to having a smaller amount of active material, which can reduce the capacity of the cell and, as a consequence, decreases the total energy density.

Planar thin-film SSBs then require the deposition of thicker cathode layers, which is a problematic factor in terms of production time and cost. For instance, the deposition of oxide materials from PVD techniques, such as sputtering deposition, or by Atomic Layer Deposition (ALD) can be very expensive due to the required technology, and their fabrication may take several hours for completion. An alternative way to improve both power and energy densities in a SSB is to lay on the development of 3D battery architectures, which will be presented in the next section.

1.2.2. 3D Solid-State Batteries

The ANSLab (ALD Nanostructures Laboratory at the University of Maryland) has devoted a significant effort in recent years to elaborate new architectures that can overcome those SSB challenges. The concept of creating 3D thin-film SSBs relies on increasing the internal surface area at the same footprint that a planar thin-film battery might have. Pearse *et al*^{66,68} have previously demonstrated that the use of fabrication methods that produce highly-conformal thin films, such as ALD and Chemical Vapor Deposition (CVD), combined with high-precise etching steps, can form 3D structures like nanopores and micropores filled with thin-film SSBs, like the ones showed in **Figure 1.2**.

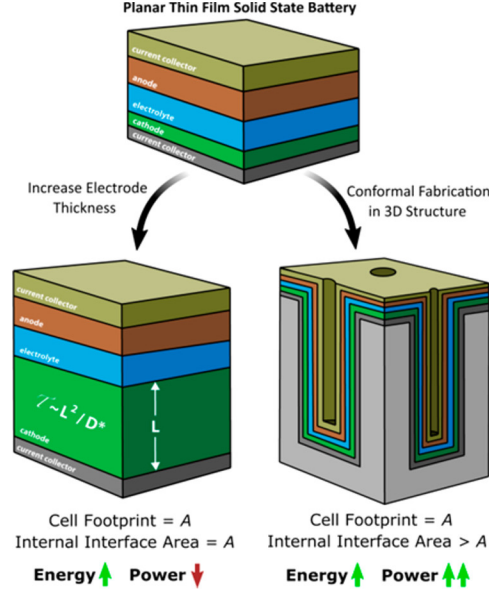


Figure 1.2. Planar versus 3D thin-film solid-state batteries. Reproduced from Pearse *et al.*⁶⁸

The drawback of having to compromise the power density in a planar SSB by increasing the cathode thickness to maintain a high energy density does not exist in this 3D battery configuration. In fact, more power is expected to be delivered since SSBs can be fabricated having $\sim$ hundreds of nanometers in total length.

While different 3D architectures can be implemented to fabricate SSBs, most of the reports are focusing on the use of micromachining methods and etching for creation of holes and trenches that will end up forming a 3D substrate.^{69–76} Then, pores with uniform dimensions are filled in with battery components, so that the capacity of the device can be tuned according to the geometry of the pores, having more or less material to be deposited relative to their length and diameter, and by the electrical connection of multiple pores sharing the same substrate.^{77,78}

Hence, to maximize energy and power density, thin electrode-electrolyte-electrode layers should be configured to maximize the surface area, and so the interfaces become the dominant part of the system. The biggest issue arising in the

design of the 3D batteries that were aforementioned relies on the complexity of such interfaces that will be formed. Due to the geometry of the 3D SSBs, non-uniform electric field lines are expected, so the charge transport involves some complications. For instance, those interfaces may suffer from electrochemical degradation, and they might act as energy barriers for charge transfer. Therefore, it is important to distinguish the processes occurring at interfaces from those involving the bulk of the components, and the effect of each individual interface on the overall electrochemical performance of a thin-film SSB.

1.3.Types of Interfaces in Solid-State Batteries

There are many reports in the literature describing the importance of investigating the role of interfaces in SSBs.^{49,64,79–86} It is important to note, however, that most of the published reports have focused on studying electrode/electrolyte interfaces, while little attention has been given to current collector/electrode interfaces, even though insulating thin layers can be formed at their interfaces and could affect the electronic charge transfer.⁸⁷ The interfaces are commonly divided into three categories, according to their electrochemical stability:^{49,81,88,89}

1.3.1. Thermodynamically Stable Interfaces

When there are no driving forces for reactions at an interface in a SSB, this heterojunction is intrinsically, thermodynamically stable. This is the ideal type of interface, in which low or negligible impedances are expected due to the

electrochemical compatibility of the materials while maintaining constant interfacial contact.

There are few examples in the literature showing electrode/electrolyte interfaces that are considered to be thermodynamically stable. For instance, a first principles study conducted by Zhu *et al*⁸⁸ indicated that solid oxide electrolytes upon contact with lithium cobalt oxide (LCO), one of the most studied cathode materials in SSBs, have a minimum interfacial reaction energy, indicating their thermodynamic equilibrium. However, an electrochemical stability could not be maintained at high cell voltages, where side reactions would take place. For the case of lithium lanthanum zirconium oxide (LLZO) and lithium aluminum titanium phosphate (LATP) contacting LCO, side reactions above 4 V *vs* Li/Li⁺ are expected to happen and will decompose the electrolytes at the interface, resulting in undesirable phases that are electronically conducting. However, the same study has shown that other oxides such as lithium phosphorus oxynitride (LiPON) are expected to form stable, electronically-insulating interfaces with LCO at above 4 V *vs* Li/Li⁺. Hence, it is almost inevitable to form thermodynamically unstable interfaces in SSBs, but their kinetic stabilization may vary according to the choice of electrode/electrolyte materials.

1.3.2. Kinetically Stable Interfaces

When the chemistry of an interface diverges from the present phases in the materials that are in direct contact at the heterojunction, the interface can then be described as an **interphase** arising from the kinetics of species. Decomposition of materials under electrochemical cycling, as well as intermixing of charges during

deposition or after annealing processes can create interphases in SSBs.^{49,81,88} Usually, those interphases will result in an increase in local impedance (in comparison to thermodynamically stable interfaces) and measurable space-charge layers (SCL) due to charge accumulation/charge depletion.⁸⁹

When a SSB is charged/discharged, its interphase is considered to be kinetically stable if the conductivity remains fairly constant on the full range of the applied voltage window.⁸⁹ Since the conductivity of an interphase can be related to its impedance and SCL, those are two very important parameters that can be experimentally measured and analyzed to provide good diagnostics of the nature of the interface.

With respect to its electric properties, a kinetically stable electrode/electrolyte interface in a SSB should be *ion-conducting, electronically insulating* for optimization of charge transfer. In addition, kinetically stable interfaces are expected to have a different phase, but no sign of chemical decomposition should be observed upon cycling.

1.3.3. Kinetically Unstable Interfaces

On the other hand, the electric conductivity of an electrode/electrolyte interface that varies according to the applied voltage is a characteristic of a non-passivating, kinetically unstable interphase, which should be avoided in SSBs⁸¹. In general, this interphase is a mixed conductor, meaning that ionic and electronic conductivities have comparable values. Since the electronic mobility is significant, side reactions are favorable to occur, leading to a decrease in the number of available charges for battery operation and electrochemical decomposition of active materials in a SSB. In a long

term, capacity fading can be observed with further cycling due to the evolution of the unstable interphase, leading to a fast device degradation.

1.4.Strategies for Stabilization of Interfaces

Kinetically unstable interfaces can lead to local impedances as high as $\text{k}\Omega\cdot\text{cm}^2$ during cycling, and sometimes choosing materials that have electrochemical compatibility to form kinetically stable interfaces is not an option in terms of device performance due to low ionic conductivity and capacity values of battery components. Protective layers that are deposited between the electrode and the electrolyte act as *artificial interfaces* that could provide the desired electric properties and electrochemical compatibility in SSBs, and many different options in terms of materials are being used as a way to stabilize the interface.

ALD aluminum oxide (Al_2O_3) as thin as 14 nm has been used as a protective layer of Li metal pellets due to its ability to mitigate corrosion reactions with atmosphere and with liquid electrolytes containing sulfur species in a coin cell.²³ A reaction takes place when aluminum oxide is in contact with Li metal, creating a stable, uniform and pinhole-free ion-conducting $\text{Li}_x\text{Al}_2\text{O}_3$ alloy that still allows the electrochemical reactions of the battery to happen.

LiPON has been employed as an artificial interface for kinetic stabilization of conversion reaction electrodes and liquid electrolytes. 3D ruthenium oxide (RuO_2) electrodes coated with 18 nm of LiPON showed a decrease in total impedance in comparison to uncoated electrodes, besides a remarkable capacity retention.²⁹ Composite iron oxyfluoride (FeOF) electrodes coated with LiPON also showed an

extended capacity retention through the battery cycle lifetime due to the suppression of formation of an undesirable, irreversible phase.³⁰

Organic compounds have demonstrated as well their effective use as protective layers. 1,3-dioxolane, in combination with LiPON, created a hybrid artificial interface between Li metal and liquid electrolyte that suppressed the dendrite formation.²⁵ Recently, the same organic compound has showed that can stabilize the contact between Li metal and $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS) pellets with an extension of the capacity retention in comparison to the unprotected Li/electrolyte interphase.⁴¹

These were examples of strategies that can be employed to stabilize the electrode/electrolyte interface, which have demonstrated the importance of studying interfaces in LIBs. For the case of thin-film SSBs, in particular, the length of the existing interfaces is comparable to the thickness of battery constituents and, therefore, the need of investigating their electrical, structural and chemical properties by coupling different characterization techniques is essential for optimization of charge-transfer mechanisms.

When Prof. Herbert Kroemer said in his Nobel lecture that “*the interface is the device*”,⁹⁰ he was referring to heterostructures built from two different semiconductors that enabled a revolution in microelectronics. The same statement can then be used to denote thin-film SSBs, where the role of interfaces dictates the performance of the device. This key lecture and the challenges encountered in materials science and engineering to design innovative and efficient SSBs served as motivation to conduct a dissertation on **fundamental science aspects of interfaces in thin-film SSBs**.

Chapter 2: The Multibattery Prototype

For instance, another interesting 3D architecture that exemplifies how pivotal the role of interfaces is for the operation of thin-film electrochemical devices is called the “multibattery” system. As indicated in **Figure 2.1**, it consists of stacking multiple planar thin-film batteries with an appropriate electrical connection between them to maximize their energy and power density.^{91,92}

In this case, the cathode can be as thin as the other battery constituents, then promoting fast transport of charges, without compromising the total energy density because multiple batteries will contribute to the final energy to be delivered. Series connections of individual planar batteries can improve the energy density of the device by increasing its total voltage; a parallel connection between 2D batteries increases the total generated current (so a capacity can be maximized), also effectively improving both the power and energy density values.

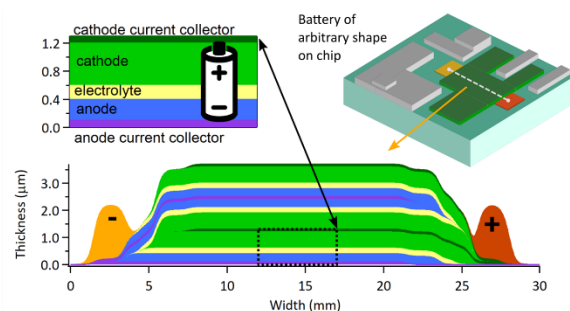


Figure 2.1. Cross section of a representation of a multibattery, which leverages thin film processing to stack multiple layers of anode, electrolyte, and cathode in a manner which magnifies the energy storage for a given device footprint. Such batteries may be made in arbitrary shapes and intimately integrated into micro-electronics devices. The total number of battery layers depicted is small, but would scale depending on the desired performance. Reproduced from Ferrari *et al.*⁹¹

2.1. Consequences of Fabrication Process on Interface/Interphase Formation

A three-layer multibattery, as depicted in **Figure 2.1**, was manufactured using a PVD process (sputtering deposition) that involved sequential steps of *in-situ* patterning to establish a parallel connection between the individual battery stacks. This prototype was fabricated to evaluate its performance *versus* a single planar SSB using the same battery constituents. However, problems encountered after completion of the fabrication process have served as a motivation to investigate the nature of the different interfaces existing in the device.

Figure 2.2-a shows a real picture of a silicon substrate sharing nine identical multibattery prototypes. Regions at every multibattery showed severe delamination after annealing at 300 °C, which has compromised the quality and the operation of the multibatteries. While the expected layered structure of final devices should correspond to the schematics from **Figure 2.2-b**, cross-sectional images taken using Scanning Electron Microscopy (SEM) revealed different problems occurring at interfaces.

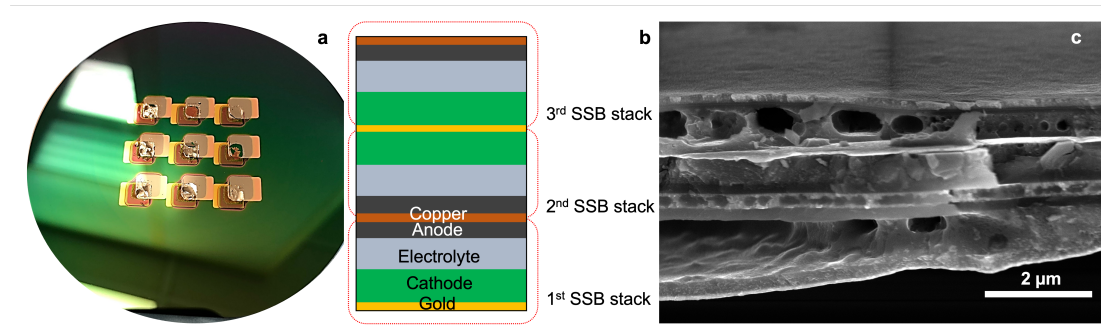


Figure 2.2. A three-layer multibattery prototype. a) Top-view of 9 identical devices, fabricated by *in-situ* patterning of sputtering depositions; b) expected layered structure of a multibattery. Gold and copper served as the cathode and anode current collectors, respectively; c) cross-sectional SEM image of a multibattery.

Figure 2.2-c showed that voids were formed inside the cathode layer, and they eventually reached large sizes that may have induced a contact loss between the cathode

and the electrolyte. It is unclear if those voids were established after a thermal stress from the post-annealing step or if there was a gas evolution at the cathode-electrolyte interface during the deposition. In addition, there was no distinction between the anode and copper layers, indicating an occurrence of an undesirable intermixing. Lastly, both the electrolyte and the anode layers had an unexpected decrease in the growth rate after completion of the first SSB stack deposition, which suggested that the parameters of these depositions were not fully optimized.

2.2. Summary of the Chapter

Although it was impractical to evaluate the performance of the multibattery prototype, this case study highlighted that “*the interface is the device*”⁹⁰ in many different ways. The compatibility of the materials at the heterojunctions, and the optimization of the fabrication process are fundamental aspects that have to be extensively investigated for the integration of advanced 3D SSB architectures with other micro-electronic devices.

Interfaces in a thin-film SSB must be studied after their fabrication and also during battery operation. Important information regarding the chemical compatibility of battery materials, with evaluation of properties of interfaces, can be extracted by pre-cycle analysis. The combination of multiple experimental techniques *in operando* can reveal the kinetics of those interfaces. The next two chapters will then present a novel approach to investigate the formation of interfaces in a thin-film SSB and their evolution upon cycling using a well-known experimental technique coupled with a unique fabrication strategy.

Chapter 3: Methodology: Electric Circuit Modeling of Solid-State Batteries

Many elaborated techniques have been implemented for in-situ characterization of heterostructures present in SSBs, like cryo-STEM (Scanning Transmission Electron Microscopy) combined with EELS (Electron Energy Loss Spectroscopy), which can provide important visualization of the systems, but may not entirely preserve the nature of interfaces due to ion-beam damage and the nature of the free surfaces produced by cross sectioning.^{93,94} KPFM (Kelvin Probe Force Microscopy) measurement has been emerging as a powerful technique that can describe local potential differences across interfaces,⁹⁵ but there is still an incomplete understanding of the quantitative analysis, and the sample preparation using FIB may still interfere on the chemistry and local distribution of charges at the exposed surface.⁸⁵

A simpler, non-destructive, characterization technique that has been used to describe reactions and materials properties in battery systems is Electrochemical Impedance Spectroscopy (EIS),^{96,97} which can be implemented in a dynamic mode for evaluation of electrical responses of a device at different states-of-charge.^{97–103}

3.1. Fundamentals on Electrochemical Impedance Spectroscopy

The response of any electrical system to a sinusoidal input signal (either voltage or current) is represented by its impedance (Z), which can be expressed in terms of magnitude and phase angle:

$$Z = |Z|e^{j\phi} \quad (3.1)$$

Where the magnitude of Z corresponds to the ratio between the voltage and current magnitudes, and ϕ is the phase shift between the voltage and current signals. The impedance is also commonly represented as a complex number for better visualization in a 2D representation such that:

$$Z = Z' + jZ'' \quad (3.2)$$

$$|Z| = \sqrt{Z'^2 + Z''^2} \quad (3.3)$$

$$\phi = \tan^{-1} \left(\frac{Z''}{Z'} \right) \quad (3.4)$$

In real electrochemical systems, like batteries, electrical contacts at the current collectors can be used to measure the total impedance of the device, which is a combination of impedances from its bulk constituents and impedances at interfaces. Since this is a type of device that multiple electrochemical reactions and charge transfer are occurring simultaneously at different locations, and depend on the charge transport properties of individual components, its total impedance is expected to vary under different frequency regimes. The evaluation of how an electrochemical system (and its equivalent impedance) responds to a sinusoidal signal that oscillates under different frequencies is called **Electrochemical Impedance Spectroscopy (EIS)**.

One of the ways to evaluate the response of an electrochemical system consists of applying a sinusoidal voltage perturbation and measuring its impedance at OCV, in

which the input signal will vary its frequency in orders of magnitude (ranging from mHz to MHz). This experiment is then called Potentiostatic EIS, illustrated in **Figure 3.1**, which will be the main experimental technique employed in this dissertation.

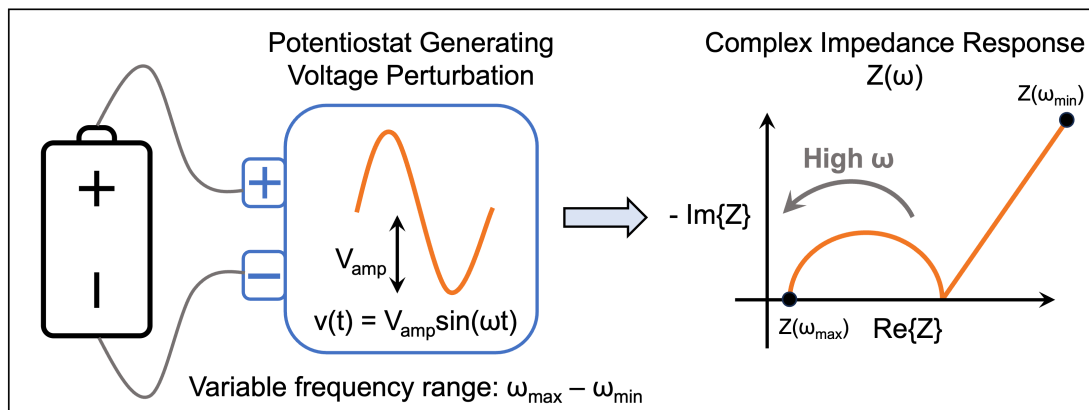


Figure 3.1. An Illustration of Potentiostatic Electrochemical Impedance Spectroscopy technique.

Evaluation of impedance profiles in electrochemical devices can also reveal important information regarding charge kinetics, cell degradation and electrochemical reactions. A more complex experimental technique, called **Staircase Potentiostatic Electrochemical Impedance Spectroscopy** (SPEIS), allows the analysis of impedance evolution under a desired voltage window, i.e., as a function of state-of-charge, as illustrated by **Figure 3.2**.

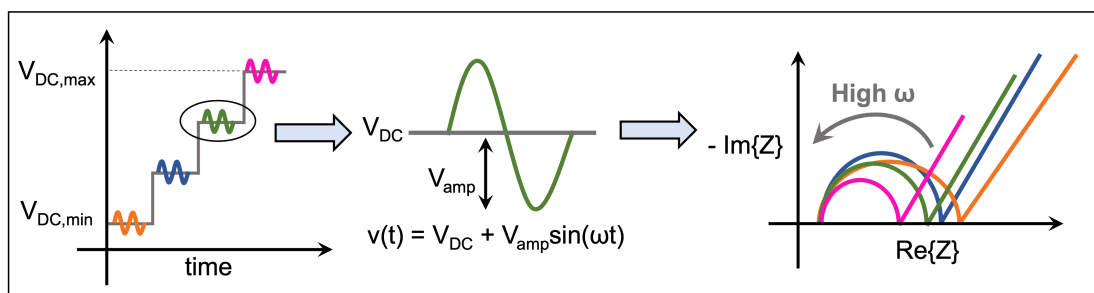


Figure 3.2. An illustration of a Staircase Potentiostatic Electrochemical Impedance Spectroscopy.

In the SPEIS technique, a voltage perturbation is generated by a potentiostat under a certain DC voltage to acquire an impedance spectrum. The number of voltage

steps that are chosen to analyze a certain electrical response of a device equals to the number of impedance spectra generated by completion of the experiment.

For most of the studied electrochemical devices, their total impedances have negative imaginary components, which is characteristic of energy storage electric components like a capacitor. Therefore, it is usual to display the impedance response using a Nyquist plot, as it is shown in **Figure 3.1** and **Figure 3.2**, and build electric circuit models using elements like resistors and capacitors for interpretation of the data.

Depending on the electric circuit element, Z might or not be frequency-dependent. Electrical resistances, for example, are purely real, while capacitors and inductors are purely imaginary impedances that are frequency-dependent. When they are combined in an electric circuit arrangement, the total (or equivalent) impedance will have both real and imaginary parts that will reflect their association in series and/or in parallel. **Figure 3.3** illustrates the impedance profile of a resistor and a capacitor, both in series and in parallel, as a practical example of expected behaviors of these arrangements as a function of frequency.

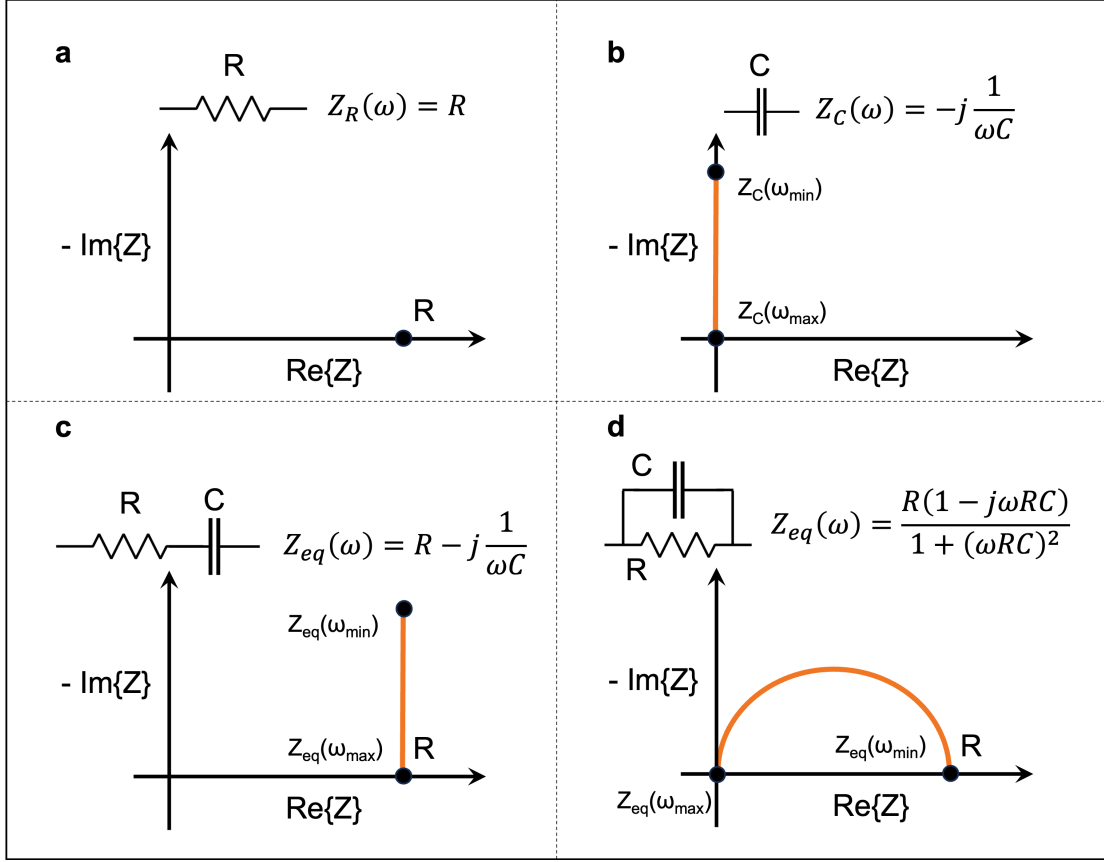


Figure 3.3. Nyquist plots of a resistor and a capacitor under different associations.

Physical phenomena that happen inside an electrochemical device such a battery, like charge accumulation, charge transfer and diffusion of active species can be represented by resistors and capacitors in series and in parallel associations. Hence, fitting an acquired impedance spectra using an electric circuit model could be used to extract information about the materials properties and charge kinetics at interfaces from the numerical values of the implemented electric circuit parameters.

3.2.A Physical Approach to Decouple Interfacial and Bulk Properties

3.2.1. Ambiguities Arising from Unrealistic Electric Circuit Models

The biggest challenge in using PEIS and SPEIS for characterization of electrochemical devices comes from the fact that multilayered structures like SSBs have an entanglement of different physical and chemical reactions occurring simultaneously. Hence, ambiguities may arise from a naive or unrealistic interpretation of electric circuit models for description of a battery upon cycling.^{104,105}

For instance, an impedance diagram of a real SSB was fitted using two distinct electric circuit models, showed in **Figure 3.4**. Constant Phase Elements (CPEs) were used in the models instead of capacitors to accommodate the possible inhomogeneities of materials' fabrication, porosity, and roughness of solid-solid interfaces that are commonly described in SSBs.¹⁰⁶

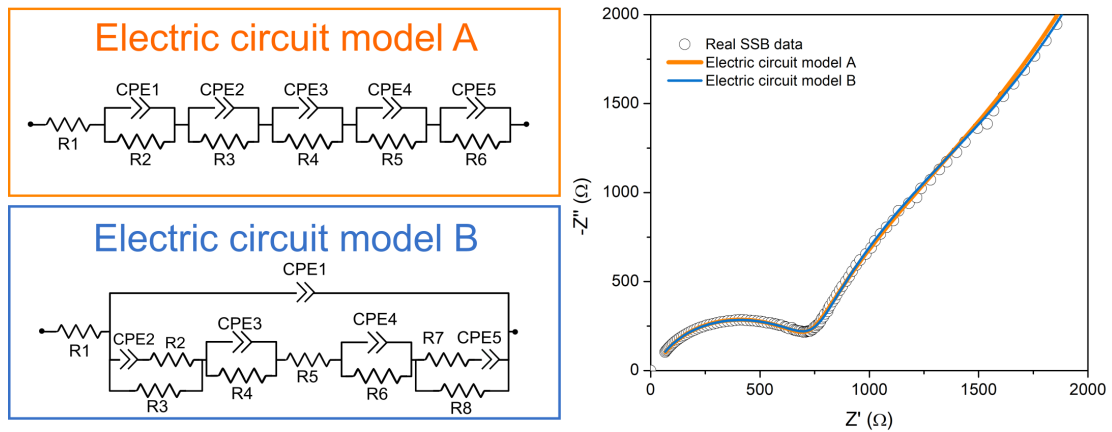


Figure 3.4. Two different electric circuit models fitting the same SSB data.

Both electric circuits provide a satisfactory fitting, exemplifying that there are multiple (and in fact, infinite) ways to model an equivalent impedance. However, the numerical values of the electric circuit parameters will be substantially different in different models and, sometimes, may not represent accurate properties of bulk

materials and interfaces. The *Electric Circuit Model A* from **Figure 3.4** fits the SSB impedance data by a series association of individual resistor-CPE elements in parallel. These five parallel lines are identical on their construction of the circuit; hence, although they may represent different parts of a SSB (cathode; cathode-electrolyte interface; electrolyte; electrolyte-anode interface; anode layers), it is very difficult to ascribe the circuit elements with charge transport mechanisms at different layers (and length scales) inside a battery. The *Electric Circuit Model B* from **Figure 3.4** has distinct associations of electric circuit parameters and, indeed, it was built using a physics-based interpretation that will be summarized in the following section.

3.2.2. Physics-Based Electric Circuit Model: the Huggins Approach

Each battery component can be associated with electric circuit parameters based on their physical properties.¹⁰⁷ Three general assumptions were made for the purpose of electric circuit modeling of thin-film battery materials: i) the current collectors are electronic conducting and ion-blocking; ii) both the cathode and the anode are mixed conductors, while the electrolyte is assumed to be electronically insulating and ion conducting; and iii) all the active layers (cathode, electrolyte and anode) are amorphous. The absence of grain boundaries simplifies the system, so it was a scientific choice to start building electric circuit models using materials with less complexity in their morphology for a first validation of the model.

The motion of charges inside each battery element is represented by a resistor (R). In particular, the electron transport inside the external wires and the thin film metal contacts is combined and represented by R_{wiring} . Extra electrical parameters need to be

added to include the effect of charge storage between the two metal contacts, i.e., the bulk capacity of the layer(s) to be studied, and also the space-charge regions that exist at interfaces upon contact of different materials. CPEs will be used to represent these bulk and interfacial charge storage mechanisms. The impedance of a CPE is described by the following equation:

$$Z_{CPE}(\omega) = \frac{1}{(j\omega)^a Q} = \frac{\cos\left(\frac{\pi}{2}a\right)}{\omega^a Q} - j \frac{\sin\left(\frac{\pi}{2}a\right)}{\omega^a Q} \quad (3.5)$$

Where ω is the angular frequency (rad/s), Q has units of F/s^{1-a} , and a is unitless. From equation (3.5), the impedance of a CPE has both real and imaginary parts that are frequency-dependent, such that:

$$Re\{Z_{CPE}\} = Z' = \frac{\cos\left(\frac{\pi}{2}a\right)}{\omega^a Q} \quad (3.6)$$

$$Im\{Z_{CPE}\} = Z'' = -\frac{\sin\left(\frac{\pi}{2}a\right)}{\omega^a Q} \quad (3.7)$$

And the magnitude of the impedance can be calculated as well:

$$|Z_{CPE}| = \sqrt{Z'^2 + Z''^2} = \frac{1}{\omega^a Q} \quad (3.8)$$

In practice, a ranges from 0.5 (ideal diffusion mechanism¹⁰⁸) to 1 (ideal capacitor behavior). While Q has similarities with a capacitance (C), they are not equal.¹⁰⁹ Nevertheless, it is possible to calculate a corresponding capacitance of a CPE from the impedance equation for a capacitor:

$$C = \frac{1}{j\omega Z} = -j \frac{1}{\omega Z} \quad (3.9)$$

And therefore:

$$C_{CPE}(\omega) = -j \frac{1}{\omega Z_{CPE}} = C'(\omega) + jC''(\omega) \quad (3.10)$$

Hence, when modeling materials that require the use of a CPE, its equivalent capacitance is a complex number with both real and imaginary parts.¹¹⁰ Equation (3.10) can be further derived in terms of Z_{CPE} to calculate the real and imaginary parts of its capacitance using equations (3.6), (3.7) and (3.8):

$$C'(\omega) = -\frac{1}{\omega} \frac{Z''}{|Z|^2} = \frac{Q}{\omega^{1-a}} \sin\left(\frac{\pi}{2}a\right) \quad (3.11)$$

$$C''(\omega) = -\frac{1}{\omega} \frac{Z'}{|Z|^2} = -\frac{Q}{\omega^{1-a}} \cos\left(\frac{\pi}{2}a\right) \quad (3.12)$$

Therefore, C is directly proportional to Q , and equations (3.11) and (3.12) also show the relation between the capacitance and the frequency.

The bulk capacitance of a layer is directly related to the geometry of the device, and it is delimited by the thickness of the material (d), active area (A), vacuum permittivity (ϵ_0) and its relative permittivity (ϵ_r) for the case of a parallel-plate capacitor, according to equation (3.13):

$$C_{Bulk}(\omega) = \frac{\epsilon_r \epsilon_0 A}{d} \Rightarrow \epsilon_r = \left(\frac{d}{\epsilon_0 A} \right) C_{Bulk}(\omega) = \epsilon'_r(\omega) + j\epsilon''_r(\omega) \quad (3.13)$$

Where ϵ_r has a frequency dependence due to the nature of the complex capacitance, which can be computed using equations (3.11), (3.12) and (3.13):

$$\epsilon'_r(\omega) = \left(\frac{d}{\epsilon_0 A} \right) C'_{Bulk}(\omega) = \left(\frac{d}{\epsilon_0 A} \right) \frac{Q}{\omega^{1-a}} \sin\left(\frac{\pi}{2}a\right) \quad (3.14)$$

$$\epsilon''_r(\omega) = \left(\frac{d}{\epsilon_0 A} \right) C''_{Bulk}(\omega) = -\left(\frac{d}{\epsilon_0 A} \right) \frac{Q}{\omega^{1-a}} \cos\left(\frac{\pi}{2}a\right) \quad (3.15)$$

From the real and imaginary components of the relative permittivity complex number, the real part, indicated by equation (3.14), corresponds to the dielectric function, while the ratio between the imaginary part and the real part is called the dielectric loss.^{111,112} The dielectric function decreases at high frequencies because of the reduced space-charge polarization effect. The dielectric loss is directly related to the electromagnetic energy loss due to the nature of the material in the presence of an applied electrical field.¹¹³

At interfaces (and interphases), charges can be accumulated or depleted according to the applied bias. CPEs are implemented to model this charge dynamics at different heterojunctions in a thin-film device, and the width of these created space-charge layers (d_{SCL}) can be derived from equation (3.14):

$$d_{SCL} = \frac{\epsilon'_r(\omega) \epsilon_0 A}{C'_{interface}(\omega)} \quad (3.16)$$

Like the relative permittivity and the capacitance, d_{SCL} is mathematically frequency-dependent. In practice, accumulation of charges and depletion of them will

be studied at minimum frequencies for evaluation of the effect of SCL during charge-transfer reactions.

Using a physical interpretation of charge transport at different materials and interfaces, as well as at different frequency domains, electric circuit models can be built for two fundamental electrochemical devices: *a) a metal-electrolyte-metal device*; and *b) a metal-electrode-metal device*, where the electrode is either the cathode or the anode. Specifications of these two basic models will be described below, which can be associated in a full battery electric circuit model.

a) Metal-electrolyte-metal device: electric circuit model

Charge dynamics can be predicted in this metal-electrolyte-metal system according to the diffusivity of ionic species (like Li^+) in two different regimes: bulk domain and interfacial domain. When the frequencies of the input sinusoidal voltage from PEIS are large enough, less time is given for Li^+ to diffuse inside the electrolyte, and they tend to get localized, which contributes to bulk polarization. In this case (bulk domain), accumulation of ion charges at the Electrolyte-Metal Interfaces (EMIs) is very small or nonexistent. When the frequencies are small (interfacial domain), Li^+ are diffusing according to the applied electric field, with no significant bulk polarization while the charge polarization happens mainly at the EMIs.

As it was previously mentioned in this section, CPEs can be used to model both the bulk polarization and the local accumulation of charges at the interfaces with metal layers. Denoting $\text{CPE}_{\text{electrolyte}}$ and $\text{CPE}_{\text{interface}}$ as the electrical parameters that will model the bulk and interfacial charge polarization, these CPEs will have different behaviors under different frequency ranges, which can be represented by their association in

parallel. $R_{\text{electrolyte}}$, i.e., the electrolyte resistance of Li^+ , should have a series association with $\text{CPE}_{\text{interface}}$ because these two processes (diffusion and charge accumulation/depletion at EMIs) occur in a sequential progression at lower frequencies. **Figure 3.5** illustrates the complete electric circuit modelling for the Al/LiPON/Cu device derived from the physical considerations and aforementioned approximations.

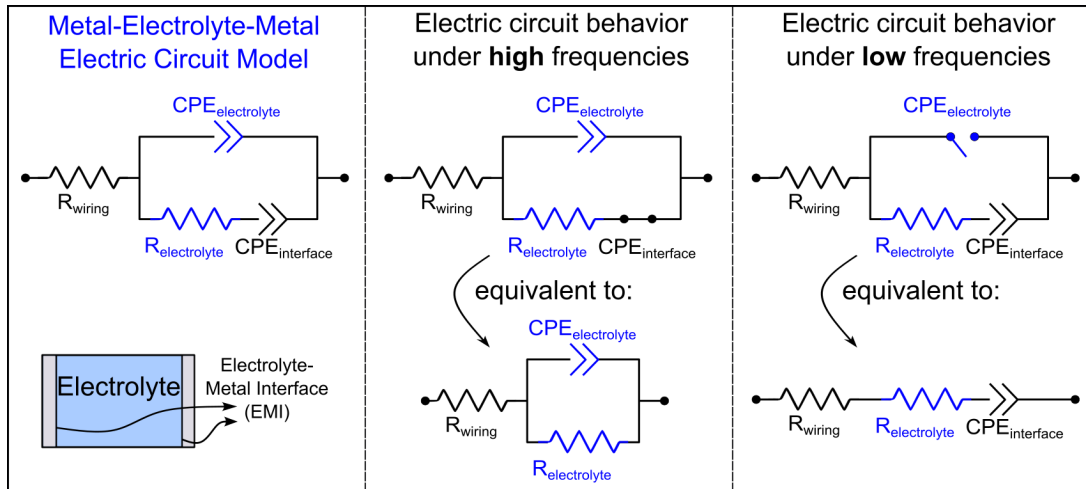


Figure 3.5. Metal-Electrolyte-Metal electric circuit model based on physical properties of charge transport.

Therefore, at lower frequencies, the series association of resistances and $\text{CPE}_{\text{interface}}$ results in a “diffusion tail” in a Nyquist plot, which should be a straight line parallel to the y-axis if such interface could be modeled as an ideal capacitor. For CPEs with a smaller than 1, that diffusion tail will have an angle with respect to the x-axis that arises from the frequency-dependent real impedance showed in equation (3.6). At high frequencies, the parallel $R_{\text{electrolyte}}/\text{CPE}_{\text{electrolyte}}$ association will result in a depressed semicircle shape in a Nyquist plot (which eccentricity depends on factor a). That arc, at extremely elevated frequencies, would intercept zero at the x-axis, but the

presence of a finite resistance due to the wiring (R_{wiring}) shifts the arc to this resistance value.

b) Metal-electrode-metal device: electric circuit model

The conduction of electrons in the anode and in the cathode should be comparable to the conduction of Li^+ in them. Therefore, the electric circuit model of a metal-electrode-metal device should include an extra resistor ($R_{\text{electronic}}$) in the electric circuit shown in **Figure 3.5** to properly model the electric pathway for electronic conduction. Since electrons and Li^+ will be flowing in opposite directions, $R_{\text{electronic}}$ is connected in parallel to the resistor that models the ionic conduction inside an electrode (R_{ionic}).

Although Li^+ will still be blocked at interfaces due to the ion-blocking nature of the chosen metals to serve as current collectors, electrons will be allowed to be transferred from the electrode to the metal layer and vice-versa, according to the direction of the generated electric field. Hence, it is expected that electrons will not be able to reach the electrode-metal interface at high frequencies, and less accumulation of charges might happen at this interface under lower frequencies since there is an electronic charge transfer. The electric circuit model from **Figure 3.6** considers all of these physical processes with respect to conduction of ions and electrons inside an electrode, and the electronic charge transfer at interfaces.

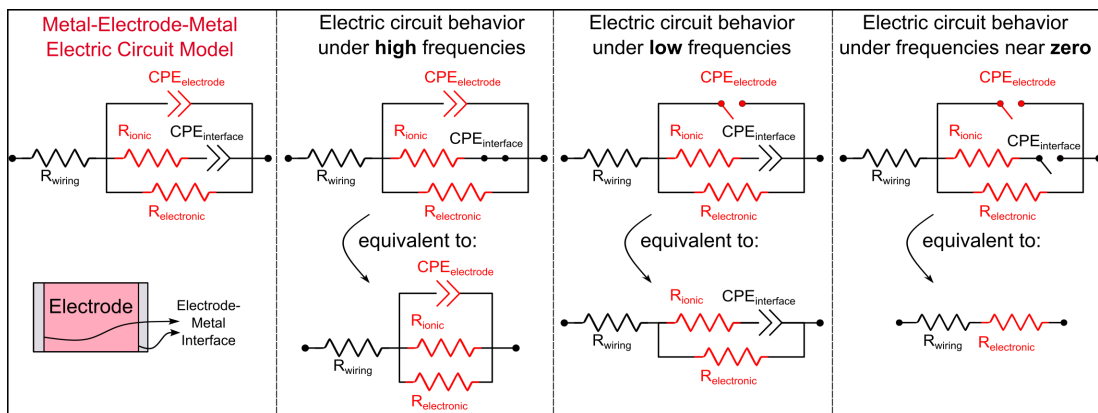


Figure 3.6. Metal-electrode-metal electric circuit model based on physical properties of charge transport.

3.3. Summary of the Chapter

The use of appropriate electric circuit models to fit the SSB impedance response during an EIS experiment can provide important information about charge transport in bulk and interfacial regions. In order to eliminate ambiguities arising from the data interpretation, electric circuit models must be built using physical assumptions.

Using the Huggins' approach,¹⁰⁷ battery constituents with different electrical properties like the anode and the cathode (mixed conductors), and the electrolyte (ion-conducting dielectric) can be individually modeled using electric circuit parameters. This basic knowledge of how to model diffusion of species and charge transfer/charge accumulation at interfaces can be used as a building block for more complex electrical devices. For instance, an anode-free device consisting of a cathode and an electrolyte in contact and between current collectors will take into account the electric circuit models of these materials separately. Therefore, a realistic electric circuit model of a thin-film SSB will take use of these building block units studied in **Figure 3.5** and **Figure 3.6** to model the bulk layers and all the present interfaces (and interphases).

A closer look at the *electric circuit model B* based on a physical interpretation of charge transport from **Figure 3.4** reveals the existence of identical electric circuit parameter associations, so in order to completely decouple the charge transport properties of individual battery constituents and interfaces, a previous knowledge of the materials properties is necessary, like conductivities and relative permittivity values. Chapter 4 will then introduce a new methodology protocol to independently extract basic properties of materials of interest for evaluation of SSB performance and interface evolution using EIS and electric circuit modeling.

Chapter 4: Design of a Platform to Decouple Interfacial and Bulk Properties of a Thin-Film Solid-State Battery

4.1. The Concept of Diagnostic Test Devices

In this chapter, a new protocol for fabrication of thin-film SSBs that allows the evaluation of the formation and evolution of different interfaces across a device while providing a facile diagnosis of the final device performance will be presented. Full SSBs and a permutation of their isolated components and interfaces were manufactured in the same process step, so that it was possible to deconvolute the role of each material and interface in a stepwise fashion. A careful and systematic analysis arising from electric circuit modeling served as a good estimate of bulk properties, like conductivity and relative permittivity, and once the ambiguity in the EIS dispersion is removed, the models can also be used to predict space-charge layers at many different heterojunctions. **Figure 4.1** describes the steps used in the methodology analysis to build a complete SSB model:

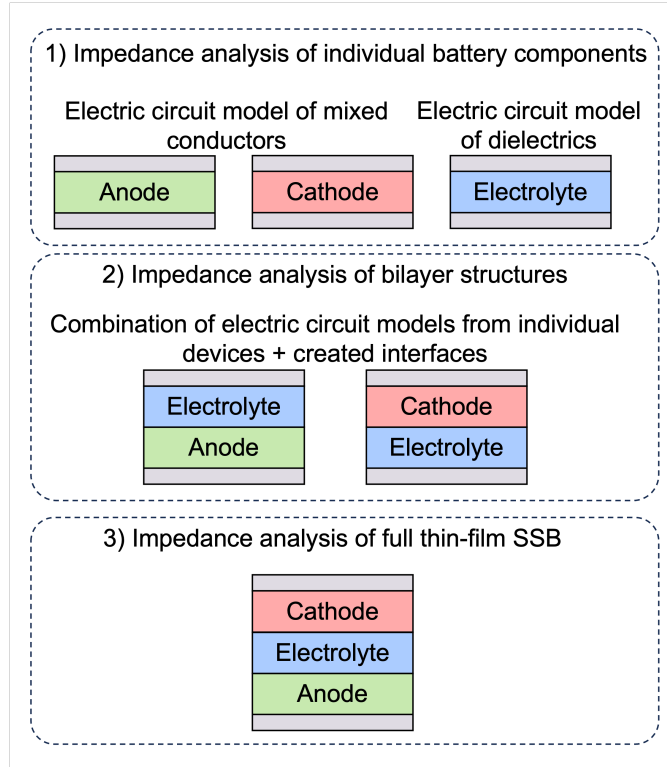


Figure 4.1. Description of methodology used for impedance analysis.

Equivalent electric circuits composed of resistors and constant phase elements that account for various physical parameters of the electrolyte, cathode, and anode in our device that were introduced in Chapter 3 will be modeled. Then, materials properties will be extracted from fitting these equivalent circuits to the measured EISs of the individual layers (called as the diagnostic test devices) depicted in **Figure 4.1**. Next, these parameters will be transferred to bilayers, and finally assembling the layers and interphases to describe the full cell EIS. Ultimately, the performance and capacity degradation of a full thin-film SSB after 500 cycles will be explained by analysis of the EIS through the lens of the individual components.

4.2. *Prototype Fabrication Using Simple Materials*

A 4x4 array of thin-film SSBs, as well as diagnostic test devices that are permutations of individual battery components and their interfaces, was fabricated using a sputtering tool (AJA ATC Orion 8) with a UHV-coupled mask exchanger. The process involved a sequence of in-situ patterning using three different shadow masks and substrate rotation so that both SSBs and the diagnostic test devices could be fabricated in the same run, with no air exposure at any time, and sharing a single substrate (3-inch silicon wafer with a 500 nm layer of thermally grown silicon dioxide). Shadow masks were designed such that an offset of their patterns allowed substrate rotation and reutilization of 2 masks for following deposition steps, illustrated by **Figure 4.2**, which also shows a real image of a set of devices after fabrication.

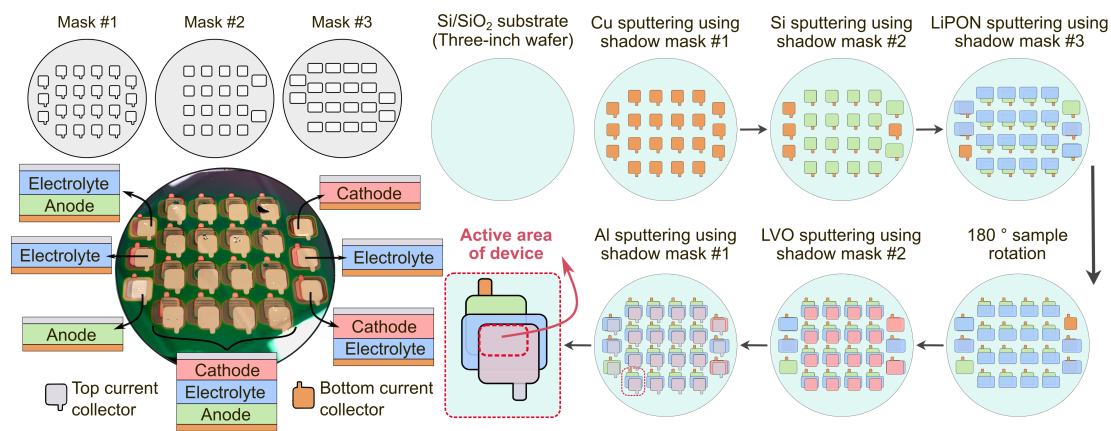


Figure 4.2. *New methodology for fabrication of thin-film SSBs and diagnostic test devices.* Illustration of shadow masks used for in-situ patterning of devices, and an image of a real batch of devices. In this case, 16 SSBs and auxiliary devices were fabricated simultaneously in a 3-inch silicon wafer. Materials: Copper as anode current collector, amorphous silicon (a-Si) as anode, lithium phosphorus oxynitride (LiPON) as electrolyte, lithium vanadium oxide (LVO) as cathode, and aluminum as cathode current collector.

50 nm of copper was sputtered using a shadow mask for bottom electrical contact of all the devices. rf-sputtering was used to deposit 45 nm of amorphous silicon using a power of 3.7 W/cm² under a 3 mTorr argon atmosphere for the anode layer.

570 nm of lithium phosphorous oxy-nitride (LiPON) was chosen to be the electrolyte, which was deposited by reactive rf-sputtering, using a lithium phosphate (Li_3PO_4) target with an applied power density of 3.2 W/cm^2 under a 1.5 mTorr nitrogen (N_2) atmosphere. Lithium vanadium oxide (LVO) was deposited to serve as the cathode layer using a previously developed co-sputtering process.⁹¹ To do so, Li_2O and V_2O_5 targets were simultaneously sputtered under a 1.5 mTorr argon (Ar) atmosphere. Their respective power densities during deposition were 5.9 W/cm^2 and 7.6 W/cm^2 . At the end, a 60 nm-thick aluminum layer was sputtered for top electrical contact, and the substrate was then post-annealed at 300°C for 3 hours under low-pressure N_2 atmosphere (5mTorr) after completing all the deposition steps. Thicknesses of the deposited materials were measured from cross-sectional SEM images (Hitachi SU-70 FEG).

The choice of materials for fabrication of thin-film SSBs was based on their previously reported compatibility^{22,66,67,85,91,114} and due to their simple structure with no grain boundaries, which simplifies the electric circuit model of the final SSB. Amorphous silicon (a-Si), lithium phosphorus oxynitride (LiPON), and lithium vanadium oxide (LVO) were chosen to be the anode, electrolyte and cathode layers of the devices in Figure 1. Copper and aluminum were sputtered as the anode and cathode current collectors, respectively, due to their electrochemical stability at respectively low and high voltages.

4.3. Properties of Interfaces and Interphases

In a complete thin-film SSB, many interfaces are created during the fabrication process, and each one of them will have distinct electrical properties based on the created space-charge layers (SCLs) upon contact of the materials. Having diagnostic test devices that correspond to individual battery components shown in **Figure 4.2** promotes the investigation of every interface in a thin-film SSB and the interfacial stability before and after cycling.

One of these test devices relies on the metal-insulator-metal arrangement, in which the insulator is the electrolyte (LiPON). Although the **Electrolyte-Metal Interface (EMI)** present in such a test device does not exist in the full thin-film SSB, important properties related to the permittivity and ionic resistance of LiPON can be extracted when this interface is decoupled from the rest. During an EIS measurement, a sinusoidal voltage input creates an electric field such that a majority of Li^+ inside LiPON diffuses towards one of the EMIs when the frequency range is sufficiently small. On the other metal side, there is a higher concentration of lithium-ion vacancies,⁴⁸ which also creates a SCL in which its thickness denotes the Li^+ depletion width.

The **Anode-Metal Interface (AMI)** and the **Cathode-Metal Interface (CMI)** will generate SCLs with distinct electrical properties in comparison to EMI. Li^+ diffusing inside LVO and/or a-Si during cell charge/discharge will accumulate at their interfaces with the metal layers, while electrons are not blocked. While this type of interface has not been widely studied in the battery field, its behavior under different states-of-charge might reveal important features about the rate of reaction between Li^+

and electrons, and if the ionic and electronic conductivity at these interfaces remains constant. As it was discussed in Chapter 1, kinetically stable interfaces should maintain their electrical properties, and variations of their conductivities can therefore reflect on degradation of batteries during their lifetimes.

The other two remaining interfaces that are created during fabrication are the **Anode-Electrolyte Interface (AEI)** and the **Cathode-Electrolyte Interface (CEI)**. They are very challenging to be modeled in an electric circuit since intermixing is likely to occur and interphases can be formed during fabrication and under cycling. Previous studies have demonstrated that a wide intermixing region between ALD V_2O_5 and NaPON electrolyte developed in the course of the deposition process.¹¹⁵ In another study, interdiffusion between lithium manganese oxide and LLZO occurred after electrochemical cycling.¹¹⁶ In addition, Li^+ diffusion was reported to occur during sputtering when depositing LiPON on V_2O_5 ,¹¹⁷ so an interphase is likely to be formed between the cathode and electrolyte thin films in this current prototype.

Preferably, these interphases will have high ionic conductivities with low electronic conductivities to allow the charge transfer of Li^+ from the electrolyte to the anode/cathode and vice-versa while suppressing the diffusion of electrons to minimize charge accumulation in those interphase regions and side reactions that could lead to lithium immobilization, resulting then in capacity fading.^{81,118} They are the most widely studied interfaces in a SSB because their local impedances can compromise the total performance of the device. In this work, both AEI and CEI will be modeled as a resistance in parallel to a CPE, in which the resistance is attributed to the charge transfer, and the CPE will inform about their SCLs according to equation (3.16).

4.4. Summary of the Chapter

By combination of impedance spectroscopy analysis and a singular device fabrication methodology, it is now possible to systematically deconvolute charge dynamics in the bulk and at interfaces of a thin-film SSB. Patterned diagnostic devices that represented isolated battery components were used to build electric circuit models that enabled a realistic interpretation of the electrochemical reactions and properties of materials in these devices. The next chapter begins with an explanation of the electric circuits that were built for each studied device, as well as the correlations that can be made with electric circuit parameters and the physics of materials and interfaces under an applied bias. Then, main results will showcase how it was possible to diagnose the main cause of capacity fading of thin-film SSBs by using impedance spectroscopy analysis.

Chapter 5: Electric Circuit Modeling Implementation on the Platform for Thin-Film Solid-State Battery Diagnostics

The investigation of different interfaces that are formed in a SSB and their evolution under different states-of-charge was primarily based on impedance spectroscopy data. For every device manufactured in **Figure 4.2**, an equivalent electric circuit was modeled by considering the materials properties and the mechanisms of charge dynamics under different frequency ranges.^{107,119–121} Then, the acquired impedance spectra of the measured devices were fitted using the proposed electric circuit models for an estimate of the physical properties, like conductivities and relative permittivity values of bulk materials, as well as the width of space-charge regions at interfaces.

For each analyzed set of impedance data, the complete frequency range (250 kHz – 250 mHz) was fitted to the respective electric circuit model, which is a very important aspect when discussing charge accumulation or depletion of charges at small frequencies. More information about the error propagation of the fitted values can be found in the Appendix.

Electrochemical measurements were done using a potentiostat (BioLogic, SP-300) with electrical feedthrough connections inside an argon-filled glovebox, using a probe station with micromanipulators in a two-electrode configuration, in which the copper contact was both the counter and reference electrodes, and the aluminum contact side was the working electrode for all the tested devices. PEIS was used for evaluation

of impedance profiles for the diagnostic test devices and the SSBs. A sinusoidal voltage signal with 10 mV amplitude was applied as a perturbation about each device's OCV.

For some of the devices, an impedance spectrum was obtained at multiple voltage steps, from 0 V to 3.6 V (vs. Cu), with an increment of 180 mV using the SPEIS technique. A wait time of 5 seconds was used after incrementing the voltage before each EIS measurement, and the total time for a complete measurement under this voltage window was 1.5 hours. The frequency of the input signal varied from 250 kHz to 250 mHz (30 points per decade), and the total impedance was recorded at every measured datapoint. The collected impedances of the devices were then fitted using Z-fit, from the Biologic EC-lab software, for circuit element parameter estimation. For each tested device, an appropriate electric circuit model was designed to associate the electric parameters to the physics of the devices during operation. The Simplex+Monte-Carlo method in Z-Fit was used to minimize the fitting.

5.1. Full-Cell Electric Circuit Model Built from Component EIS Signatures

5.1.1. Electrolyte-Only Diagnostic Test Device

The diagnostic test devices composed of individual battery layers were used to extract information about materials properties of LiPON, LVO and a-Si. In **Figure 5.1-a**, the impedance data of the LiPON-only test device was fitted using the electric circuit model shown in the same graph. At frequencies lower than 9 kHz, diffusion of Li^+ to the EMI inside LiPON occurs, while at higher frequencies there is not a substantial concentration of charge but rather polarization of charges within the bulk of the LiPON.

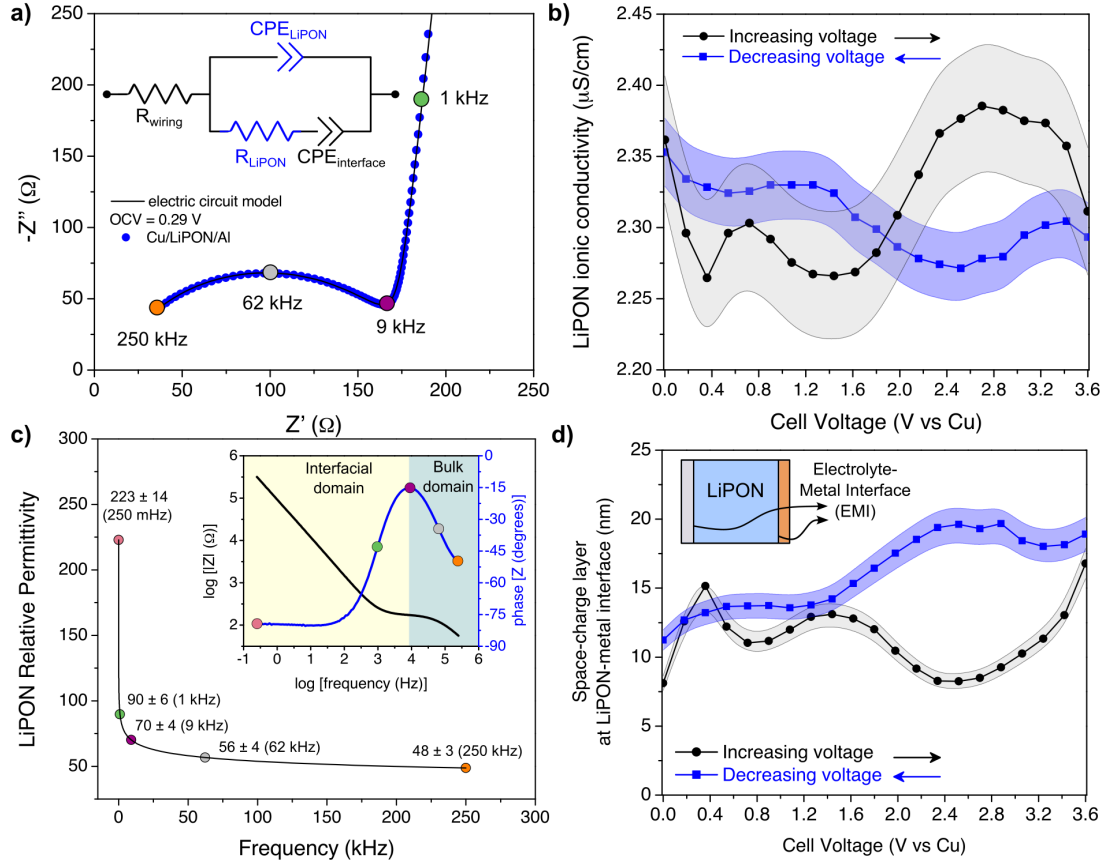


Figure 5.1. Impedance profile of LiPON-only device. a) Impedance spectrum of LiPON-only diagnostic test device at OCV with the representation of the electric circuit model for data analysis; b) LiPON ionic conductivity on different applied voltages; c) relative permittivity of LiPON on different frequencies at OCV; inset: Bode diagram of device at OCV, in which the blue line corresponds to the phase of the total impedance, and the black line is the log of the total impedance modulus; d) computed SCL width at the Electrolyte-Metal Interface (EMI) under different applied voltages calculated at the lowest frequency measurement (250 mHz).

The proposed electric circuit model can also be used for dynamic impedance analysis, i.e., when varying the applied voltage. In this case, for every increase or decrease in the applied bias, an impedance spectrum is acquired, and the parameters of the electric circuit model are minimized. Hence, any changes in the LiPON properties or interfacial reactions are reflected on the variation of the electric circuit parameters.

Figure 5.1-b shows the calculation of ionic conductivity of LiPON (σ_{LiPON}) at a voltage window of 0 – 3.6 V, according to equation (5.1):

$$\sigma_{LiPON} = \frac{1}{R_{LiPON}} \left(\frac{d_{LiPON}}{A} \right) \quad (5.1)$$

Where R_{LiPON} is the resistance obtained from the fitting analysis using the electric circuit model, d_{LiPON} is the thickness of the deposited LiPON layer, and A is the active area of the device. Although there is a fluctuation of σ_{LiPON} as the voltage is increased, it relaxes back to its initial value when the voltage was decreased. The average ionic conductivity in this voltage range was $(2.3 \pm 0.1) \times 10^{-6}$ S/cm, which shows the electrochemical stability of the electrolyte, and it agrees with the literature values for σ_{LiPON} .³⁷

Since bulk properties can now be distinguished from interfacial reactions using the electric circuit model proposed here, the relative permittivity of LiPON (ϵ_{LiPON}) could be computed as a function of frequency (see equation (3.14)). **Figure 5.1-c** shows that above 9 kHz ϵ_{LiPON} smoothly decreases towards values close to 48. Although reported values of ϵ_{LiPON} are usually smaller^{39,110,122,123} than the one estimated here, direct comparisons are imprecise because calculations are made using different frequencies in the literature, and compositional changes like Li and N content should affect ϵ_{LiPON} as well.^{124,125} Below 9 kHz, interfacial reactions are dominant, and ϵ_{LiPON} gets exponentially higher. The inset graph (Bode plot) confirms the bulk domain vs. interfacial domain over the studied frequency range.

SCL width at the two EMIs were monitored over different applied biases. Any changes in the electric circuit parameters of $CPE_{interface}$ (both a and Q , see equations (3.11) and (3.16)) resulted in changes to charge accumulation and interfacial kinetics. It was assumed that the width of the Li^+ accumulation at one EMI has the same length

as Li^+ vacancies on the other EMI, even though the metal contacts are different (copper and aluminum), so the width of each SCL in **Figure 5.1-d** is an approximate and average result. Adding 2 $\text{CPE}_{\text{interface}}$ parameters to the electric circuit model, where each of them would correspond to one EMI, could be more accurate but it would not be possible to fit them without a high degree of correlation, giving rise to ambiguities in data analysis. At low voltages, the SCL is 7–12 nm wide, and towards 3.6 V (vs Cu) there was an increase of this layer up to 20 nm. Those larger values are consistent with a similar direct measurement of the Cu/LiPON interface using electron holography.¹²⁶ The increase in the width of the SCL at higher potentials might indicate a higher accumulation of charges and an eventual LiPON decomposition due to its electrochemical instability above 2.5 V vs Li/Li^+ .^{63,127}

5.1.2. Cathode-Only and Anode-Only Diagnostic Test Devices

After obtaining information about the properties of LiPON, the cathode-only and anode-only diagnostic test devices were analyzed. In **Figure 5.2-a**, two semi-arcs are found in the impedance spectrum of the LVO-only diagnostic test device. The size of each arc depends on the conduction of ions and electrons in a mixed conductor. Two arcs are usually visible¹⁰⁷ when both ionic and electronic conductivities are comparable. In the case of LVO, a similar concentration ratio between free electrons and Li^+ is expected, so the semi-arc at lower frequencies found with a smaller size is mainly due to a higher electron mobility in comparison to Li^+ .¹²⁸ The relative permittivity of LVO was estimated to be (37 ± 5) at 250 kHz, using equation (3.14).

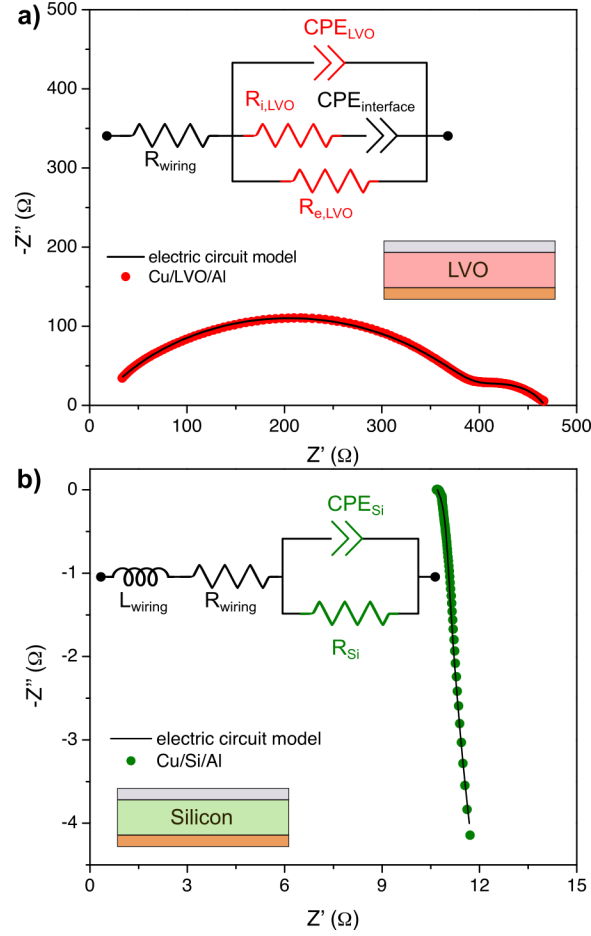


Figure 5.2. Impedance profile of LVO-only and Si-only devices. a) Electric circuit model for the LVO-only test device and impedance spectrum at OCV. b) Impedance spectrum of Si-only diagnostic device at OCV and the electric circuit model that represents this device.

In contrast to the low-frequency profile of the LiPON-only diagnostic device, which showed a linear function between real and imaginary impedance components, a second and smaller semi-arc appears in the impedance profile of the LVO device. This is explained by the fact that although Li^+ are blocked when they get accumulated at the cathode-metal interface (CMI), electrons will be transferred. For the LiPON-only diagnostic test device, charge accumulation at the interfaces took place below 9 kHz, while for LVO it was ~ 150 Hz. This is meaningful because it shows that the time constant for LVO is bigger than the LiPON-only device, i.e., a shorter time is needed for Li^+ inside LiPON to reach the EMI in comparison to the Li^+ diffusion in LVO.

Indeed, this is confirmed when the resistances of the electric circuit model are used to compute conductivity values for each charged species in LVO. The calculated LVO ionic conductivity was $\sigma_{i,LVO} = 0.12 \times 10^{-6}$ S/cm while its electronic conductivity was $\sigma_{e,LVO} = 0.71 \times 10^{-6}$ S/cm. Therefore, σ_{LiPON} is about 20 times bigger than $\sigma_{i,LVO}$, which explains the fast Li^+ accumulation at the EMI on the LiPON-only diagnostic device. At the minimum measured frequency (250 mHz), the width of SCL at the CMI was estimated to be (38 ± 6) nm. The SCL width at the CMI is bigger than the value found for EMI due to the fact that $\epsilon_{LVO} > \epsilon_{LiPON}$. Because $\sigma_{e,LVO}$ is ~ 6 times larger than $\sigma_{i,LVO}$, it is possible that, under an EIS experiment, electrons are diffusing from the metal layer to the LVO and reducing more Li^+ at the interface.

In **Figure 5.2-b**, the impedance spectrum of the Si-only diagnostic test device and the electric circuit model used for its fitting analysis are shown. After a-Si deposition, no Li^+ are present, so there is conduction of electrons only (there could be mobile holes from defects, but the impedance spectrum shows no evidence, so they can be considered as minority carriers). Since the deposited a-Si layer is thin (~ 45 nm), the total impedance is reduced, so wiring effects are more pronounced, which were modeled using a series inductor.^{106,121} At low frequencies, the impedance tends to a resistor behavior, with an area-specific resistance of $1.6 \text{ } \Omega \cdot \text{cm}^2$. The relative permittivity of a-Si was estimated to be (13 ± 1) at 250 kHz, and the SCL width at the Silicon-metal interface could not be modeled in this device due to the pronounced wiring effect previously described.

5.1.3. Electrolyte-Cathode (Anode-Free) Diagnostic Device

Using the information learned from the diagnostic devices of individual battery components, properties such as relative permittivity and ionic and electronic resistances can be used to analyze more interesting interfaces under cycling. Electric circuit parameters previously fitted on these test devices are transferred to the more complex electric circuit models of diagnostic devices where the AEI and CEI are present.

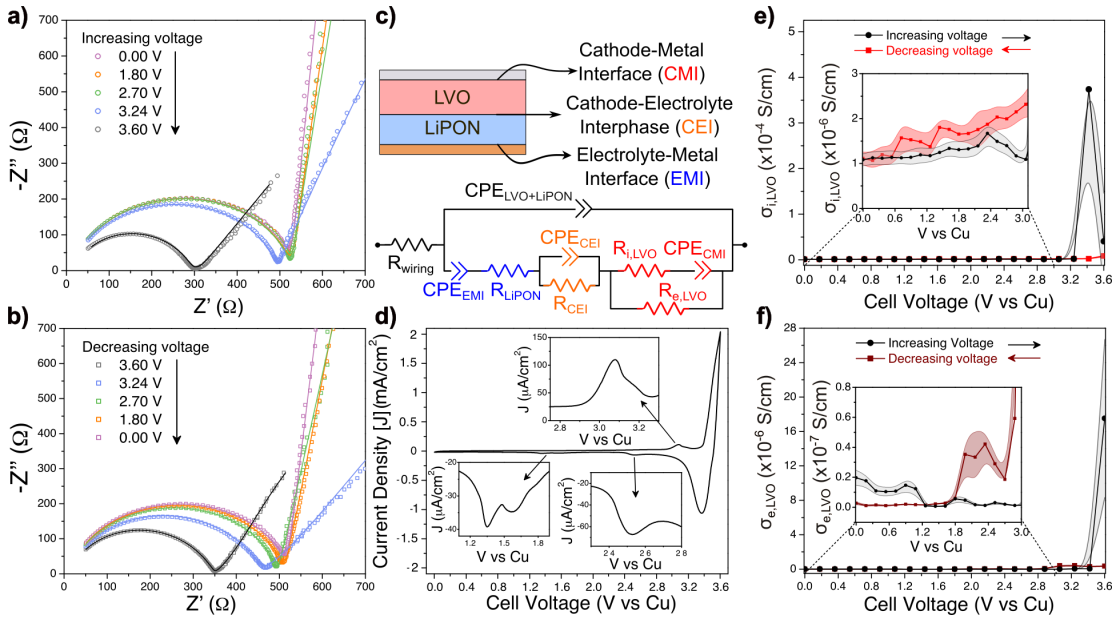


Figure 5.3. *Impedance profile of LVO-LiPON device.* Impedance spectra of LiPON-LVO diagnostic test device when a) increasing the voltage, and b) decreasing the voltage gradient; c) schematics of the device and the electrically modeled interfaces (and interphase). The values of circuit parameters in blue were taken from the LiPON-only device, and the same applies for circuit parameters in red, taken from the LVO-only device. Circuit parameters in orange are representing the CEI; d) cyclic voltammogram of LiPON-LVO device; e) LVO ionic conductivity and f) LVO electronic conductivity as a function of applied bias.

For instance, when LVO is in contact with LiPON, a redistribution of charges is expected to happen, resulting in a CEI formation that may have distinct electrical properties. Now, it is possible to distinguish the properties of this interphase (and SCLs at metal interfaces) from the electric dynamics of the single layers using the electric

circuit models from the isolated LVO and LiPON devices. The estimated circuit parameters from LiPON-only (shown in blue in **Figure 5.3-c**) and LVO-only (shown in red in **Figure 5.3-c**) diagnostic devices are plugged into the electric circuit model of LiPON-LVO diagnostic device for data fitting and analysis. Using this methodology, every parameter is allowed to relax to its appropriate value. The great benefit behind this approach is that the isolated LVO and LiPON diagnostic test devices provided initial guesses for the LVO-LiPON device that are representative of the physical/chemical properties.

Hence, charge dynamics and internal impedances can now be fully resolved under different states-of-charge. By increasing the applied voltage in this system, Li^+ will be moving from LVO to LiPON. Decreasing the applied voltage will result in Li^+ transfer in the opposite direction. Impedance diagrams from **Figure 5.3-a** and **Figure 5.3-b** show that the LiPON-LVO test device can be modeled using the electric circuit from **Figure 5.3-c**, and a significant change in the impedance spectra was observed at voltages higher than 2.7 V. In **Figure 5.3-d**, the cyclic voltammetry taken from this device revealed that an electrochemical peak at ~ 3.1 V is observed when the bias is increased that can be ascribed to a partial extraction of Li^+ from LVO.^{91,129} Above 3.3 V, the remaining amount of mobile Li^+ inside LVO should be diffusing through the CEI and the LiPON layer, and a current density spike in the mA/cm^2 range is noted. The shape and magnitude of this peak is representative of lithium plating¹³⁰ at the LiPON/Cu interface (EMI), so there should be a convolution of two different reactions happening at the same time: Li^+ diffusing out of LVO and Li^+ reduction at the EMI.

When the applied bias becomes smaller, Li oxidation from EMI and subsequent Li^+ diffusion towards the LVO side is observed in the cyclic voltammogram.

While it could be challenging to decouple these two different mechanisms (lithium oxidation/reduction at EMI and Li^+ diffusion inside the device), this is now possible to be made with the novel diagnostics approach. An evaluation of the changes to the electric circuit parameters from the impedance analysis showed, for example, that $\sigma_{\text{i,LVO}}$ and $\sigma_{\text{e,LVO}}$ vary according to the applied bias in the device. In **Figure 5.3-e**, $\sigma_{\text{i,LVO}}$ ranges from $1\text{-}3 \times 10^{-6}$ S/cm from 0-3 V. In contrast, the conductivity during the last portion of the sweep is ~ 102 times greater. A similar behavior was also observed in electrochemically lithiated V_2O_5 thin films by Shibuya et al,¹³¹ in which the V_2O_5 conductivity substantially decreased below 3.0 V vs Li/Li⁺ due to a possible irreversible change in its crystal structure.

Interface kinetics was also evaluated using this diagnostic device and the numerical values of the electric circuit parameters. From the data in **Figure 5.4-a** and **Figure 5.4-b**, it is evident that the CEI is mostly stable from 0-3 V, despite some fluctuations of its resistance. The CEI SCL shown in **Figure 5.4-b** is significantly wide, ranging from 80-160 nm. That may be caused by a Li^+ gradient at the interphase,¹³² in which the LiPON-side of LVO has a high concentration of Li^+ , and heightened by the ready transfer of Li^+ between LiPON and LVO.

At higher voltage biases, up to 3.6 V, it seems that the CEI resistance is affected by the charge polarization and the SCL width at the CEI drops to small values. This could possibly be explained by the small concentration of Li^+ in this region at high voltages, since the majority of mobile Li^+ have diffused towards the EMI at 3.6 V.

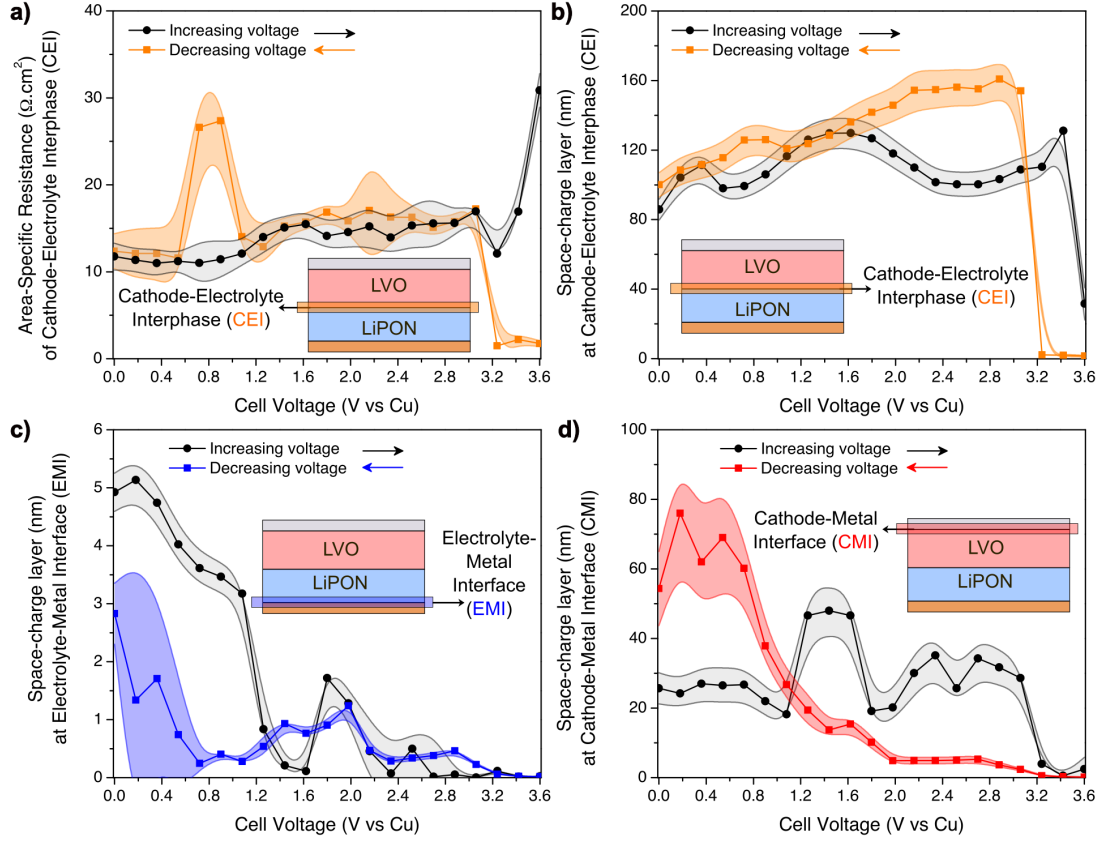


Figure 5.4. Interface kinetics of the LVO-LiPON diagnostic test device. Evolution of a) Cathode-Electrolyte Interphase (CEI) resistance; b) Space-Charge Layer (SCL) formed at the CEI; c) SCL at Electrolyte-Metal Interface (EMI); d) SCL at the Cathode-Metal Interface (CMI) of the LiPON-LVO diagnostic test device.

The average conductivity of the CEI between 0 and 3.6 V can be estimated assuming that its thickness is equivalent to the SCL width (see equation (3.16)). In this case, the average σ_{CEI} is $(0.8 \pm 0.2) \times 10^{-6}$ S/cm, which is lower than the ionic conductivity of LVO and LiPON. Hence, charge transfer of Li^+ in this multiscale process ($\text{LVO} \leftrightarrow \text{CEI} \leftrightarrow \text{LiPON}$) can be negatively affected by the sluggish motion of Li^+ at the CEI.

The hypothesis of Li oxidation/reduction at the EMI at higher biases is now confirmed by the evolution of the SCL at the EMI seen in **Figure 5.4-c**. As the applied voltage was increased, the width of the SCL of LiPON-Cu interface decreased to a sub-

nm range. Above 2 V, it was already very small, which most likely indicates a beginning of LiPON decomposition into Li_3PO_4 and Li_3N .⁹⁴ Above 3.2 V, lithium reduction has occurred. When the applied bias was reversed, Li was stripped from LiPON/Cu interface and the initial SCL was slowly restored.

Another interesting, and yet uncommonly reported interface that was decoupled using this diagnostics approach was the LVO-Al interface (CMI). While increasing the voltage bias, its SCL was mostly stable (20-40 nm wide, see **Figure 5.4-d**), until the last fraction of mobile Li^+ from LVO were transferred to CEI and LiPON, which then decreased the width of the SCL to only a few nanometers. At this point, the CMI does not accumulate charges anymore, since Li^+ is depleted and electrons can be easily transferred because $\sigma_{\text{e,LVO}}$ is significantly higher at this voltage (see **Figure 5.3-f**). When the applied bias was reversed, the SCL slowly increased, and below 1.2 V it was even wider than the initial state (about 3-4 times wider), possibly due to the smaller electronic conductivity of LVO at this voltage, as shown in **Figure 5.3-f**.

5.1.4. Anode-Electrolyte (Cathode-Free) Diagnostic Device

Upon contact of unlithiated a-Si and LiPON, the Silicon-LiPON interface (AEI) appears to be thermodynamically stable.⁸⁹ An electric circuit based on the LiPON-LVO diagnostic device was built (see the following **Figure 5.5**), in which the addition of circuit parameters to represent the AEI were not giving satisfactory fitting of the data. Hence, to avoid over-parametrization¹⁰⁴ we did not include circuit elements to denote that specific interface.

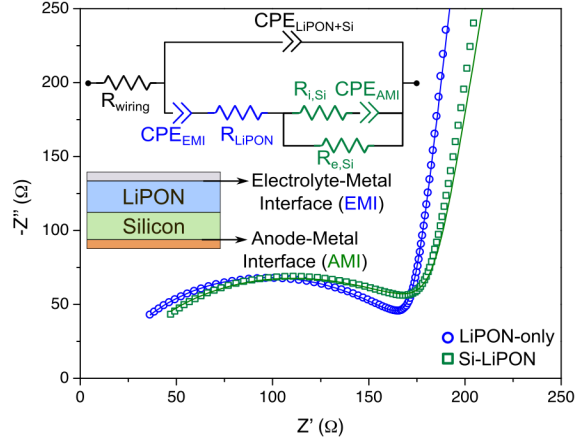


Figure 5.5. Impedance spectrum of Si-LiPON diagnostic device (green curve), and the electric circuit model that was built for data analysis. Values of the electric circuit parameters in green were extracted from the Si-only test device, and the blue ones were taken from the LiPON-only test device. The impedance data of LiPON-only device is shown in blue for visual comparison.

Two resistors were included to represent the electronic flow inside the Silicon layer ($R_{e,Si}$) and the eventual ionic flow ($R_{i,Si}$) under equilibrium if there was a spontaneous diffusion of Li^+ from the LiPON layer. In the as-deposited state, the silicon electronic resistance was estimated at $1.4 \Omega.cm^2$, which agrees with the value found on the Si-only diagnostic device, while the ionic resistance was $\sim 140 k\Omega.cm^2$, confirming that the thermodynamically stable AEI prevented Li^+ from flowing from the LiPON layer to the a-Si during deposition. It is important to note that the deposition sequence is reversed from that of the LiPON/LVO device, so the Si is deposited beneath the LiPON.

The fitting of the electric circuit model to the real data from the Si-LiPON diagnostic device revealed interesting information about the interfaces. The contact between a-Si and copper (Anode-Metal Interface – AMI) created a SCL with an estimated width of $(8 \pm 1) nm$. On the other side of this device, the EMI (in this case, LiPON-Al interface) SCL width was calculated to be $(30 \pm 2) nm$. The data for the LiPON-LVO test device (**Figure 5.4-c**) showed that the LiPON-Cu interface was 5 nm-

thick, at most. The combination of these results from different auxiliary devices can help us conclude that a thicker SCL exists when LiPON is in contact with Al rather than Cu, and that the average of these two EMI SCLs is ~ 17.5 nm, which is in good agreement with the values in **Figure 5.1-d** when studying the interfaces from the Al/LiPON/Cu diagnostic device.

5.2. Describing the EIS of the Thin-Film SSB Full Cell

5.2.1. Building an Electric Circuit Model for a Full Cell from Impedance Signatures of Diagnostic Devices

Having previously analyzed the EIS of each diagnostic test device, now those fitted circuit parameters can be applied to an equivalent circuit for the complete thin-film SSB. The circuit, therefore, includes bulk and interfacial parameters, and the knowledge of how the properties evolve under different applied biases. For each parameter added to the circuit in **Figure 5.6-a**, their initial values were extracted from the electric circuits of the diagnostic test devices. This ensures that the impedance analysis is robust, because it considers the different physical properties and chemical reactions happening at the bulk and at different interfaces, at the same time, that are now fully distinguished.

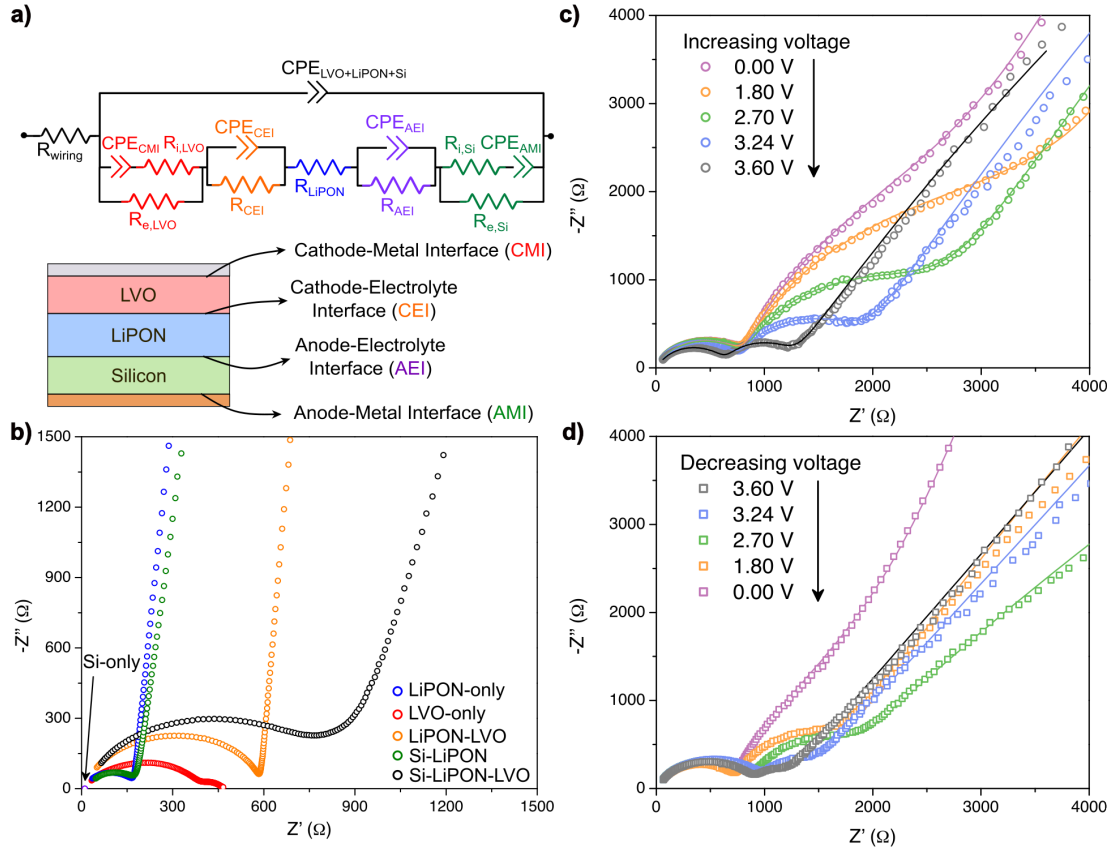


Figure 5.6. *Electric circuit model and impedance profile of a full thin-film SSB.* a) Description of the proposed electric circuit model for interpretation of the thin-film SSB impedance analysis; b) Impedance spectra of every auxiliary device at OCV, including the impedance profile of the SSB stack as-deposited; Impedance of the SSB after several galvanostatic charge/discharge cycles at 8C recorded at different biases during c) charge; and d) discharge half cycles. A discrepancy in the impedance curves at 3.6 V when applying the bias in reverse directions possibly occurred due to relaxation between the charge and discharge measurements.

Figure 5.6-b shows that the impedance profile of the SSB is a convolution of the impedances of isolated battery components and interfaces, and lacks any discrete features that would allow a decomposition of the spectrum without the systematic approach we have taken. The impedance data in black corresponds to the total impedance of the thin-film SSB after fabrication, at OCV. The Si-LiPON interface (AEI) in that specific EIS curve (as-deposited cell) was not modeled in the electric circuit to avoid over-parameterization, like it was observed on the Si-LiPON device (see **Figure 5.5**). The absence of electric circuit parameters to model the AEI suggests

that little or no reactivity exists between LiPON and a-Si before electrochemical cycling on the full cell, which is a characteristic of thermodynamically stable interface. The LiPON-LVO interface (CEI) in the SSB before cycling had a fitted resistance of $14 \Omega \cdot \text{cm}^2$, which is comparable to what was found at the LiPON-LVO test device (see **Figure 5.4-a**), and the ionic resistance of a-Si was within the same order of magnitude ($117 \text{ k}\Omega \cdot \text{cm}^2$) of what was calculated for the Si-LiPON diagnostic device. Overall, it appears that the characteristics found in the diagnostic devices were not affected after completion of the deposition process to form a thin-film SSB.

After galvanostatically cycling the battery 545 times at faster rates (8C, which corresponded to a current density of $50 \mu\text{A}/\text{cm}^2$) for the purpose of studying kinetic effects, we analyzed the evolution of the internal impedances as a function of the applied bias. Overall, the total impedance of the SSB before cycling (**Figure 5.6-b**, black curve) looks different than any of the impedances after 550 cycles taken at different applied biases (**Figure 5.6-c** and **Figure 5.6-d**). While the as-deposited device exhibits a single semi-circle with a low-frequency tail, after cycling there was a split of the impedance profile into two semicircles at high frequencies with a distinct low-frequency tail angle. Furthermore, the impedance data at different biases (**Figure 5.6-c** and **Figure 5.6-d**) shows that the properties of the thin-film SSB are not perfectly reversible during each half cycle. In fact, the two 0 V spectra have different low-frequency tails. It is possible that there is a kinetic factor that delays some restoration of the impedance, or this irreversibility in the EIS is indicative of continuing side reactions somewhere in the device.

5.2.2. Cathode Interfaces During Cycling

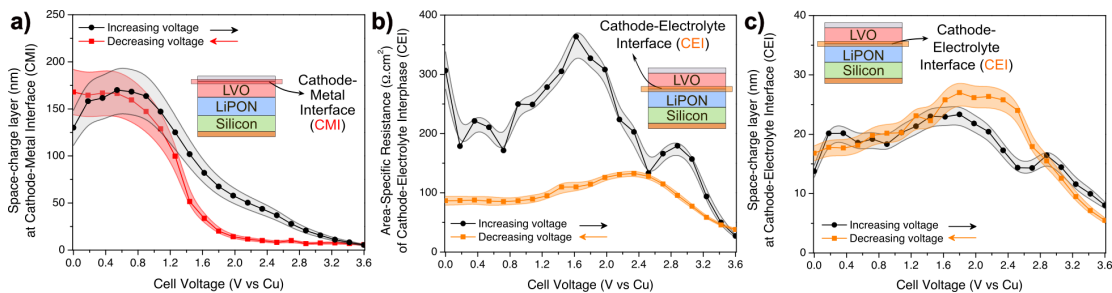


Figure 5.7. SSB cathode interfaces after cycling. a) SCL at the LVO-Al interface; b) resistance of LVO-LiPON interphase; c) SCL at the LVO-LiPON interphase.

The many different interfaces (and interphases) inside the thin-film SSB showed electrochemical instabilities under different applied biases. The LVO-Al interface (CMI) in **Figure 5.7-a** had a SCL width estimated up to 170 nm at low cell voltages (Li^+ insertion in LVO), while that width decreased at higher voltages to values close to 5 nm (Li^+ extracted from LVO). The general trend in SCL is in accordance with the same interface in the LiPON-LVO diagnostic device (see **Figure 5.4-d**). However, the CMI is around two times wider at low cell voltages in the case of the thin-film SSB.

Interestingly, the width of the LiPON-LVO interphase (CEI) from the full cell (**Figure 5.7-c**) agrees with the Li^+ gradient observed from an XPS depth profiling data of electrochemically lithiated V_2O_5 -LiPON interface,¹³² which then validates the deconvolution of impedance profiles performed in this report. A remarkable increase in the CEI resistance with comparison to the uncycled SSB (14 $\Omega \cdot \text{cm}^2$) is shown in **Figure 5.7-b**, and an asymmetry in the charge transfer is noted. In particular, when the applied voltage was being increased, this interphase had a resistance that reached 400 $\Omega \cdot \text{cm}^2$ at 1.6 V. When the applied voltage was decreased, the resistance was about 4

times smaller. This indicates that the transfer of Li^+ has a higher energy barrier to go from the LVO to the LiPON than the reverse direction.

The ionic conductivity of the CEI in the SSB was estimated to be on the order of 10^{-9} S/cm, which is one order of magnitude higher than the value calculated for the LiPON-LVO diagnostic device. Therefore, the difference in the CEI conductivity values predicts a drop in performance after the device begins to be cycled.

5.2.3. Anode Interfaces During Cycling

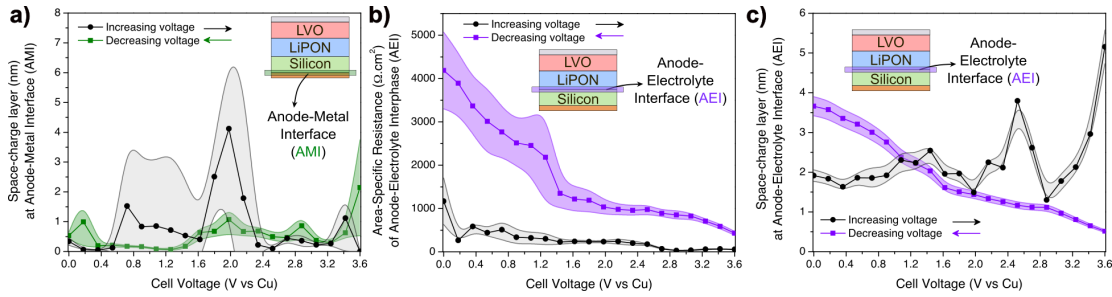


Figure 5.8. SSB anode interfaces after cycling. a) SCL at the Si-Cu interface; b) resistance of Si-LiPON interphase; c) SCL of Si-LiPON interphase.

The anode side of the thin-film SSB also contributed to a decrease in energy during the device operation. The SCL at the Si-Cu interface (AMI) was estimated to be 8 nm in the Si-LiPON diagnostic device (**Figure 5.5**), while the same interface was below 5 nm during cycling (**Figure 5.8-a**). The increase in SCL width is attributable to an increase in charge accumulation as long as the relative permittivity is held constant (see equation (3.16)). It is expected that ϵ_{Si} should increase as a function of lithiation, but no such information could be extracted from this set of diagnostic devices and no references in literature were found to describe $\epsilon_{\text{Li}_x\text{Si}}$. Therefore, no conclusions can be made about the AMI as a function of state-of-charge with this lack of information on silicon properties. Indeed, this illustrates how it is important to propose new

experiments for evaluation of properties of battery materials as a function of lithium insertion for modeling purposes and better data interpretation.

Lastly, the Si-LiPON interface (AEI) that was previously modeled to be thermodynamically stable before cycling has become kinetically unstable during charge/discharge cycles. **Figure 5.8-b** shows that its resistance reached $4 \text{ k}\Omega\cdot\text{cm}^2$ after fully discharging the battery, i.e., when a-Si is delithiated. During the beginning of a charge process, the same interface had a resistance 4 times smaller than the discharge cycle. Hence, the resistance to transfer Li^+ across the AEI slowly decreases as the silicon gets more lithiated, and Li^+ transfer from Si to LiPON appears to be more favorable at cell voltages above 1.4 V.

The width of the AEI SCL was found to be below 10 nm during both charge and discharge processes (**Figure 5.8-c**), and the estimated conductivity at the AEI is 10^{-10} S/cm . The increased AEI resistance contributes to ohmic losses, reducing the measured capacity of the device in this voltage window. While it is still not clear whether these high-impedance interphases with the electrolyte (CEI and AEI) in a SSB are intrinsically dependent one of another, at least now there is evidence that the major sources of capacity fading in the thin-film SSB are ohmic losses at the AEI and CEI.

5.3. Performance of the Full Thin-Film SSB

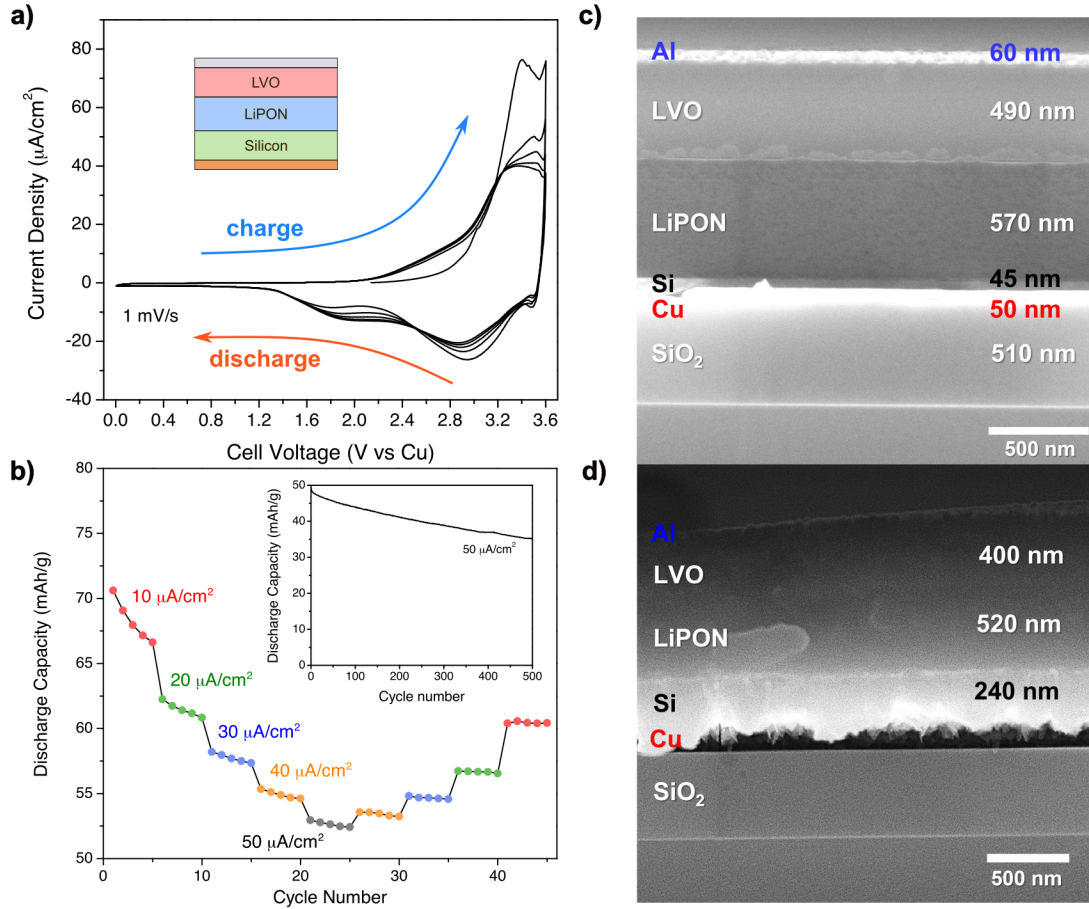


Figure 5.9. Charge-discharge cycles of thin-film SSB and cross-sectional SEM images. a) Cyclic voltammogram of a thin-film SSB, right after deposition. Under the 2-electrode configuration, the copper contact was used both as reference and as a counter electrode. Increasing the total cell voltage refers to charging; b) discharge capacity under different constant current densities (so different C-rates) for 45 cycles in a fresh, yet uncycled SSB. Inset: capacity fading at fast charging/discharging for 500 cycles at 8.5 C (50 $\mu\text{A}/\text{cm}^2$) after cycling 45 times under variable C-rates; cross-sectional SEM images of the thin-film SSB atop the SiO_2 substrate c) before any electrochemical cycling; and d) after 545 cycles at 8.5 C at a charging state.

Figure 5.9-a shows cyclic voltammetry of the thin-film SSB right after fabrication, in which broad peaks are observed between 3 – 3.6 V during charge, and at 2.9 V and 1.8 V during the discharge. Those peaks can be correlated to the insertion/extraction of Li^+ from the LVO, which were also seen on **Figure 5.3-d** in the LVO-LiPON test device. In the thin-film SSB, the peaks are broader and shifted ~ 0.4

V with respect to the LiPON-LVO diagnostic device, likely because of the silicon-Li alloying/dealloying reactions happening at the same time. A first sign of degradation of the SSB was observed in the cyclic voltammogram in **Figure 5.9-a** by the continuous decrease in the current density over subsequent cycles, which was further investigated in a fresh device.

On another thin-film SSB that was not yet electrochemically tested from the 4x4 array of fabricated devices, a series of 545 galvanostatic charge/discharge cycles was performed under variable C-rates, as shown in **Figure 5.9-b**. A larger capacity loss was observed at the initial cycling of the SSB, regardless of the value of the applied currents (e.g. $10 \mu\text{A}/\text{cm}^2 = 1.7 \text{ C}$). From cycle 1 to 45 under variable C-rates, there was a loss of discharge capacity $\sim 15 \%$. Interestingly, the first 45 cycles from the follow-up 500-series at a high C-rate of 8.5 C ($50 \mu\text{A}/\text{cm}^2$) resulted in a discharge capacity loss of $\sim 8 \%$. This evidence shows that fast charging was not the only factor contributing to the device performance below the expected. Apparently, problems occurring at the beginning of the battery lifetime have caused irreversible changes on the device.

SEM analysis of the fractured cross section of an uncycled, as-deposited thin-film SSB (**Figure 5.9-c**) revealed that most of the interfaces were smooth after completion of the fabrication process, besides some irregular patterns that were noted at the LVO-LiPON interface possibly due to the fracture, or because of an interphase that formed during the deposition of the LVO onto the LiPON. The interfaces of the full stack looked completely different after 545 cycles, here shown in a charged state (**Figure 5.9-d**). There is an evident volume expansion of silicon (about 4.33 times)

when it gets lithiated that is in accordance with the literature²¹, which had possibly caused a contact loss between Si and Cu. Also, a LiPON decomposition at the AEI¹³³ could have caused shrinking of $\sim 9\%$ of the total LiPON layer. LVO had an 18% thickness reduction, but this could be due to Li^+ extraction from its structure.

Overall, electrochemical measurements and SEM images are in accordance with the results observed from the impedance analysis. The Si-LiPON interface was not included in the electric circuit models of the Si-LiPON diagnostic device, nor in the full SSB before cycling, because unphysical and suspicious fitting of their EISs was found whenever this interface was included in the models. Our hypothesis for this case was that the interface was thermodynamically stable during/after fabrication, and the SEM images shown in **Figure 5.9-c** presented a smooth contact between Si and LiPON that agrees with our premise.

After cycling, the SEM in **Figure 5.9-d** revealed a volume expansion of Li_xSi at a charged state that drastically affected the stability of the Si-LiPON interface, which was confirmed by the capacity fading observed on electrochemical measurements. The calculation of the AEI conductivity from the impedance analysis reinforces the argument that this interface was a major source of battery degradation. The direct relationship between cell performance and interface kinetics in this report was only possible due to our diagnostics protocol for systematic decoupling of internal impedances in a thin-film SSB.

5.4.Prognosis

A battery is more than the sum of its parts. The properties of interfaces/interphases are important parameters for device performance, and the fact that many properties vary with ion concentration further complicates the analysis. By using thin film deposition to break up the battery into component parts, and analyzing each in turn, we find that changes in material properties and interphases can be fully accounted for. Furthermore, these fitted parameters do not become wild or highly correlated when examining the full cell, implying that the model is not overfitting the data, and verifies the hypothesis that the thin film full cell can be described by its component parts, once they are all accounted for.

The use of diagnostic devices to deconvolute impedances in a SSB also proposes that *in-situ* experiments can be done using this technique. For example, internal impedances can be spatially resolved by performing a 2D-mapping of a SSB using KPFM analysis to probe the behavior of charge transfer at interfaces in different locations. For the case of crystalline materials and/or interfaces, coupling X-Ray Diffraction (XRD) measurements with impedance analysis over different states-of-charge can evaluate the mobility of majority charge carriers at grain boundaries versus in bulk. And, in general, this protocol using individual and isolated test devices can provide comparisons of battery health while simultaneously performing morphological, structural, mechanical, and electrochemical characterization techniques on sibling devices.

While a complete study of interface kinetics in a SSB still requires in-situ experimental techniques such as SEM (Scanning Electron Microscopy), XPS (X-Ray Photoelectron Spectroscopy), ToF-SIMS (Time-of-Flight Secondary Ion Mass Spectroscopy), KPFM, AES (Auger Electron Spectroscopy), RBS (Rutherford Backscattering Spectroscopy), and/or TEM,^{9,50,114,116,134–136} an electrochemical impedance analysis coupled with an appropriate system of devices can reveal features of the interfaces during cycling, as well as indicate possible issues occurring during processing that were yet unreported. Hence, a direct, non-destructive measurement of the physical properties of interfaces is now feasible for a wider range of thin-film devices, which can substantially improve the design of next-generation ionic devices.^{105,137}

For the first time, the kinetics of interfaces in a SSB was monitored and reported from impedance analysis to diagnose full cell performance and degradation during fast cycling. The simple premise of decoupling bulk and interfacial internal impedances by building single and bilayer devices, deriving physics-based electric circuit models for every layer (and interface) individually, and combining their circuit parameters into a robust and complete electric circuit for the full battery, has proven to work successfully. Circuit parameters from the diagnostic test devices fully explain the behavior of the full cell, with minimal drift in the fitted values from test device to full cell.

In the previous sections, we have shown that equivalent circuit analysis can provide models and parameters that are transferable from simple systems to complex ones. For instance, important material properties were calculated under different

applied biases, such as the relative permittivity of the active materials, conductivities of bulk layers and across at interphases, and the width of space-charge regions at heterojunctions. Variations in these material properties can be explained by well-known dynamics in solid-state batteries, and provide quantitative measurements of parameters necessary for advanced modeling of electrochemical systems.

There are several beneficial impacts to the field of electrochemical devices coming from these calculated properties. Conductivity measurements at interfaces can determine whether or not protective layers must be incorporated to adjust the electrical properties of interfaces closer to ideal values. Also, different combinations of promising materials can now be tested using this diagnostic protocol to investigate compatibility. And, more broadly, the calculated values of materials properties can now be included in computational simulations for a better prediction of device performance.

Simple materials with simple interfaces were studied as a proof-of-concept. Adding materials with more complex structures like grain boundaries, or intrinsic tortuosity, porosity, and voids that exist in particulate SSBs will require extra assumptions to be made when building the electric circuit models. The inclusion of inactive materials such as carbon black will also add more challenges to fully deconvolute the internal impedances, so additional diagnostic test devices may be required to be fabricated and studied. Lastly, thin-film batteries with unique architectures like AAO-nanopore arrays for fabrication of 3D thin-film SSBs⁷⁵ will have to be carefully studied because the electric field lines are not as uniform as they

are in planar batteries, so the calculations of space-charge layers have to be derived considering the nature of their architectures.

Although this dissertation only performs diagnostics of simple thin-film SSBs, the challenges previously described for more complex systems only require some understanding of the structure of the system to include important chemical and physical properties into the electric circuit modeling. Hence, the benefits of using this diagnostics protocol for other battery systems can potentially increase the understanding of the battery community in local interfaces and impedances and their consequences for capacity retention, cell degradation and compatibility of promising materials.

5.5. Summary of the Chapter

Interface (and interphase) kinetics were proven to affect the overall performance of thin-film SSBs using the new diagnostics protocol presented in this work. By combination of impedance spectroscopy analysis, conventional electrochemical measurements, and a singular device fabrication methodology, we provided a systematic deconvolution of charge dynamics in the bulk and at interfaces of a thin-film SSB.

Patterned auxiliary devices that represented isolated battery components were used to build electric circuit models that enabled a realistic interpretation of the electrochemical reactions and properties of materials in these devices. Accumulation of charges at interfaces and conductivities of Li^+ and electrons across different layers were monitored at different states-of-charge, and, for instance, a space-charge layer in

the range of 100 nm was observed at the cathode-metal interface and the cathode-electrolyte interphase after completion of the fabrication process. The anode-electrolyte interface was found to be stable only before cycling using both impedance analysis and cross-sectional SEM imaging.

The determination of how the interfaces changed with different applied voltages was only possible by the implementation of the auxiliary device diagnostics approach. For instance, the LVO-LiPON interphase was found to be resistive to Li^+ transfer, especially during charging, but the LiPON-Si interphase was 10 times more resistive.

The information extracted from the auxiliary devices served as initial input for the electric circuit model of the full thin-film SSB. A $\sim 15\%$ decrease in capacity was observed as a function of charge/discharge cycles during the first 45 cycles, which indicated that charge transfer across the entire SSB modified the nature of the as-deposited interfaces. In addition, a large volume expansion of silicon, once it gets lithiated, was a major contributor to the low capacity of the device.

Hence, this work demonstrated how important it is to incorporate diagnostics of batteries to understand possible fabrication inconsistencies and kinetic behavior during their operation. For the particular choice of materials studied in this prototype, volume expansion of silicon upon lithiation caused contact loss with the current collector and a kinetically unstable Si-LiPON interphase was present during cycling of the battery. In the future, different artificial interfaces could be deposited using the methodology described here between silicon and LiPON to provide mechanical strength while maintaining a reasonable low ionic resistivity for further battery operation without loss of capacity. Interfacial stabilization of the cathode-electrolyte

interphase has also proven to be necessary to improve charge transfer. We believe, therefore, that the combination of this novel and robust diagnostics protocol coupled with interfacial engineering will enable the implementation of more complex architectures for the next generation of SSBs.

Chapter 6: Conclusions and Perspectives

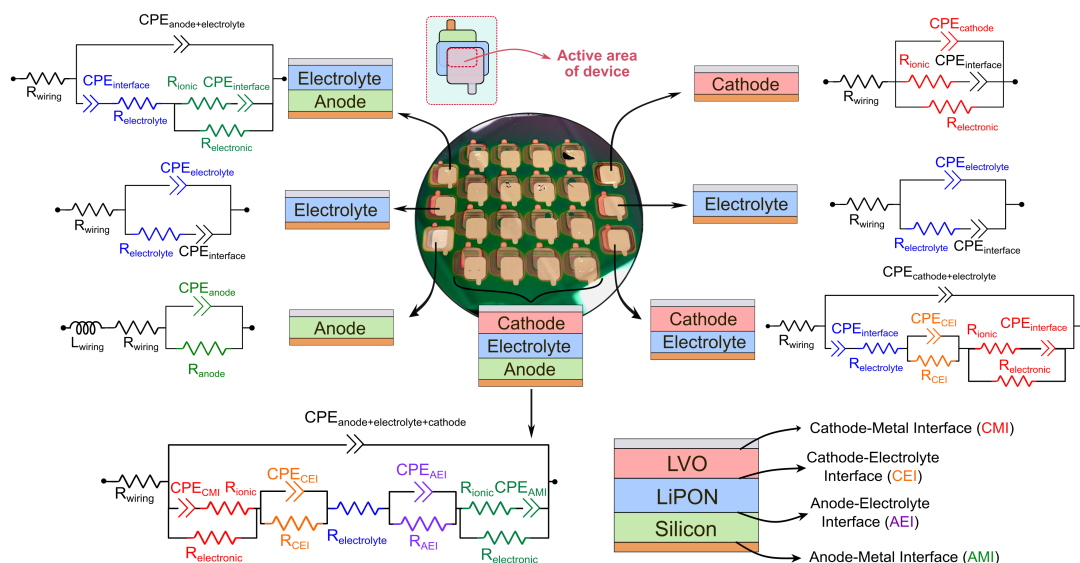


Figure 7.1. Electric circuit models for diagnostic devices and SSB.

For the first time ever reported, evolution of interfaces in a thin-film SSB and their kinetics were reported using a new device fabrication methodology coupled to electric circuit modeling. The protocol involving the simultaneous fabrication of diagnostic test devices and complete stacks of thin-film SSBs serves as a **multipurpose platform**, in which the following subjects can be investigated:

- Compatibility of promising materials for electrochemical systems
- Extraction of materials properties as a function of charge/discharge, like electrical conductivities and relative permittivity
- Estimation of interfacial properties, like space-charge layer widths and electrical conductivity
- Deconvolution of individual bulk and interfacial parameters

- Identification of localized layers that potentially contribute to device degradation and capacity fading

Using a system of materials with well-studied structural and morphological properties, an electric circuit model based on physical assumptions validated the hypothesis that interfacial kinetics in thin-film SSBs can be studied using a non-destructive technique. For example, one of the studied interfaces using this new approach for data analysis has presented a thermodynamically stable behavior after fabrication of the device that evolved to form a kinetically unstable interface upon charging and discharging. Another interphase from the same device has proven to be kinetically stable at different applied voltages, and the distinction between these discrepant interfaces was due to the diagnostic test devices that allowed a deconvolution of information acquired from an impedance spectrum. It is expected, therefore, that material scientists can make use of this protocol for promotion of interfacial engineering in SSBs.

6.1. Contributions to Scientific Publications During the Doctoral Degree

Ferrari, V.C., Lee, S.B., Rubloff, G.R., Stewart, D.M. Fabrication Diagnostics of Thin-Film Solid-State Batteries from The Deconvolution of Their Interfacial and Bulk Impedances. *In preparation.*

Ferrari, V.C., Rubloff, G.R., Stewart, D.M. Lithium ion diffusion from different solid electrolytes to thin-film cathode layers at early stages of sputtering deposition. *In preparation.*

- **Contribution:** fabrication of devices, interpretation of EIS data, XPS depth profiling analysis and discussions related to interphase formation between V_2O_5 and LiPON:

Warecki, Z., **Ferrari, V.C.**, Robinson, D.A., Sugar, J.D., Lee, J., Ievlev, A.V., Kim, N.S., Stewart, D.M., Lee, S.B., Albertus, P., Rubloff, G., Talin, A.A. Simultaneous Solid Electrolyte Deposition and Cathode Lithiation for Thin Film Batteries and Lithium Iontronic Devices, *ACS Energy Letters*, 9, **2024**, 2065-2074.

- **Contribution:** conduction of XPS measurements and data analysis, and discussions related to the reactions occurred to form a stable tin fluoride protective layer:

Damircheli, R., Hoang, B., **Ferrari, V.C.**, Lin, C.F. Fluorinated Artificial Solid-Electrolyte-Interphase Layer for Long-Life Sodium Metal Batteries, *ACS Applied Materials and Interfaces*, 15, 47, **2023**, 54915-54922.

- **Contribution:** provided my expertise in sputtering deposition for process development of thin-film iron fluoride:

Hoang, B., **Ferrari, V.C.**, Wang, H., Stewart, D., Damircheli, R., Lin, C.F. From Amorphous to Crystalline Thin-Film FeF_3 Conversion Electrodes by Sputtering Deposition, *ACS Applied Energy Materials*, 6, 19, **2023**, 10005-10011.

- **Contribution:** discussions on electrochemical analysis of lithium insertion in Si:

Wang, H., Song, Y., **Ferrari, V.C.**, Kim, N., Lee, S.B., Albertus, P., Rubloff, G., Stewart, D. In-situ Raman mapping of Si island electrodes and stress modeling as a

function of lithiation and size, *ACS Applied Materials and Interfaces*, 15, 34, **2023**, 40409-40418.

- **Contribution:** provided my expertise in Spectroscopic Ellipsometry for generation of physical models of optical parameters:

Huang, Y.S., Lee, C.Y., Rath, M., **Ferrari, V.**, Yu, H., Woehl, T.J., Ni, J.H., Takeuchi, I., Ríos, C. Tunable structural transmissive color in fano-resonant optical coatings employing phase-change materials, *Materials Today Advances*, 18, **2023**, 100364.

- **Contribution:** fabrication of all analyzed samples, conduction of electrochemical cycling, and general data discussions:

Levy, Z., **Ferrari, V.C.**, Rosas, P., Walker, M.J., Duddella, K., Haseman, M., Stewart, D., Rubloff, G., Brillson, L.J. Lithium Spatial Distribution and Split-Off Electronic Bands at Nanoscale V₂O₅/LiPON Interfaces, *ACS Applied Energy Materials*, 6, 9, **2023**, 4538-4548.

- **Contribution:** main investigator of this project – process development of pre-lithiated cathode material during sputtering deposition; electrochemical, structural and composition analysis of materials.

Ferrari, V.C., Kim, N.S., Lee, S.B., Rubloff, G.W. and Stewart, D.M. Co-sputtering of lithium vanadium oxide thin-films with variable lithium content to enable advanced solid-state batteries, *Journal of Materials Chemistry A*, 10, **2022**, 12518-12531.

Appendix

Error propagation of derived parameters from electric circuit modeling

Some properties of materials were calculated using geometrical values (active surface area and film thickness) and also parameters extracted from the electric circuit modeling. Hence, those properties have associated uncertainties that were calculated based on error propagation.

a) Uncertainty of a CPE capacitance ($\sigma_{C'}$)

From equation (3.11), the real part of the capacitance of a CPE has an uncertainty that depends on the parameters a and Q :

$$\sigma_{C'} = \sqrt{\sigma_a^2 \left(\frac{\partial C'}{\partial a} \right)^2 + \sigma_Q^2 \left(\frac{\partial C'}{\partial Q} \right)^2} \quad (\text{A.1})$$

Where σ_a and σ_Q are the fitting errors of a and Q parameters. Equation (A.1) can be simplified using the value of the imaginary part of the capacitance from equation (3.12):

$$\sigma_{C'} = \sqrt{\sigma_a^2 \left[\ln(\omega) C' - \frac{\pi}{2} C'' \right]^2 + \sigma_Q^2 \left(\frac{C'}{Q} \right)^2} \quad (\text{A.2})$$

b) Uncertainty of relative permittivity ($\sigma_{\varepsilon'_r}$)

The relative permittivity (ε_r) of a material depends on its bulk capacitance, C_{Bulk} , surface area A , and thickness d , according to equation (3.14). For this error estimation, the associated area error was neglected since A could be determined by the design of devices and it was easily measured. The uncertainty of C_{Bulk} was calculated using equation (A.2), and the thickness error was estimated from cross-sectional measurements taken by SEM. Hence, only C_{Bulk} and d will contribute to the uncertainty of the ε_r :

$$\sigma_{\varepsilon'_r} = \sqrt{\sigma_{C'_{Bulk}}^2 \left(\frac{\partial \varepsilon'_r}{\partial C'_{Bulk}} \right)^2 + \sigma_d^2 \left(\frac{\partial \varepsilon'_r}{\partial d} \right)^2} \quad (A.3)$$

Which can be further derived into the following equation:

$$\sigma_{\varepsilon'_r} = \varepsilon'_r \sqrt{\left(\frac{\sigma_{C'_{Bulk}}}{C'_{Bulk}} \right)^2 + \left(\frac{\sigma_d}{d} \right)^2} \quad (A.4)$$

c) Uncertainty of the width of space-charge layer ($\sigma_{d_{SCL}}$)

From equation (3.16), d_{SCL} depends on the relative permittivity of the material, its surface area and interfacial capacitance. Using equations (A.2) and (A.4), the associated error of d_{SCL} can be calculated as:

$$\sigma_{d_{SCL}} = \sqrt{\sigma_{C'_{Interface}}^2 \left(\frac{\partial d_{SCL}}{\partial C'_{Interface}} \right)^2 + \sigma_{\varepsilon'_r}^2 \left(\frac{\partial d_{SCL}}{\partial \varepsilon'_r} \right)^2} \quad (A.5)$$

Which is simply calculated as:

$$\sigma_{d_{SCL}} = d_{SCL} \sqrt{\left(\frac{\sigma_{C'_{Interface}}}{C'_{Interface}}\right)^2 + \left(\frac{\sigma_{\epsilon'_r}}{\epsilon'_r}\right)^2} \quad (A.6)$$

d) Uncertainty of ionic and electronic conductivities of bulk materials and interfaces ($\sigma_{\sigma_e}, \sigma_{\sigma_i}$)

From equation (5.1), the associated error of conductivity calculations will depend on the resistance (R) and the thickness (d) of the layer. For bulk materials, d was measured by cross-sectional SEM images:

$$\sigma_{\sigma_{Bulk}} = \sigma_{Bulk} \sqrt{\left(\frac{\sigma_{d_{Bulk}}}{d_{Bulk}}\right)^2 + \left(\frac{\sigma_{R_{Bulk}}}{R_{Bulk}}\right)^2} \quad (A.7)$$

For interfaces/interphases, d corresponds to the space-charge layer that was calculated using equations (3.16) and (A.6):

$$\sigma_{\sigma_{interface}} = \sigma_{interface} \sqrt{\left(\frac{\sigma_{d_{SCL}}}{d_{SCL}}\right)^2 + \left(\frac{\sigma_{R_{interface}}}{R_{interface}}\right)^2} \quad (A.8)$$

Bibliography

1. Tan, D. H. S., Banerjee, A., Chen, Z. & Meng, Y. S. From nanoscale interface characterization to sustainable energy storage using all-solid-state batteries. *Nat. Nanotechnol.* **15**, 170–180 (2020).
2. Kim, J. G. *et al.* A review of lithium and non-lithium based solid state batteries. *Journal of Power Sources* **282**, 299–322 (2015).
3. Manthiram, A., Yu, X. & Wang, S. Lithium battery chemistries enabled by solid-state electrolytes. *Nature Reviews Materials* **2**, 1–16 (2017).
4. Randau, S. *et al.* Benchmarking the performance of all-solid-state lithium batteries. *Nature Energy* **5**, 259–270 (2020).
5. Armand, M. & Tarascon, J.-M. Building better batteries. *Nature* **451**, 652–657 (2008).
6. Janek, J. & Zeier, W. G. Challenges in speeding up solid-state battery development. *Nat Energy* **8**, 230–240 (2023).
7. Janek, J. & Zeier, W. G. A solid future for battery development. *Nat Energy* **1**, 16141 (2016).
8. Jung, K., Shin, H., Park, M. & Lee, J. Solid-State Lithium Batteries: Bipolar Design, Fabrication, and Electrochemistry. *ChemElectroChem* **6**, 3842–3859 (2019).
9. Pearse, A. J., Gillette, E., Lee, S. B. & Rubloff, G. W. The reaction current distribution in battery electrode materials revealed by XPS-based state-of-charge mapping. *Phys. Chem. Chem. Phys.* **18**, 19093–19102 (2016).

10. Asano, T., Yubuchi, S., Sakuda, A., Hayashi, A. & Tatsumisago, M. Electronic and Ionic Conductivities of $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2\text{-Li}_3\text{PS}_4$ Positive Composite Electrodes for All-Solid-State Lithium Batteries. *J. Electrochem. Soc.* **164**, A3960–A3963 (2017).
11. Ma, W. Y., Zhou, B., Wang, J. F., Zhang, X. D. & Jiang, Z. Y. Effect of oxygen vacancy on Li-ion diffusion in a V_2O_5 cathode: A first-principles study. *Journal of Physics D: Applied Physics* **46**, (2013).
12. Weiss, M. *et al.* From Liquid- to Solid-State Batteries: Ion Transfer Kinetics of Heteroionic Interfaces. *Electrochemical Energy Reviews* **3**, 221–238 (2020).
13. Chen, X., Xie, J., Zhao, X. & Zhu, T. Electrochemical Compatibility of Solid-State Electrolytes with Cathodes and Anodes for All-Solid-State Lithium Batteries: A Review. *Adv Energy and Sustain Res* **2**, 2000101 (2021).
14. Hwang, B. J., Wang, C. Y., Cheng, M. Y. & Santhanam, R. Structure, morphology, and electrochemical investigation of LiMn_2O_4 thin film cathodes deposited by radio frequency sputtering for lithium microbatteries. *Journal of Physical Chemistry C* **113**, 11373–11380 (2009).
15. Zhang, Y., Ouyang, L. Z., Chung, C. Y. & Zhu, M. Sputtered Al-doped lithium manganese oxide films for the cathode of lithium ion battery: The post-deposition annealing temperature effect. *Journal of Alloys and Compounds* **480**, 981–986 (2009).
16. Kawasoko, H. *et al.* Low Interface Resistance in Solid-State Lithium Batteries Using Spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4(111)$ Epitaxial Thin Films. *ACS Applied Energy Materials* **3**, 1358–1363 (2020).

17. Wang, L. *et al.* Spontaneous Lithiation of Binary Oxides during Epitaxial Growth on LiCoO_2 . *Nano Lett.* **22**, 5530–5537 (2022).
18. Luais, E. *et al.* Mesoporous silicon negative electrode for thin film lithium-ion microbatteries. *Journal of Power Sources* **274**, 693–700 (2015).
19. Mu, T. *et al.* Stable Silicon Anodes by Molecular Layer Deposited Artificial Zincone Coatings. *Adv Funct Materials* **31**, 2010526 (2021).
20. Xu, K. *et al.* Research Progress on Coating Structure of Silicon Anode Materials for Lithium-Ion Batteries. *ChemSusChem* **14**, 5135–5160 (2021).
21. Koerver, R. *et al.* Chemo-mechanical expansion of lithium electrode materials – on the route to mechanically optimized all-solid-state batteries. *Energy Environ. Sci.* **11**, 2142–2158 (2018).
22. Wang, H. *et al.* In Situ Raman Mapping of Si Island Electrodes and Stress Modeling as a Function of Lithiation and Size. *ACS Appl. Mater. Interfaces* **15**, 40409–40418 (2023).
23. Kozen, A. C. *et al.* Next-Generation Lithium Metal Anode Engineering via Atomic Layer Deposition. *ACS Nano* **9**, 5884–5892 (2015).
24. Vishnugopi, B. S. *et al.* Challenges and Opportunities for Fast Charging of Solid-State Lithium Metal Batteries. *ACS Energy Lett.* **6**, 3734–3749 (2021).
25. Kozen, A. C. *et al.* Stabilization of Lithium Metal Anodes by Hybrid Artificial Solid Electrolyte Interphase. *Chem. Mater.* **29**, 6298–6307 (2017).
26. Han, S. Y. *et al.* Stress evolution during cycling of alloy-anode solid-state batteries. *Joule* **5**, 2450–2465 (2021).

27. McDowell, M. T., Cortes, F. J. Q., Thenuwara, A. C. & Lewis, J. A. Toward High-Capacity Battery Anode Materials: Chemistry and Mechanics Intertwined. *Chem. Mater.* **32**, 8755–8771 (2020).
28. Wang, H. *et al.* Micro-Raman Stress Characterization of Crystalline Si as a Function of the Lithiation State. *ACS Appl. Mater. Interfaces* **15**, 10752–10760 (2023).
29. Lin, C. F. *et al.* Solid Electrolyte Lithium Phosphous Oxynitride as a Protective Nanocladding Layer for 3D High-Capacity Conversion Electrodes. *ACS Nano* **10**, 2693–2701 (2016).
30. Lin, C. F. *et al.* Highly Reversible Conversion-Type FeOF Composite Electrode with Extended Lithium Insertion by Atomic Layer Deposition LiPON Protection. *Chemistry of Materials* **29**, 8780–8791 (2017).
31. Cabana, J., Monconduit, L., Larcher, D. & Palacín, M. R. Beyond Intercalation-Based Li-Ion Batteries: The State of the Art and Challenges of Electrode Materials Reacting Through Conversion Reactions. *Advanced Materials* **22**, (2010).
32. Li, J. *et al.* Phase evolution of conversion-type electrode for lithium ion batteries. *Nat Commun* **10**, 2224 (2019).
33. Wang, H. *et al.* Recent Advances in Conversion-Type Electrode Materials for Post Lithium-Ion Batteries. *ACS Materials Lett.* **3**, 956–977 (2021).
34. Wang, F. *et al.* Conversion Reaction Mechanisms in Lithium Ion Batteries: Study of the Binary Metal Fluoride Electrodes. *J. Am. Chem. Soc.* **133**, 18828–18836 (2011).

35. Stewart, D. M. *et al.* Tin Oxynitride Anodes by Atomic Layer Deposition for Solid-State Batteries. *Chem. Mater.* **30**, 2526–2534 (2018).
36. Zhao, Q., Stalin, S., Zhao, C.-Z. & Archer, L. A. Designing solid-state electrolytes for safe, energy-dense batteries. *Nat Rev Mater* **5**, 229–252 (2020).
37. LaCoste, J. D., Zakutayev, A. & Fei, L. A Review on Lithium Phosphorus Oxynitride. *J. Phys. Chem. C* **125**, 3651–3667 (2021).
38. Lacivita, V., Artrith, N. & Ceder, G. Structural and Compositional Factors That Control the Li-Ion Conductivity in LiPON Electrolytes. *Chemistry of Materials* **30**, 7077–7090 (2018).
39. Le Van-Jodin, L., Ducroquet, F., Sabary, F. & Chevalier, I. Dielectric properties, conductivity and Li⁺ ion motion in LiPON thin films. *Solid State Ionics* **253**, 151–156 (2013).
40. Balaish, M. *et al.* Processing thin but robust electrolytes for solid-state batteries. *Nat Energy* **6**, 227–239 (2021).
41. Wang, Y. *et al.* Suppression of Electrochemical and Chemical Degradation of Li₁₀GeP₂S₁₂ by an Elastomeric Artificial Solid Electrolyte Interphase. *ACS Appl. Energy Mater.* **6**, 8266–8276 (2023).
42. Sastre, J. *et al.* Lithium Garnet Li₇La₃Zr₂O₁₂ Electrolyte for All-Solid-State Batteries: Closing the Gap between Bulk and Thin Film Li-Ion Conductivities. *Adv Materials Inter* **7**, 2000425 (2020).
43. Luo, S. *et al.* Growth of lithium-indium dendrites in all-solid-state lithium-based batteries with sulfide electrolytes. *Nat Commun* **12**, 6968 (2021).

44. Pfenninger, R., Struzik, M., Garbayo, I., Stilp, E. & Rupp, J. L. M. A low ride on processing temperature for fast lithium conduction in garnet solid-state battery films. *Nat Energy* **4**, 475–483 (2019).
45. Butler, K. T., Sai Gautam, G. & Canepa, P. Designing interfaces in energy materials applications with first-principles calculations. *npj Comput Mater* **5**, 19 (2019).
46. Weiss, M. *et al.* Fast Charging of Lithium-Ion Batteries: A Review of Materials Aspects. *Advanced Energy Materials* **11**, 2101126 (2021).
47. Swift, M. W. *et al.* Predicting low-impedance interfaces for solid-state batteries. *Current Opinion in Solid State and Materials Science* **26**, 100990 (2022).
48. Swift, M. W. & Qi, Y. First-Principles Prediction of Potentials and Space-Charge Layers in All-Solid-State Batteries. *Phys. Rev. Lett.* **122**, 167701 (2019).
49. Luntz, A. C., Voss, J. & Reuter, K. Interfacial Challenges in Solid-State Li Ion Batteries. *J. Phys. Chem. Lett.* **6**, 4599–4604 (2015).
50. Kato, Y. *et al.* All-Solid-State Batteries with Thick Electrode Configurations. *J. Phys. Chem. Lett.* **9**, 607–613 (2018).
51. Froboese, L., Sichel, J. F. V. D., Loellhoeffel, T., Helmers, L. & Kwade, A. Effect of Microstructure on the Ionic Conductivity of an All Solid-State Battery Electrode. *J. Electrochem. Soc.* **166**, A318–A328 (2019).
52. Zhu, C., Usiskin, R. E., Yu, Y. & Maier, J. The nanoscale circuitry of battery electrodes. *Science* **358**, eaao2808-10 (2017).
53. Wang, Y. *et al.* Lithium and lithium ion batteries for applications in microelectronic devices: A review. *Journal of Power Sources* **286**, 330–345 (2015).

54. Lobe, S., Bauer, A., Uhlenbruck, S. & Fattakhova-Rohlfing, D. Physical Vapor Deposition in Solid-State Battery Development: From Materials to Devices. *Advanced Science* **8**, 2002044 (2021).
55. Blomgren, G. E. The Development and Future of Lithium Ion Batteries. *Journal of The Electrochemical Society* **164**, A5019–A5025 (2017).
56. Bates, J. B., Dudney, N. J., Neudecker, B., Ueda, A. & Evans, C. D. Thin-film lithium and lithium-ion batteries. *Solid State Ionics* **135**, 33–45 (2000).
57. Rubloff, G. W., Kozen, A. C. & Bok Lee, S. From nanoscience to solutions in electrochemical energy storage. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* **31**, 058503 (2013).
58. Noked, M. *et al.* Electrochemical Thin Layers in Nanostructures for Energy Storage. *Accounts of Chemical Research* **49**, 2336–2346 (2016).
59. Dudney, N. J. Thin Film Micro-Batteries. *ECS Interface* **17**, 44–48 (2008).
60. Chen, R., Li, Q., Yu, X., Chen, L. & Li, H. Approaching Practically Accessible Solid-State Batteries: Stability Issues Related to Solid Electrolytes and Interfaces. *Chem. Rev.* **120**, 6820–6877 (2020).
61. Boaretto, N. *et al.* Lithium solid-state batteries: State-of-the-art and challenges for materials, interfaces and processing. *Journal of Power Sources* **502**, 229919 (2021).
62. Baggetto, L., Niessen, R. A. H., Roozeboom, F. & Notten, P. H. L. High Energy Density All-Solid-State Batteries: A Challenging Concept Towards 3D Integration. *Adv Funct Materials* **18**, 1057–1066 (2008).

63. Zhu, Y. *et al.* Lithium-film ceramics for solid-state lithionic devices. *Nature Reviews Materials* **6**, 313–331 (2021).
64. Lim, H.-D. *et al.* A review of challenges and issues concerning interfaces for all-solid-state batteries. *Energy Storage Materials* **25**, 224–250 (2020).
65. Kerman, K., Luntz, A., Viswanathan, V., Chiang, Y.-M. & Chen, Z. Review—Practical Challenges Hindering the Development of Solid State Li Ion Batteries. *J. Electrochem. Soc.* **164**, A1731–A1744 (2017).
66. Pearse, A. J. *et al.* Nanoscale Solid State Batteries Enabled by Thermal Atomic Layer Deposition of a Lithium Polyphosphazene Solid State Electrolyte. *Chem. Mater.* **29**, 3740–3753 (2017).
67. Bates, J., Gruzalski, G., Dudney, N., Luck, C. & Yu, X. Rechargeable thin-film lithium batteries. *Solid State Ionics* **70–71**, 619–628 (1994).
68. Pearse, A. *et al.* Three-Dimensional Solid-State Lithium-Ion Batteries Fabricated by Conformal Vapor-Phase Chemistry. *ACS Nano* **12**, 4286–4294 (2018).
69. Arthur, T. S. *et al.* Three-dimensional electrodes and battery architectures. *MRS Bull.* **36**, 523–531 (2011).
70. Long, J. W., Dunn, B., Rolison, D. R. & White, H. S. Three-dimensional battery architectures. *Chemical Reviews* **104**, 4463–4492 (2004).
71. Kim, N. *et al.* On-Wafer Wide-Pore Anodic Aluminum Oxide. *J. Electrochem. Soc.* **170**, 063507 (2023).
72. Gillette, E. I., Kim, N., Rubloff, G. W. & Lee, S. B. Interconnected mesoporous V₂O₅ electrode: Impact on lithium ion insertion rate. *Physical Chemistry Chemical Physics* **18**, 30605–30611 (2016).

73. Talin, A. A. *et al.* Fabrication, Testing, and Simulation of All-Solid-State Three-Dimensional Li-Ion Batteries. *ACS Appl. Mater. Interfaces* **8**, 32385–32391 (2016).
74. Gillette, E. *et al.* Anodization control for barrier-oxide thinning and 3D interconnected pores and direct electrodeposition of nanowire networks on native aluminium substrates. *Phys. Chem. Chem. Phys.* **17**, 3873–3879 (2015).
75. Liu, C. *et al.* An all-in-one nanopore battery array. *Nature Nanotech* **9**, 1031–1039 (2014).
76. Hart, R. W., White, H. S., Dunn, B. & Rolison, D. R. 3-D Microbatteries. *Electrochemistry Communications* **5**, 120–123 (2003).
77. Kim, N. *et al.* Impact of pore size, interconnections, and dynamic conductivity on the electrochemistry of vanadium pentoxide in well defined porous structures. *Phys. Chem. Chem. Phys.* **20**, 29708–29716 (2018).
78. Liu, C., Kim, N., Rubloff, G. W. & Lee, S. B. High performance asymmetric V₂O₅-SnO₂ nanopore battery by atomic layer deposition. *Nanoscale* **9**, 11566–11573 (2017).
79. Yu, C. *et al.* Accessing the bottleneck in all-solid state batteries, lithium-ion transport over the solid-electrolyte-electrode interface. *Nat Commun* **8**, 1086 (2017).
80. Lou, S. *et al.* Interface Issues and Challenges in All-Solid-State Batteries: Lithium, Sodium, and Beyond. *Advanced Materials* **33**, 2000721 (2021).
81. Xiao, Y. *et al.* Understanding interface stability in solid-state batteries. *Nat Rev Mater* **5**, 105–126 (2019).

82. Zehiri, B. *et al.* Revealing the role of the cathode–electrolyte interface on solid-state batteries. *Nat. Mater.* **20**, 1392–1400 (2021).
83. Lewis, J. A., Tipples, J., Cortes, F. J. Q. & McDowell, M. T. Chemo-Mechanical Challenges in Solid-State Batteries. *Trends in Chemistry* **1**, 845–857 (2019).
84. Chen, K. *et al.* Effect of introducing interlayers into electrode/electrolyte interface in all-solid-state battery using sulfide electrolyte. *Solid State Ionics* **327**, 150–156 (2018).
85. Fuller, E. J. *et al.* Spatially Resolved Potential and Li-Ion Distributions Reveal Performance-Limiting Regions in Solid-State Batteries. *ACS Energy Lett.* **6**, 3944–3951 (2021).
86. Pervez, S. A., Cambaz, M. A., Thangadurai, V. & Fichtner, M. Interface in Solid-State Lithium Battery: Challenges, Progress, and Outlook. *ACS Appl. Mater. Interfaces* **11**, 22029–22050 (2019).
87. Gong, C. *et al.* Surface/Interface Effects on High-Performance Thin-Film All-Solid-State Li-Ion Batteries. *ACS Appl. Mater. Interfaces* **7**, 26007–26011 (2015).
88. Zhu, Y., He, X. & Mo, Y. First principles study on electrochemical and chemical stability of solid electrolyte–electrode interfaces in all-solid-state Li-ion batteries. *J. Mater. Chem. A* **4**, 3253–3266 (2016).
89. Famprikis, T., Canepa, P., Dawson, J. A., Islam, M. S. & Masquelier, C. Fundamentals of inorganic solid-state electrolytes for batteries. *Nat. Mater.* **18**, 1278–1291 (2019).
90. Kroemer, H. Nobel Lecture: Quasielectric fields and band offsets: teaching electrons new tricks. *Rev. Mod. Phys.* **73**, 783–793 (2001).

91. Ferrari, V. C., Kim, N. S., Lee, S. B., Rubloff, G. W. & Stewart, D. M. Co-sputtering of lithium vanadium oxide thin films with variable lithium content to enable advanced solid-state batteries. *J. Mater. Chem. A* **10**, 12518–12531 (2022).
92. Futscher, M. H. *et al.* Monolithically-stacked thin-film solid-state batteries. *Commun Chem* **6**, 110 (2023).
93. Wang, Z. *et al.* In Situ STEM-EELS Observation of Nanoscale Interfacial Phenomena in All-Solid-State Batteries. *Nano Lett.* **16**, 3760–3767 (2016).
94. Cheng, D. *et al.* Unveiling the Stable Nature of the Solid Electrolyte Interphase between Lithium Metal and LiPON via Cryogenic Electron Microscopy. *Joule* **4**, 2484–2500 (2020).
95. Qi, Y., Swift, M. W., Fuller, E. J. & Talin, A. A. Interface potentials inside solid-state batteries: Origins and implications. *MRS Bulletin* **48**, 1239–1246 (2023).
96. Ogihara, N., Itou, Y., Sasaki, T. & Takeuchi, Y. Impedance Spectroscopy Characterization of Porous Electrodes under Different Electrode Thickness Using a Symmetric Cell for High-Performance Lithium-Ion Batteries. *J. Phys. Chem. C* **119**, 4612–4619 (2015).
97. Momma, T., Yokoshima, T., Nara, H., Gima, Y. & Osaka, T. Distinction of impedance responses of Li-ion batteries for individual electrodes using symmetric cells. *Electrochimica Acta* **131**, 195–201 (2014).
98. Huang, J., Li, Z. & Zhang, J. Dynamic electrochemical impedance spectroscopy reconstructed from continuous impedance measurement of single frequency during charging/discharging. *Journal of Power Sources* **273**, 1098–1102 (2015).

99. Teo, L., Subramanian, V. R. & Schwartz, D. T. Dynamic Electrochemical Impedance Spectroscopy of Lithium-ion Batteries: Revealing Underlying Physics through Efficient Joint Time-Frequency Modeling. *J. Electrochem. Soc.* **168**, 010526 (2021).
100. Choi, Y. & Pyun, S. Effects of intercalation-induced stress on lithium transport through porous LiCoO₂ electrode. *Solid State Ionics* **99**, 173–183 (1997).
101. Watanabe, H., Omoto, S., Hoshi, Y., Shitanda, I. & Itagaki, M. Electrochemical impedance analysis on positive electrode in lithium-ion battery with galvanostatic control. *Journal of Power Sources* **507**, 230258 (2021).
102. Murbach, M. D., Hu, V. W. & Schwartz, D. T. Nonlinear Electrochemical Impedance Spectroscopy of Lithium-Ion Batteries: Experimental Approach, Analysis, and Initial Findings. *J. Electrochem. Soc.* **165**, A2758–A2765 (2018).
103. Koerver, R. *et al.* Redox-active cathode interphases in solid-state batteries. *J. Mater. Chem. A* **5**, 22750–22760 (2017).
104. Meddings, N. *et al.* Application of electrochemical impedance spectroscopy to commercial Li-ion cells: A review. *Journal of Power Sources* **480**, 228742 (2020).
105. Gabersček, M. Understanding Li-based battery materials via electrochemical impedance spectroscopy. *Nat Commun* **12**, 6513 (2021).
106. Nara, H., Yokoshima, T. & Osaka, T. Technology of electrochemical impedance spectroscopy for an energy-sustainable society. *Current Opinion in Electrochemistry* **20**, 66–77 (2020).
107. Huggins, R. A. Simple method to determine electronic and ionic components of the conductivity in mixed conductors a review. *Ionics* **8**, 300–313 (2002).

108. Randles, J. E. B. Kinetics of rapid electrode reactions. *Discuss. Faraday Soc.* **1**, 11 (1947).
109. Orazem, M. E. *et al.* Dielectric Properties of Materials Showing Constant-Phase-Element (CPE) Impedance Response. *J. Electrochem. Soc.* **160**, C215–C225 (2013).
110. Ahuja, K. *et al.* Ultra-thin on-chip ALD LiPON capacitors for high frequency application. *Journal of Power Sources* **575**, 233056 (2023).
111. Kadri, E. *et al.* Ac conductivity and dielectric behavior of a-Si:H/c-Si_{1-y}Ge_y/p-Si thin films synthesized by molecular beam epitaxial method. *Journal of Alloys and Compounds* **705**, 708–713 (2017).
112. Sallaz, V., Oukassi, S., Voiron, F., Salot, R. & Berardan, D. Assessing the potential of LiPON-based electrical double layer microsupercapacitors for on-chip power storage. *Journal of Power Sources* **451**, 227786 (2020).
113. Gaabour, L. H. Study of the structural, AC electrical conductivity, electric modulus, and dielectric properties of novel PVDF/LiCoO₂ nanocomposites for Li-ion batteries. *AIP Advances* **11**, 095114 (2021).
114. Santhanagopalan, D. *et al.* Interface Limited Lithium Transport in Solid-State Batteries. *J. Phys. Chem. Lett.* **5**, 298–303 (2014).
115. Nuwayhid, R. B. *et al.* Dynamic Electrode–Electrolyte Intermixing in Solid-State Sodium Nano-Batteries. *ACS Appl. Mater. Interfaces* **15**, 24271–24283 (2023).
116. Delluva, A. A., Dudoff, J., Teeter, G. & Holewinski, A. Cathode Interface Compatibility of Amorphous LiMn₂O₄ (LMO) and Li₇La₃Zr₂O₁₂ (LLZO)

- Characterized with Thin-Film Solid-State Electrochemical Cells. *ACS Appl. Mater. Interfaces* **12**, 24992–24999 (2020).
117. Warecki, Z. *et al.* Simultaneous Solid Electrolyte Deposition and Cathode Lithiation for Thin Film Batteries and Lithium Iontronic Devices. *ACS Energy Lett.* **9**, 2065–2074 (2024).
118. Chen, C. *et al.* Interface Aspects in All-Solid-State Li-Based Batteries Reviewed. *Advanced Energy Materials* **11**, 2003939 (2021).
119. Gabersček, M. Impedance spectroscopy of battery cells: Theory versus experiment. *Current Opinion in Electrochemistry* **32**, 100917 (2022).
120. Gaddam, R. R., Katzenmeier, L., Lamprecht, X. & Bandarenka, A. S. Review on physical impedance models in modern battery research. *Phys. Chem. Chem. Phys.* **23**, 12926–12944 (2021).
121. Nelms, R. M. & Tatarchuk, B. J. Using a Debye polarization cell to predict double-layer capacitor performance. *IEEE Transactions on Industry Applications* **37**, 4–9 (2001).
122. Le Van-Jodin, L. *et al.* Role of the chemical composition and structure on the electrical properties of a solid state electrolyte: Case of a highly conductive LiPON. *Electrochimica Acta* **259**, 742–751 (2018).
123. Tsuruoka, T., Su, J. & Terabe, K. A Voltage-Controlled Oscillator Using Variable Capacitors with a Thin Dielectric Electrolyte Film. *ACS Appl. Electron. Mater.* **2**, 2788–2797 (2020).

124. López-Grande, A., Mather, G. C. & Muñoz, F. Thermodynamic calculation of the ionic conductivity of LiPON glasses and solid electrolytes. *J. Mater. Chem. A* **11**, 12282–12296 (2023).
125. Fu, Z.-W. *et al.* High- k lithium phosphorous oxynitride thin films. *Applied Physics Letters* **83**, 5008–5010 (2003).
126. Aizawa, Y. *et al.* In situ electron holography of electric potentials inside a solid-state electrolyte: Effect of electric-field leakage. *Ultramicroscopy* **178**, 20–26 (2017).
127. Swift, M. W., Swift, J. W. & Qi, Y. Modeling the electrical double layer at solid-state electrochemical interfaces. *Nat Comput Sci* **1**, 212–220 (2021).
128. Jamnik, J. & Maier, J. Treatment of the Impedance of Mixed Conductors Equivalent Circuit Model and Explicit Approximate Solutions. *J. Electrochem. Soc.* **146**, 4183–4188 (1999).
129. Navone, C., Baddour-Hadjean, R., Pereira-Ramos, J. P. & Salot, R. A kinetic study of electrochemical lithium insertion into oriented V_2O_5 thin films prepared by rf sputtering. *Electrochimica Acta* **53**, 3329–3336 (2008).
130. West, W. C., Whitacre, J. F. & Lim, J. R. Chemical stability enhancement of lithium conducting solid electrolyte plates using sputtered LiPON thin films. *Journal of Power Sources* **126**, 134–138 (2004).
131. Shibuya, M., Yamamura, S., Matsue, T. & Uchida, I. *In Situ* Conductivity Measurements during Lithium Intercalation/Deintercalation on V_2O_5 Thin Film by Using Interdigitated Microarray Electrodes. *Chemistry Letters* **24**, 749–750 (1995).

132. Levy, Z. *et al.* Lithium Spatial Distribution and Split-Off Electronic Bands at Nanoscale V₂O₅/LiPON Interfaces. *ACS Appl. Energy Mater.* **6**, 4538–4548 (2023).
133. Tian, H.-K., Chakraborty, A., Talin, A. A., Eisenlohr, P. & Qi, Y. Evaluation of The Electrochemo-Mechanically Induced Stress in All-Solid-State Li-Ion Batteries. *J. Electrochem. Soc.* **167**, 090541 (2020).
134. Hood, Z. D. *et al.* Elucidating Interfacial Stability between Lithium Metal Anode and Li Phosphorus Oxynitride via *In Situ* Electron Microscopy. *Nano Lett.* **21**, 151–157 (2021).
135. Wang, S., Xu, H., Li, W., Dolocan, A. & Manthiram, A. Interfacial Chemistry in Solid-State Batteries: Formation of Interphase and Its Consequences. *J. Am. Chem. Soc.* **140**, 250–257 (2018).
136. Horopanitis, E. E. *et al.* Preparation by e-gun evaporation and study of cathode-electrolyte thin-film bi-layers for solid state microbatteries. *Journal of Solid State Electrochemistry* **8**, 55–58 (2003).
137. Qi, Y. Measuring is believing. *Nat Energy* **8**, 1307–1308 (2023).