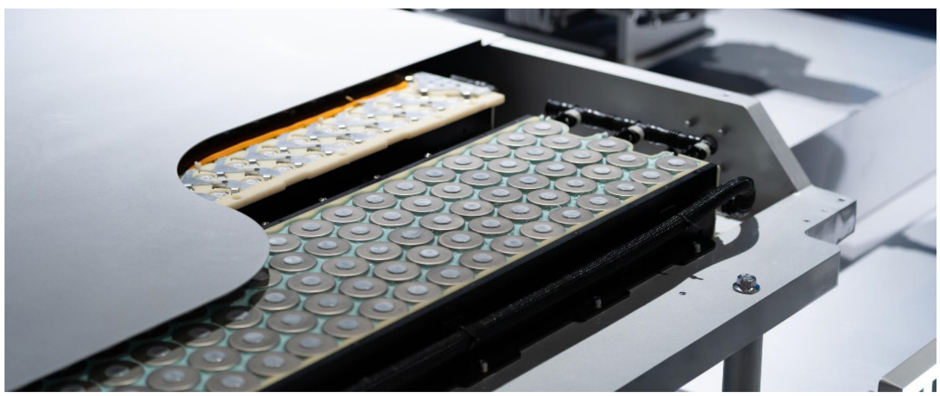
White Paper

# Advancing Research of Rechargeable Batteries Using Agilent UV-Vis Spectrophotometers

## Rechargeable battery studies published by global research groups



## Introduction

Rechargeable batteries are at the forefront of global discussions as an alternative to typical combustion engines, as they offer a cost-effective solution to reducing carbon emissions and dependance on fossil fuels. The focus of many research groups centers around alkali metals such as lithium, sodium, and potassium due to their high theoretical specific capacities and exceptionally low electrochemical potentials.[1] This white paper provides examples of how Agilent UV-Vis/NIR spectrophotometers have been used by leading research groups for the characterization of rechargeable battery materials and components.

## Agilent UV-Vis/NIR spectrophotometers

Agilent's range of UV-Vis/NIR spectrophotometers cater to a variety of analysis needs, from routine applications to high-end experiments (Table 1). UV-Vis/NIR instruments can perform a range of analyses in the rechargeable batteries space such as:[2,3]

- Quantitative analysis of electrolytes
- Qualitative analysis (materials characterization)
- Degradation studies
- Color measurements of electrolytes and other components
- Spectroelectrochemistry
- Band gap calculations
- Operando optical spectroscopy
- Leaching studies

A number of accessories are available to be paired with Agilent UV-Vis/NIR spectrophotometers for enhanced scalability, flexibility, cost efficiency, and measurement capability. Accessories such as the fiber optic dip probe provide a unique solution to analyzing volatile or moisture-sensitive rechargeable battery materials, such as lithium hexafluorophosphate ($LiPF_6$), in the controlled environment of a glovebox.

## Rechargeable battery research applications using UV-Vis/NIR

Research groups located around the world have used Agilent UV-Vis/NIR instrumentation as an integral solution for the analysis and characterization of various battery components, as summarized in the following examples.

### A Facile Method to Improve the Photocatalytic and Lithium-Ion Rechargeable Battery Performance of $TiO_2$ Nanocrystals[4]

Ting Xia and the research team have displayed that subjecting crystalline $TiO_2$ nanocrystals to a vacuum treatment at moderate temperatures and low vacuum levels can lead to significant alterations in their structural, optical, electronic, and chemical characteristics. Compared to untreated $TiO_2$ nanocrystals, these vacuum-treated counterparts exhibit notably enhanced photocatalytic activity and superior performance in storing lithium ions. Consequently, this innovative approach presents a promising avenue for enhancing the functionality of $TiO_2$ and other oxide nanocrystals for various practical applications. The reflectance spectra of the $TiO_2$ particles were measured using an Agilent Cary 60 UV-Vis spectrometer with an optical reflectance fiber unit, which revealed that vacuum-treated $TiO_2$ nanocrystals extended their absorption from UV into near-infrared.

### Lithium Bis(Trifluoromethanesulfonyl)imide Blended in Polyurethane Acrylate Photocurable Solid Polymer Electrolytes for Lithium-Ion Batteries[5]

Cristian Mendes-Felipe and collaborators formulated a UV-photocurable polyurethane acrylate (PUA) resin incorporating lithium bis(trifluoromethanesulfonyl)imide (LiTFSI). The conductivity levels enabled the application of the developed materials as photocurable solid polymer electrolytes (SPE) in Li/C-$LiFePO_4$ half-cells, resulting in a substantial battery discharge capacity. These findings, coupled with theoretical assessments of discharge capacity across various C-rates and temperatures for batteries using LiTFSI/PUA SPE underscore the potential of the developed photocurable SPE for lithium-ion battery (LIB) applications. Optical characterization of the pristine photo resin and the LiTFSI/PUA samples was characterized using ultraviolet-visible (UV-Vis) spectroscopy measurements. The UV-Vis spectroscopy was conducted using an Agilent Cary 60 spectrophotometer, covering the range from 200 to 800 nm with a sampling interval of 1 nm and 25 accumulation scans, and showed that the pristine photo resin presents the maximum light transmittance.

### Iodine-Containing Additive Engineering for Rejuvenating Inactive Lithium and Constructing Highly Stable Lithium Metal Anodes[6]

In their investigation, Wenchang Ma and colleagues conducted a series of redox reactions using the redox couple to effectively remove inactive lithium, thereby enhancing the capacity and Coulombic efficiency of the cell in a reversible manner. The capability of the redox couple to rejuvenate inactive lithium was confirmed through UV spectroscopy conducted on an Agilent Cary 3500 instrument, where signals were observed between 200 and 400 nm.

### Tuning the Azo Location in Conjugated Polymers Toward High-Performance Lithium-Ion Batteries[7]

Sen Zhang, *et al.* investigated how the positioning of azo units (para versus meta linkage, main chain versus side chain) within conjugated polymers influences electrochemical properties and battery performance. Both experimental and theoretical analyses highlight "redox-pendant" and "meta junction" as effective features for designing redox-conjugated polymers for superior energy storage capabilities. The practical viability of the resulting full battery to power an LED bulb was successfully demonstrated, highlighting its real-world application potential. This study offers valuable insights into structurally optimizing polymers for enhanced battery performance. UV-Vis absorption spectra from 250 to 700 nm were acquired using a Cary 3500 spectrophotometer. The spectra allowed the characterization of the polymers; two had identical peaks at 322 nm, while the third had a peak at 337 nm.

### Electrospun Core-Shell Microfiber Separator with Thermal-Triggered Flame-Retardant Properties for Lithium-Ion Batteries[8]

Kai Liu and colleagues investigated to determine whether encapsulating a flame retardant within a protective polymer shell could prevent its direct dissolution into the electrolyte, thereby mitigating potential adverse effects on battery performance. In the event of a thermal runaway in the lithium-ion battery, the protective polymer shell would melt in response to elevated temperatures, facilitating the release of the flame retardant. This mechanism effectively suppresses the combustion of highly flammable electrolytes. A UV-Vis absorbance spectrum was used to quantitatively monitor the triphenyl phosphate release behavior upon thermal triggering. TPP exhibits three explicit absorption bands whose peaks are located at 266, 260, and 255 nm. The spectra facilitate a quantitative estimate of the amount of TPP that has been released into the electrolyte. Measurements were performed using an Agilent Cary 6000i UV-Vis-NIR spectrophotometer from 210 nm to 330 nm.

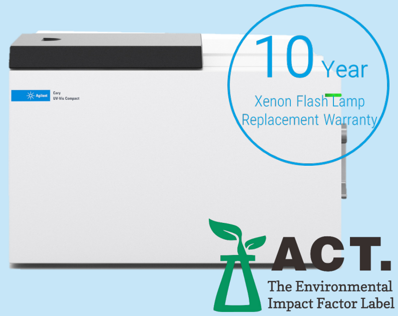
### Solvometallurgical Recovery of Cobalt from Lithium-Ion Battery Cathode Materials Using Deep-Eutectic Solvents[9]

In this work, a green, cost-effective, and safe approach is proposed by using a choline chloride-citric acid deep-eutectic solvent (DES) as a lixiviant. Aluminum and copper were evaluated as reducing agents for cobalt (III). After optimization, lithium and cobalt were quantitatively leached from $LiCoO_2$ in the presence of aluminum and copper. Copper was the most effective reducing agent for cobalt (III), so that no additional reducing agents or a pre-separation step were required. Copper (I), copper (II), and cobalt (II) chloride salts were dissolved in the DES with similar metal concentration as in the pregnant leach solution (PLS), followed by recording of the absorption spectra. These were hereafter compared with the recorded PLS spectra for qualitative analysis. A calibration curve was constructed by dissolving different amounts of cobalt (II) chloride in a 35 wt% water-diluted choline chloride solution for cobalt (II) chloride quantification in the DES. Qualitative and quantitative analysis of the pregnant leach solution was done by UV-Vis-NIR absorption spectroscopy with a Cary 6000i spectrophotometer.


### 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.

**Table 1.** An overview of the Agilent UV-Vis and UV-Vis-NIR spectrophotometers.

| System | Sample Type | Analysis Requirements |
|---|---|---|
| Cary 60 | Liquids and solids | – Routine analysis of liquid samples<br>– Remote fiber optic measurements, ideal for moisture-controlled environment (glovebox)<br>– High-throughput with the 18-cell changer<br>– Color measurements |
| Cary 3500 Multicell and Compact | Liquids | – Multiple simultaneous measurements<br>– Temperature-controlled experiments<br>– Fast data collection (250 data points per second) |
| Cary 3500 Flexible | Liquids and solids | – Variable pathlengths<br>– Fast data collection (250 data points per second)<br>– Large sample compartment |
| Cary 4000<br>Cary 5000<br>Cary 6000i<br>Cary 7000 | Liquids and solids | – Small or large samples<br>– Extended wavelength into NIR<br>– Measurement flexibility<br>– Color measurements |

## Conclusion

Agilent's range of UV-Vis/NIR spectrophotometers provide a diverse array of functions that enable important research involving metal-ion batteries to be conducted. From routine battery components research on the Cary 60, material characterization on the Cary 3500, and quantitative analysis of leach solutions on the Cary 4000/5000/6000i/7000, the Cary instruments cover a wide range of research needs with flexibility and scalability. The availability of many accessories and dynamic software make the Cary range the most powerful on the market for battery research.

## References


1. Liu, H.; Cheng, X-B.; Huang, J-Q.; Kaskel, S.; Chou, S.; Park, H. S.; Zhang, Q. Alloy Anodes for Rechargeable Alkali-Metal Batteries: Progress and Challenge. *ACS Materials Letters* **2019**, *1(2)*, 217–229.
2. Patel, M. U. M.; Dominko, R. Application of In Operando UV-Vis Spectroscopy in Lithium–Sulfur Batteries. *ChemSusChem* **2014**, *7*, 2167–2175.
3. Bouteau, G.; Van-Nhien, A. N.; Sliwa, M.; *et al.* Effect of Standard Light Illumination on Electrolyte's Stability of Lithium-Ion Batteries Based on Ethylene and Di-Methyl Carbonates. *Sci. Rep*. **2019**, *9*, 135.
4. Xia, T.; Zhang, W.; Murowchick, J. B.; Liu, G.; Chen, X. A Facile Method to Improve the Photocatalytic and Lithium-Ion Rechargeable Battery Performance of $TiO_2$ Nanocrystals. *Adv. Energy Mater.* **2013**, *3*, 1516–1523.
5. Mendes-Felipe, C.; Barbosa, J. C.; Gonçalves, R.; Miranda, D.; Costa, C. M.; Vilas-Vilela, J. L.; Lanceros-Mendez, S. Lithium Bis (Trifluoromethanesulfonyl)imide Blended in Polyurethane Acrylate Photocurable Solid Polymer Electrolytes for Lithium-Ion Batteries. *J. Energy Chem.* **2021**, *62*, 485–496.
6. Ma, W.; Li, W.; Jiang, J.; Xu, Y.; Li, W.; Liu, X.; Chen, Z.; Jiang, Y.; Zhang, J.; Zhao, B. Iodine-Containing Additive Engineering for Rejuvenating Inactive Lithium and Constructing Highly Stable Lithium Metal Anodes. *Chem. Engin. J.* **2023**, *477*, 146890–146890.
7. Sen Zhang; Fangfang Xing; Ling Chen; Xiujuan Wang; Xiaoming H. *Chemistry of Materials* **2022**, *34(20)*, 9031–9041.
8. Liu, K.; *et al.* Electrospun Core-Shell Microfiber Separator with Thermal-Triggered Flame-Retardant Properties for Lithium-Ion Batteries. *Sci. Adv.* **2017**, *3(1)*.
9. Peeters, N.; Binnemans, K.; Riaño, S. Solvometallurgical Recovery of Cobalt from Lithium-Ion Battery Cathode Materials Using Deep-Eutectic Solvents. *Green Chemistry* **2020**, *22(13)*, 4210–4221.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