White Paper

Materials Testing & Research

Spectroelectrochemistry Using Agilent UV-Vis-NIR Spectrophotometers

Advanced material studies published by global research groups

Introduction

Spectroelectrochemistry (SEC) combines electrochemistry and spectroscopy, creating a powerful analytical and versatile tool that is used in both research and industrial applications. UV-Vis- or UV-Vis near-infrared (NIR)-based SEC methods offer a path to a deeper understanding of electrochemical processes such as electrocatalysis and photoelectrocatalysis. They also enable the development of new materials and technologies. By analyzing spectral changes at different applied potentials, SEC enables real-time observation of reactions as they occur. The data allow researchers to explore the progression of reaction pathways and identify key intermediates, facilitating the development of more efficient and sustainable catalytic processes.[1]

Spectroelectrochemistry

SEC integrates electrochemistry and spectroscopy into a single tool. During the experiment, an electric potential, which is applied to the sample, is changed incrementally. After each change of the applied potential, a UV-Vis or UV-Vis-NIR spectrum is recorded.[1,2] Figure 1 shows a schematic of the setup commonly used in SEC experiments.

The key components of every SEC experiment are as follows:

- The spectrophotometer
- The potentiostat
- The electrochemical cell

The spectrophotometer

The spectrophotometer is central to the SEC setup, as it measures the optical properties of the sample, such as absorbance or transmittance of light, as the electrochemical reactions occur. The choice of spectrophotometer depends on the wavelength range required for the study. Commonly, UV-Vis spectrophotometers are used; however, depending on the application, UV-Vis-NIR spectrophotometers may be employed.

The spectrophotometer's light source generates a beam that passes through the sample in the electrochemical cell. The light interacts with the sample and any changes in the optical properties are detected by the spectrophotometer's detector. The spectrophotometer can operate in different modes, such as absorbance, transmittance, or reflectance, depending on the type of electrochemical cell and sample under investigation. A fiber optic coupler can also be used to conduct measurements outside of the sample compartment.

The potentiostat

The potentiostat plays a crucial role in SEC by controlling the potential at the working electrode in the electrochemical cell. Depending on the actual potentiostat model used, the applied potential is either changed manually or through a software interface.

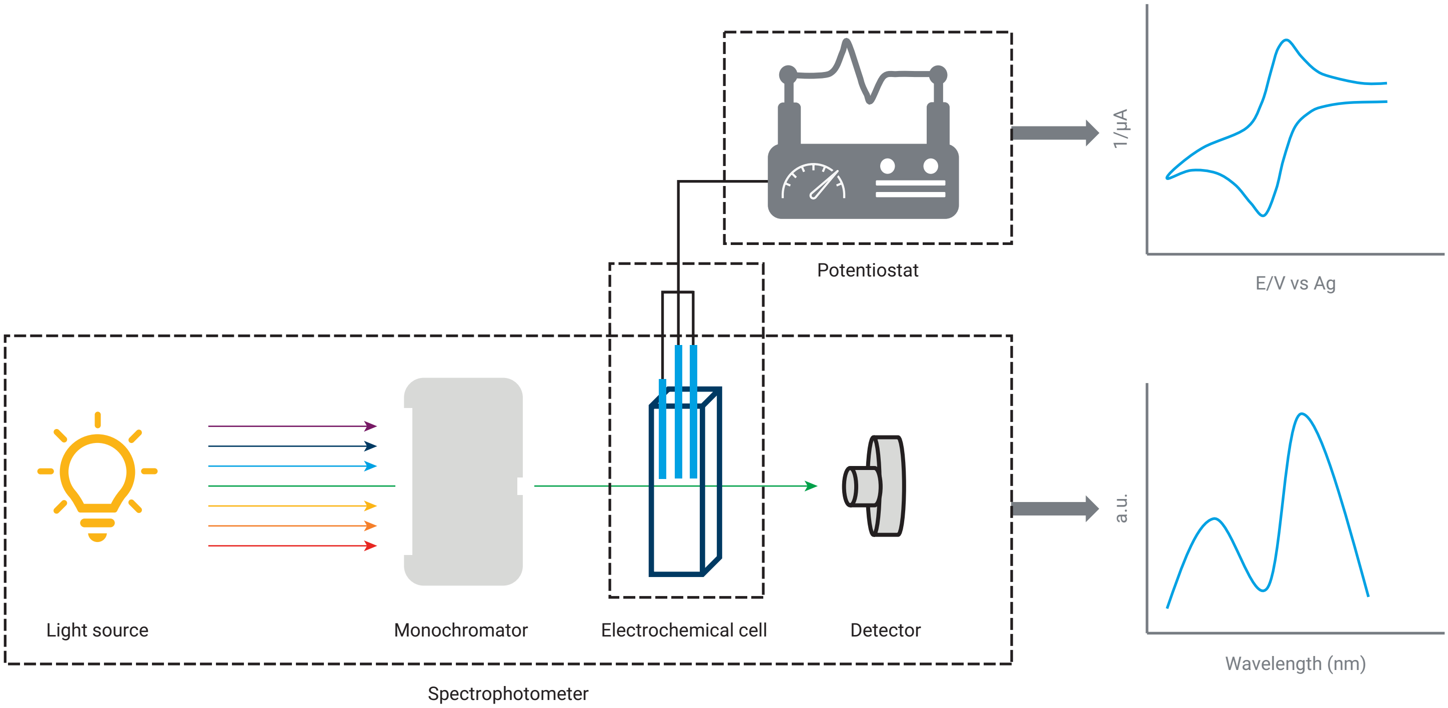

Figure 1. SEC experimental setup.

The electrochemical cell

The electrochemical cell in a SEC setup (shown in Figure 2) is a specialized component designed to integrate with the spectrophotometer. Its main function is to house the sample and facilitate the electrochemical reaction while allowing optical measurements. The composition of the cell includes several critical parts including:

1. **Electrodes**[2]
   - **Working electrode (WE)**: The WE is where the electrochemical reaction of interest occurs. For SEC, this electrode is typically made from a transparent conductive material such as indium tin oxide or fluorine-doped tin oxide coated onto glass or quartz, or conductive metal meshes such as gold or platinum. The transparency is essential for allowing the spectrophotometer's light to pass through the electrode and interact with the sample.
   - **Counter electrode (CE)**: positioned opposite the WE in the cell, the CE completes the circuit and maintains a charge balance during the electrochemical reaction. This electrode is usually made from inert materials such as platinum or gold.
   - **Reference electrode (RE)**: The RE provides a stable potential against which the working electrode's potential is measured. A common choice is the silver/silver chloride (Ag/AgCl) electrode, but others such as the saturated calomel electrode may also be used depending on the electrolyte and sample.

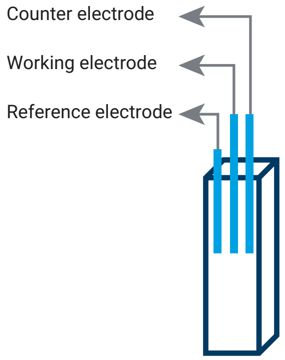

Figure 2. Setup of the three types of electrode in an electrochemical cell.

2. **Electrolyte solution**

The electrolyte is a crucial component of the cell, as it provides the ionic medium necessary for the electrochemical reaction. In SEC, the electrolyte often comprises a thin layer placed between the working electrode and a transparent counter electrode or a reflective surface, depending on the cell design. The electrolyte composition can vary widely, depending on the specific reaction being studied, but it typically includes a solvent and supporting electrolyte to ensure conductivity.

3. **Cell types**
   - **Transmission cells**: Designed for liquid samples, these cells allow light to pass through the sample and be detected on the other side. The WE in a transmission cell is typically a transparent electrode, enabling the spectrophotometer to measure changes in absorbance as the reaction progresses. Transmission cells are ideal for studying homogeneous solutions or reactions occurring in liquid phases.
   - **Reflectance cells**: In these cells, the light reflects off the surface of the sample before being detected. These versatile cells can handle liquid, solid, or thin-film samples. Reflectance measurements are particularly useful for studying surface reactions, thin films, and solid-state materials.
   - **Optically transparent thin-layer electrochemical (OTTLE) cells**: OTTLE cells are specialized cells where the WE is coated with a very thin layer of electrolyte. This design allows for high-resolution spectroscopic measurements and is particularly effective for studying rapid kinetics and short-lived intermediates in electrochemical reactions. The thin layer ensures that the entire sample is within the optical path, providing high sensitivity and rapid response times.

In a SEC setup, the electrochemical cell is carefully aligned with the spectrophotometer's optical path to ensure accurate measurements. The WE is positioned so that the light beam either passes directly through (in transmission cells) or reflects off (in reflectance cells) the electrode surface. The alignment of the WE is critical, as any misalignment could result in inaccurate readings or loss of sensitivity.

In OTTLE cells, a transparent WE is typically sandwiched between two transparent plates, with a thin layer of electrolyte confined between them. This setup minimizes the distance the light must travel through the sample, enhancing the resolution and sensitivity of the measurement. The cell design also allows easy control of the applied potential or current, enabling precise studies of electrochemical processes.

Applications

SEC is used in various areas of research including the study of redox reactions, reaction mechanisms, and the detection of intermediates in electrochemical processes.

SEC setups are therefore invaluable in a wide range of applications, such as:

- **Battery research**: SEC is essential for understanding the behavior of short-lived species, critical information for improving battery performance.
- **Corrosion studies**: SEC provides detailed insights into the processes occurring at metal surfaces, aiding in corrosion prevention.

SEC also plays a crucial role in sensor development, helping to design highly selective and sensitive devices for environmental monitoring, food safety, and medical diagnostics.

Cary UV-Vis-NIR spectrophotometers

The Agilent Cary series offers a versatile range of spectrometers designed to meet diverse research needs with flexibility and scalability, including for SEC setups.

Both the Agilent Cary 60 and Cary 3500 UV-Vis spectrophotometers are equipped with a xenon flash lamp, minimizing sample photodegradation and ensuring rapid data acquisition. The Cary 60 UV-Vis is ideal for routine analysis and is compatible with a broad range of accessories. The Cary 3500 UV-Vis has a modular design featuring three modules—Compact, Flexible, and Multicell—and enables samples to be measured under varying temperature conditions and path lengths.

For advanced analyses, the Agilent Cary 4000 UV-Vis, Cary 5000, and 6000i UV-Vis-NIR, and Cary 7000 universal measurement spectrophotometers provide exceptional sensitivity and spectral resolution, covering both UV-Vis and NIR ranges.

Together, these instruments provide comprehensive solutions for a wide array of scientific applications in the SEC space, including advanced research projects.

Spectroelectrochemistry research applications using UV-Vis/NIR

Research groups located around the world have used Agilent UV-Vis or UV-Vis-NIR instrumentation in SEC setups, as summarized in the following examples.

Redox-state kinetics in water-oxidation IrOx electrocatalysts measured by operando spectroelectrochemistry[3]

In this study, Carlota Bozal-Ginesta and co-researchers employed time-resolved operando spectroelectrochemistry to investigate the redox-state kinetics of hydrous iridium oxide (IrOx) films, renowned as the best oxygen evolution electrocatalysts in acidic environments. Using a Cary 60 UV-Vis, the absorbance of the sample was monitored under different applied potentials. The research identified and quantified three redox species: Ir^{3+}, $Ir^{3}.x^{+}$, and Ir^{4+}, along with the potential-dependent $Ir^{4}.y^{+}$ species. It was discovered that the generation of $Ir^{4}.y^{+}$ states is the potential-determining step for catalytic water oxidation, while Ir^{4+} states drive hydrogen peroxide oxidation. The kinetics for water oxidation accelerated markedly with increasing potential, while the kinetics for hydrogen peroxide oxidation remained constant, indicating a first-order reaction mechanism for the latter. This innovative approach provided unique kinetic insights into IrOx electrocatalytic mechanisms, revealing a higher-order reaction mechanism involving the cooperative interaction of multiple $Ir^{4}.y^{+}$ states for water oxidation.

The syntheses, structures, and spectroelectrochemical properties of 6-oxo-verdazyl derivatives bearing surface anchoring groups[4]

In this study, a series of 6-oxo-verdazyl radicals, functionalized at the 1- and 5-positions with tolyl, thioanisole, and iodophenyl groups, were synthesized using established methods. The verdazyl core was further elaborated with π-conjugated ethynyl groups through Sonogashira cross-coupling of terminal alkynes with a diiodo precursor. The radicals' structural and electronic properties were probed using EPR spectroscopy, single-crystal X-ray diffraction, cyclic voltammetry, and UV-Vis-NIR spectroscopy. Optical spectroscopy was performed using a Cary 5000 UV-Vis-NIR spectrophotometer, while spectroelectrochemical studies were conducted with the same instrument in conjunction with an EmStat3+ potentiostat. Cyclic voltammetry revealed chemically and electrochemically reversible redox behavior within accessible windows, enabling detailed spectroelectrochemical analysis of the closed-shell cationic and anionic states. These experimental observations were complemented by (TD-)DFT calculations, providing insights into the electronic structure and charge-transfer characteristics of the of 6-oxo-verdazyl radicals.

Neutral and anion species of quinoidal thienothiophene diketopyrrolopyrroles display a common aggregation mode[5]

This study explored two molecular triads, DPP-TT-CN and DPP-TT-PhO, incorporating the diketopyrrolopyrrole (DPP) unit into a quinoidal thienothiophene structure, end-capped with dicyanomethylene or phenoxyl groups. UV-Vis-NIR and infrared spectroelectrochemical techniques, combined with theoretical calculations, revealed the formation of H-aggregates in both neutral and charged species. Variable temperature UV-Vis-NIR electronic absorption spectra were recorded using a Cary 5000 UV-Vis-NIR spectrophotometer with a wavelength range of 175 to 3,300 nm. The reduction of DPP-TT-CN produced a series of absorption features, including bands at 1,006, 1,629, and 816 nm, indicative of radical anions and dimeric aggregates. Lowering the temperature shifted the absorption to 1,208 nm, confirming the presence of aggregated species. Further reduction led to the formation of a dianion species with a band at 754 nm, which was redshifted compared to typical dianion bands in similar compounds. These findings suggest that the DPP unit plays a significant role in modulating the electronic properties of the molecule. The study also investigated the concentration-dependent aggregation of radical anions, showing that higher concentrations promote the formation of dimers and aggregates. These results highlighted the crucial role of excitonic coupling in understanding the electronic structure of these species. Overall, this work enhances the understanding of molecular aggregation in organic π-conjugated chromophores, offering insights for the design of advanced materials in supramolecular chemistry.

Electrochemical deposition of polyviologen-reduced graphene oxide nanocomposite thin films[6]

In this study, Nianxing Wang and colleagues synthesized thin composite films of polyviologen (PV) and reduced graphene oxide (rGO) through a one-step electrochemical polymerization technique. The monomer (based on cyanopyridine) and graphene oxide flakes were dissolved in an ionic liquid, followed by electrochemical reduction. This process resulted in the formation of a branched PV film with rGO flakes reduced and immobilized within the PV network. The composite films were characterized using cyclic voltammetry, electrochemical impedance spectroscopy, UV-Vis, FT-IR, Raman spectroscopy, and SEM. The findings confirmed successful composite film formation, with enhanced redox properties attributed to the presence of graphene. The method, noted for its simplicity and use of inexpensive materials, presents a simple approach for fabricating thin composite films applicable in electrochromic devices and sensors. The UV-Vis spectra of PV and PV-rGO films were recorded between 300 and 1,000 nm using a Cary 60 UV-Vis, with measurements taken across a potential range between 0.0 and –1.0 V.

Tuning electron transfer coupling and exchange interaction in bis-triarylamine radical cations and dications by bridge electron density[7]

In this study, the authors examined how the electron density of a bridge between two redox centers affects intervalence charge transfer (IVCT) and magnetic superexchange. They focused on bridged bis-triarylamine mono- and di-cations, using a 2,7-fluorenyl bridge with modifications at the 9-position. For the mixed-valence monocations, they observed an IVCT band alongside an absorption band linked to electron transfer from the bridge to the triarylamine radical cations. This allowed for the determination of electron transfer couplings using the three-state generalized Mulliken–Hush theory. The results showed that electronic coupling improved as bridge state energy decreased. For the dicationic diradicals, both experimental and quantum chemical methods were employed to find the singlet–triplet gap (exchange interaction). It was found that antiferromagnetic coupling increased as bridge state energy decreased due to electron-donating substituents. The analysis of molecular orbitals suggested an inverse relationship between ferromagnetic coupling and the square of the bridge energy, aligning with experimental findings. Spectroelectrochemical absorption measurements were recorded in reflection mode using a custom-made cell with a platinum working electrode, a platinum counter electrode, and a leak-free Ag/AgCl reference electrode, connected to a Cary 5000 UV-Vis-NIR spectrophotometer. This investigation highlighted the considerable influence of bridge state energy on both electron transfer and magnetic exchange interactions, providing guidelines for modifying the properties of electronically coupled organic redox systems through adjustments in bridge electron density.

Effects of supporting electrolytes on spectroelectrochemical and electrochromic properties of polyaniline-poly(styrene sulfonic acid) and poly(ethylenedioxythiophene)-poly(styrene sulfonic acid)-based electrochromic device[8]

In this study, the electrochromic devices using PMMA-PC-$LiClO_2$-SiO_2 electrolytes were investigated for their electrochemical performance and electrochromic properties. The electrolyte films were synthesized via a solution-casting method, achieving a uniform morphology characterized by scanning electron microscopy (SEM). The ionic conductivity of the PMMA-PC-$LiClO_4$-SiO_2 electrolyte was measured using AC impedance spectroscopy, revealing a maximum conductivity of 1.08×10^{-3} S/cm at room temperature. Cyclic voltammetry (CV) indicated that the electrochromic device exhibits a significant redox response, demonstrating the ability to switch between transparent and colored states upon applied voltage. Spectroelectrochemical studies were conducted using a Cary 60 UV-Vis spectrophotometer to capture in situ UV-Visible spectra in time course mode, showing a strong absorption peak in the visible region upon reduction, which confirmed the electrochromic effect. The stability of the devices was evaluated through prolonged cycling tests, where minimal degradation of color change was observed after 1,000 cycles, indicating excellent durability. These findings highlight the potential of PMMA-PC-$LiClO_4$-SiO_2 electrolytes in the development of efficient and durable electrochromic devices.

In operando scanning electron microscopy and ultraviolet–visible spectroscopy studies of lithium/sulfur cells using all solid-state polymer electrolyte[9]

In the study of lithium-sulfur (Li-S) cells using solid-state thin film polymer electrolytes, distinct UV-Vis absorption bands were observed at 250, 280, 325, 385, 420, and 480 nm. Unlike previous studies with liquid electrolytes, these bands were well-resolved, indicating a clearer identification of polysulfide species. The significant absorption peaks were correlated with specific sulfur species, with the 420 nm band showing opposite trends to the 320, 385, and 480 nm bands during charge and discharge cycles. Notably, a polysulfide shuttle mechanism was identified, particularly after prolonged discharge, resulting in increased concentrations of S_4^{2-}. The formation of polysulfides was analyzed as a function of time with a Cary 60 UV-Vis, revealing that $S_x^{2-}(4 \le x \le 6)$ species were present in the electrolyte during cycling. This study highlights the differences in charge and discharge mechanisms and the improved stability of the solid-state electrolyte compared to liquid systems, contributing to a better understanding of the polysulfide equilibrium and the charge hysteresis affecting battery efficiency.

Agilent Cary 60 UV-Vis Spectrophotometer

The Cary 60 UV-Vis spectrophotometer is a powerful tool for repetitive and routine analysis. It operates within the wavelength range of 190 to 1,100 nm and can be equipped with a comprehensive range of sampling accessories. It can perform measurements without any warm-up time or room light interference and eliminates sample photodegradation to ensure a correct answer every time. This tolerance of room light and the highly focused beam make the Cary 60 UV-Vis ideal for measurements outside the sample compartment using fiber optic probes.

The Cary 60 UV-Vis comes with a 10-year warranty on the Xenon flash lamp, and the Cary 60 UV-Vis has been independently audited and verified for its environmental impact and has received the ACT (Accountability, Consistency, and Transparency) label, published by My Green Lab.

Agilent Cary 3500 UV-Vis Spectrophotometer Series

The Cary 3500 Multicell and Compact UV-Vis spectrophotometers are versatile measurement tools known for their temperature control capabilities and ultra-fast data collection rate of 250 points per second.

The Cary 3500 Flexible UV-Vis spectrophotometer features a unique large sample compartment with small footprint for analyzing liquid samples that require long pathlength cuvettes, as well as characterizing solid samples. It operates effectively within the range of 190 to 1,100 nm.

The Cary 3500 UV-Vis is another recipient of the ACT, published by My Green Lab, and boasts a 10-year warranty on the Xenon flash lamp.

Agilent Cary 4000/5000/6000i/7000 UV-Vis (-NIR) Spectrophotometers

The high-end UV spectrophotometers are fitted with the ability to measure highly absorbing samples, as well as diffuse reflection and specular reflection, operating within the range of 175 to 3,300 nm.

With superb photometric performance in the 175 to 3,300 nm range using the latest generation of detectors (PbSmart, InGaAs, and sandwich), these systems have improved sensitivity and lowered stray light in the NIR, making them powerful tools for materials science research. The Agilent Cary 7000 universal measurement spectrophotometer (UMS) will satisfy all your solid sampling needs. The Cary 7000 instrument's multiangle specular reflectance and transmittance capabilities allow you to design experiments never before possible—expanding your research—while the automated reflectance and transmission will save you time and money.

Conclusion

The summaries of seven cutting-edge research projects outlined in this white paper have shown that Agilent UV-Vis and UV-Vis-NIR spectrophotometers play a critical role in advancing spectroelectrochemistry research. From exploring redox-state kinetics in electrocatalysts to investigating complex reduction behaviors in challenging environments, these instruments enable precise, real-time analysis of electrochemical reactions. The versatility and high sensitivity of the Agilent Cary series of spectrophotometers position them as indispensable tools in both fundamental and applied electrochemical research. Their integration into diverse studies underscores their capability to meet the rigorous demands of modern scientific inquiry.

References

1. Mesa, C. A.; Pastor, E.; Francàs, L. UV–Vis Operando Spectroelectrochemistry for (Photo)electrocatalysis: Principles and Guidelines, *Curr. Opin. Electrochem.* **2022**, *35*, 101098. DOI: 10.1016/j.coelec.2022.101098
2. León, L.; Mozo, J. D. Designing Spectroelectrochemical Cells: A Review, *TrAC* **2018**, *102*, 147–169. DOI: 10.1016/j.trac.2018.02.002
3. Bozal-Ginesta, C.; Rao, R. R.; Mesa, C. A.; Liu, X.; Hillman, S. A. J.; Stephens, I. E. L; Durrant, J. R. Redox-State Kinetics in Water-Oxidation IrOx Electrocatalysts Measured by Operando Spectro electrochemistry, *ACS Catalysis* **2021**, *11(24)*, 15,013–15,025. DOI: 10.1021/acscatal.1c03290
4. Kumar, V. J.; *et al.* The syntheses, Structures and Spectroelectrochemical Properties of 6-Oxo-Verdazyl Derivatives Bearing Surface Anchoring Groups. *J. Mater. Chem. C.* **2022**, *10*, 1,896–1,915. DOI: 10.1039/D1TC05495C
5. Moles Quintero, S.; *et al.* Neutral and Anion Species of Quinoidal Thienothiophene Diketopyrrolopyrroles Display a Common Aggregation Mode. *Chem. Eur. J.* **2024**. DOI: 10.1002/chem.202402094
6. Wang, N.; Lukáacs, Z.; Gadgil, B.; Damlin, P.; Janáky, C.; Kvarnström, C. Electrochemical Deposition of Polyviologen-Reduced Graphene Oxide Nanocomposite Thin Films, *Electrochim. Acta.* **2017**, *231*. DOI: 10.1016/j.electacta.2017.02.065
7. Euringer, L.; *et al.* Tuning Electron Transfer Coupling and Exchange Interaction in Bis-triarylamine Radical Cations and Dications by Bridge Electron Density. *J. Am. Chem. Soc.* **2024**. DOI: 10.1021/jacs.4c09221
8. Kuo, C.-W.; Chen, B.-K.; Li, W.-B.; Tseng, L.-Y.; Wu, T.-Y.; Tseng, C.-G.; Chen, H.-R.; Huang, Y.-C. Effects of Supporting Electrolytes on Spectroelectrochemical and Electrochromic Properties of Polyaniline-poly(styrene sulfonic acid) and Poly(ethylenedioxythiophene)-poly(styrene sulfonic acid)-based Electrochromic Device. *J. Chin. Chem. Soc.* **2014**. DOI: 10.1002/jccs.201300479
9. Marceau, H.; Kim, Chi-Su; Paolella, A.; Ladouceur, S.; Lagacé, M.; Chaker, M.; Vijh, A.; Guerfi, A.; Julien, C. M.; Mauger, A.; *et al.* In Operando Scanning Electron Microscopy And Ultraviolet–Visible Spectroscopy Studies Of Lithium/Sulfur Cells Using All Solid-State Polymer Electrolyte, *J. Power Sources* **2016**, *319*. DOI: 10.1016/j.jpowsour.2016.03.093.

Further information

UV-Vis Spectroscopy & Spectrophotometer FAQs

UV-Vis & UV-Vis-NIR Instrument Selection Guide

UV-Vis Applications Guide

www.agilent.com/chem/uv-vis-uv-vis-nir

DE-003142

Printed in the USA, December 20, 2024
5994-8001EN

Agilent
Trusted Answers