

APPLICATION NOTE: RAMAN SPECTROSCOPY TO IMPROVE BATTERY LIFE

Techniques

- Raman Spectroscopy

Keywords

- Raman
- Cyclability
- IT-NaS
- Omega to the fourth dependency
- Autofluorescence

Introduction

Battery technology is a critical pillar in humanity's sustainable green energy future. This fact was highlighted by the International Energy Agency (IEA) in their September 2020 report titled "Innovation in Batteries and Electricity Storage: A Global Analysis Based on Patent Data."¹ In the forward, Dr. Faith Birol, IEA Executive Director, stated, "The IEA's projections for the future of global energy under-

score the critical and growing importance of developing better and cheaper electricity storage." She went on to warn, "[h]owever, energy storage – which is a critical technology – is currently not on track to achieve the levels ... both in terms of its deployment and its performance." One possible solution to the energy storage problem of current Li-ion battery technology is to explore the use of novel materials for battery production. This application note will review how one research team uses Raman spectroscopy to aid in developing alternative high storage capacity technology, known as intermediate temperature sodium-sulfur (IT-NaS) batteries.



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Improving Longterm Cyclability

In their recent publication titled "Operational strategies to improve the performance and long-term cyclability of intermediate temperature sodium-sulfur (IT-NaS) battery²," Kandhasamy et al. explained that even though the world's

largest battery storage unit utilizes NaS batteries technology, it has not been widely adopted because of the need for extremely high-temperature operation (~350°C). They went on to explain that room temperature variants have been demonstrated in the lab.

initial results showed discharge capacity far below the theoretical limit for both small and large cell configurations.

Upon further investigation, they observed that after only one charge and discharge cycle, the internal resistance of the IT-NaS cell showed a significant increase, indicating irreversible degradation to the electrolyte near the cathode (referred to as catholyte). Since Raman bands correspond to vibrational frequencies of molecular bonds, it is uniquely suited for investigations of allotropes. For this reason, the team decided to measure the initial and reclaimed catholyte using an Avantes AvaRaman-532 TEC Raman spectrometer. Based on the results shown in figure 1, it was abundantly clear by the increase in the 175cm⁻¹ band that the sulfur was undergoing a chemical change. By peak-fitting the spectra to known S bands,

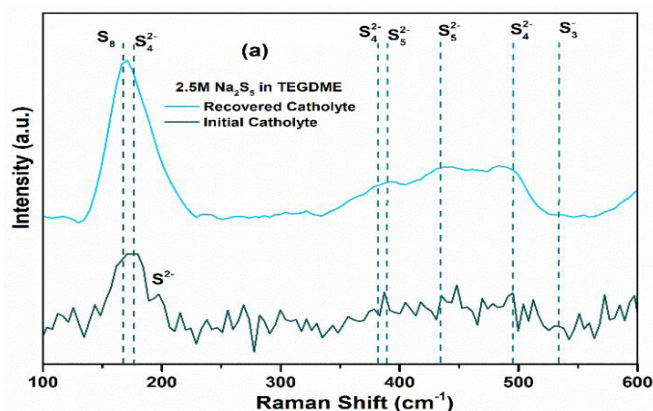


Figure 1: Raman spectrum of initial and recovered catholyte³.

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they determined that the increase in peak height was due to a rise in insulating S_8 and a decrease in active S_4 , demonstrating the high degree of specificity provided by Raman spectroscopy with regard to allo-

tropes. The insight provided by Raman spectroscopy led the team to explore various optimization strategies, including diluting the catholyte concentration and narrowing the catholyte layer. In the end, the resea-

chers managed to achieve enhanced long-term performance, stability, and a groundbreaking average total cell energy efficiency of $73 \pm 4\%$.

System-Level Requirements for Raman Spectroscopy

Since the Raman signal manifests as a change in photon energy instead of a direct absorption or emission of photons, there are several unique requirements for excitation, detection, and sampling. The first and arguably most significant requirement of any Raman system is using a narrow-line-width, wavelength-stabilized excitation laser. All Raman spectra are measured as a shift in frequency, displayed as Raman Shift (cm^{-1}) in figure 1. Therefore, it should be evident that any red or blue shift in the laser wavelength would result in a subsequent peak shift in the observed Raman spectra. Furthermore, suppose the laser linewidth is greater than the spectrometer's spectral resolution or the Raman band's linewidth.



AvaRaman system

In that case, it will result in a “blurring” of the observed spectra, ultimately reducing the spectral resolution. The [AvaRaman-532](#) utilizes an extremely stable 532 nm frequency-doubled Nd:YAG excitation laser with a linewidth of less than 0.1nm. A linewidth of 0.1 nm at 532 nm corresponds to

roughly 3.5cm^{-1} , which is significantly lower than the spectrometer 10cm^{-1} resolution of the AvaRaman-532, so as not to distort the Raman bands.

Next, it is imperative to understand that the Raman effect arises from non-linear optical phenomena, making the process extremely weak ($\sim 10^{-6}$ quantum efficiency). Therefore, requiring a tightly focused laser at the sample, as well as long integration times. Due to the relatively long integration time needed for Raman spectroscopy, all of Avantes' Raman spectrometers utilize thermoelectrically (TE) cooled detectors. The AvaRaman-532 TEC, used for the above work, incorporates the AvaSpec-ULS2048L-TEC, which is TE cooled to 5°C stable within 0.1°C , providing a signal-to-noise ratio (SNR) of 200:1 when tested using a benzene standard. The newer AvaRaman-532 HERO-EVO utilizes the AvaSpec-HERO which is capable of even deep TE cooling, down to -10°C , providing a remarkable 800:1 SNR for benzene.

Additionally, it is essential to discuss why the researchers chose to use 532 nm excitation wavelength instead of the more common 785 nm excitation for this application. There are two competing phenomena that influence wavelength choice in Raman spectroscopy. First is the so-called “omega to the fourth” dependency, which results in increased scattering efficiencies at shorter wavelengths. On the surface, this would imply that shorter wavelengths are always optimal for Raman spectroscopy, but that is not generally the case because of the second phenomenon: auto-fluorescence. In general, fluorescence is considered a weak

optical process, but it is large compared to Raman scattering. As a result, auto-fluorescence tends to mask the Raman spectrum entirely.

Since most organic molecules fluoresce when excited by visible and ultraviolet light, 785nm laser excitation is typically preferred. In this case, though, since the analyte of interest is inorganic, there is very little auto-fluorescence, allowing the researchers to take advantage of the increased Raman efficiency at 532 nm. This fact was critical to their success since the catholyte is highly absorbent and would have burned at the higher laser powers required by 785 nm excitation. For this reason, Avantes offers both 532 nm and 785 nm versions of the AvaRaman to allow researchers the flexibility they need for their application. Lastly, it should be pointed out that the $\sim 175\text{cm}^{-1}$ Raman band that they used to identify the presence of S_8 in the catholyte is relatively close to the laser line itself. Most commercial Raman spectrometers have a Raman shift cut-on of $\sim 200\text{cm}^{-1}$ because of the difficulty in filtering out amplified spontaneous emission from the laser source with standard optical filters. Fortunately, all of Avantes' Raman spectrometers, including the AvaRaman-532, use cutting-edge ultra-sharp edge filters combined with a proprietary optical design that allows for the measurement of Raman shifts down to 100cm^{-1} . This feature makes the AvaRaman ideal for the measurement of heavier atoms, like sulfur which tend to vibrate at lower frequencies.

Final Thoughts

While this application note focused mainly on end-user products, it should be pointed out that Avantes also offers both modular and OEM Raman systems as well. For more information about the full range of laboratory and OEM spectrometer options available from Avantes, including our laser sources, probes, and sample accessories, please feel free to visit the website at www.avantesusa.com or give us a call at +1 (303)-410-8668 where our knowledgeable applications specialists are standing by to help.

References

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- [2] Kandhasamy, S., Nikiforidis, G., Jongerden, G.J., Jongerden, F., van de Sanden, M.C. and Tsampas, M.N., Operational strategies to improve the performance and long term cyclability of intermediate temperature sodium sulfur (IT NaS) battery. ChemElectroChem.
- [3] Kandhasamy, S., Nikiforidis, G., Jongerden, G.J., Jongerden, F., van de Sanden, M.C. and Tsampas, M.N., Operational strategies to improve the performance and long term cyclability of intermediate temperature sodium sulfur (IT NaS) battery. ChemElectroChem. {Supporting Materials}