

Raman Spectroscopy for Lead acid Battery Analysis.

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INTRODUCTION

Lead-acid batteries remain a cornerstone of energy storage technology, valued for their reliability, low cost, and high recyclability, particularly in automotive and stationary applications. Despite their maturity, these batteries face performance limitations and degradation mechanisms such as negative plate sulfation, grid corrosion, and oxygen recombination issues that restrict their lifespan and efficiency.

To overcome these challenges and enhance performance in modern micro-hybrid systems, detailed, real-time understanding of electrochemical processes at the electrode-electrolyte interface is required.

Raman spectroscopy has emerged as a powerful, non-destructive analytical technique capable of providing high-resolution structural and chemical information on lead-acid battery components, including lead oxides, lead sulfates, and various forms of carbon additives. Raman spectroscopy is a precise, "technique of choice" for studying the formation of lead sulfate (PbSO_4) crystals, which is the primary cause of capacity loss in partial state of charge operation. Raman imaging allows for the characterization of sulfation distribution along electrode cross-sections, providing insights into uneven material degradation and inactive areas.

MATERIAL AND METHODS

Raman spectra were acquired using TechnoS IndiRAMTM CTR-300 Raman spectrometer, designed to provide high spectral resolution, wavelength stability, and excellent signal-to-noise performance for Battery analysis.

Three type of battery were analysis:

- (1) Scooter Battery : Old (Dead)
- (2) UPS Battery : Old (Dead)
- (3) Small Battery: NEW

These new and old battery is decided to see the effect of impurities (additive common material: BaSO₄ (0.5-1%), Sb, As, Cr, Cu, and Sn)) in Raman spectrum.

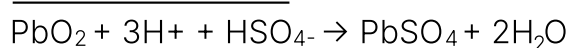
RESULT AND DISCUSSION

Chemical reaction in Lead acid battery as follows:

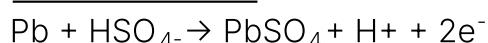
(1) Discharging state:

Product at both electrode : PbSO₄

- Cathode reaction:



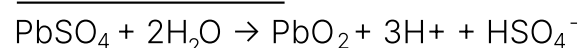
- Anode reaction:



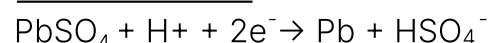
(ii) Charging state:

Cathode: PbO₂, Anode: Pb

- Cathode reaction:



- Anode reaction:



Raman mode of lead sulphate (PbSO₄), lead oxide (PbO₂) and barium sulphate (BaSO₄)

1. Raman mode of Anglesite (Pure PbSO₄)

- Tetrahedrasymm. bend mode:
[437, 449: ref 1], [436, 439, 451: ref 2]
- Tetrahedra asymm. bend mode :
[617, 640: ref 1], [605, 613, 635: ref 2]
- Tetrahedra symm. Stretch. of (SO₄)²⁻:
[977 ref 1], [974, 980, 981: ref 2]
- Tetrahedra asymm. stretching mode:
[1051, 1140, 1157: ref 1],
[1057, 1060, 1065 : ref 2],
[1148, 1154, 1160: ref 2] cm⁻¹

3. Raman mode of Barite (Pure BaSO₄: ref 4)

- Symmetry bend vibration at ~ 450 cm⁻¹
- Asymmetry bend vibration ν₄(F₂) at ~ 620 cm⁻¹
- Symmetric stretching of [SO₄]²⁻ at ~ 988-1000 cm⁻¹
- Asymmetric stretching at ~1080, 1150, 1167 cm⁻¹

2. Raman mode of lead oxides

- PbO₂:
eg : 424 cm⁻¹, a_{1g}: 515 cm⁻¹
and b_{2g}: 653 cm⁻¹ [ref 3]
- PbO: 117, 139, 270, 314, 500, 533
- Pb₃O₄: 122, 148, 540-550

PbSO ₄ (Anglesite)		PbO (Litharge)		BaSO ₄ (Barite)	
Raman shift (cm ⁻¹)	Mode assignment	Raman shift (cm ⁻¹)	Mode assignment	Raman shift (cm ⁻¹)	Mode assignment
451	ν ₂ (SO ₄ ²⁻ bending)	105	E _g (lattice mode)	456	ν ₂ (SO ₄ ²⁻ bending)
980	ν ₁ (SO ₄ ²⁻ symmetric stretching)	138	B _{1g} (lattice mode)	593	ν ₄ (SO ₄ ²⁻ bending)
1004	ν ₁ (SO ₄ ²⁻ symmetric stretching)			988	ν ₁ (SO ₄ ²⁻ symmetric stretching)
1105	ν ₃ (SO ₄ ²⁻ asymmetric stretching)			1140	ν ₃ (SO ₄ ²⁻ asymmetric stretching)
1450	ν ₃ (SO ₄ ²⁻ asymmetric stretching)			1642	ν ₃ (SO ₄ ²⁻ asymmetric stretching)

ν₁ - symmetric stretching, ν₂ - symmetric bending,
ν₃ - asymmetric stretching, ν₄ - asymmetric bending
(SO₄²⁻ = sulphate ion)

PEAK ASSIGNMENT:

Scooter old /dead battery:

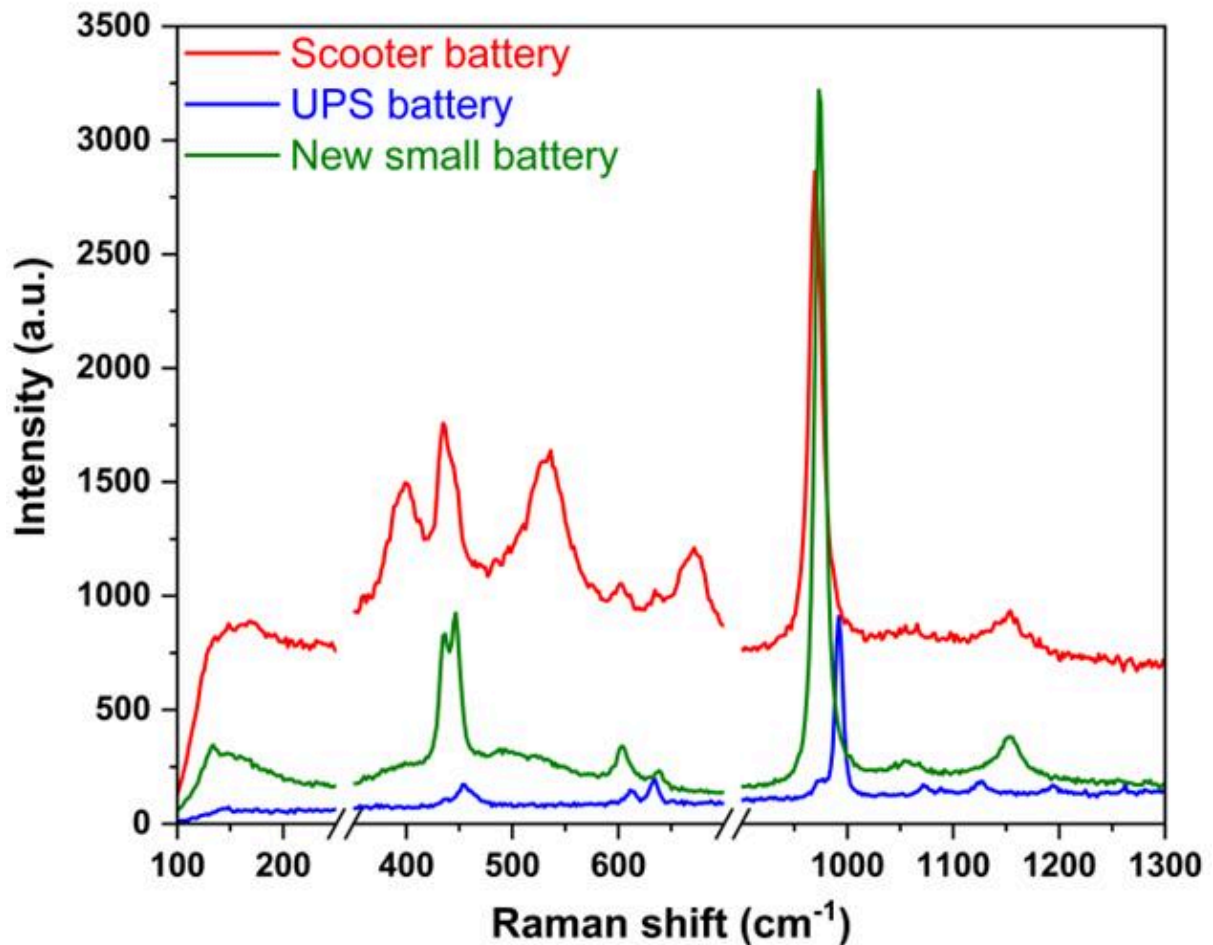
(i) (436, 454), (601, 636), (970), (1052, 1153): PbSO_4

(ii) 147, 170, 506 : PbO , PbO_2 , Pb_3O_4

(iii) 388, 400, 536, 557, 670, 688: Cr_2O_3 , Cr_8O_{21} , Fe_2O_3 , Fe_3O_4

(iii) 454, 987 : BaSO_4

Conclusion: Mainly PbSO_4 with small amount of BaSO_4 , PbO , PbO_2 , Pb_3O_4 , Cr_2O_3 , Cr_8O_{21} , Fe_2O_3 , Fe_3O_4 .



UPS old/dead battery :

(i) (437, 455), 635, 970, 1155: PbSO_4

(ii) 455, 612, 992, (1072, 1155, 1194): BaSO_4

Conclusion: Mainly BaSO_4 with PbSO_4

Portable electronic new battery:

(i) 436, 445, (603, 639), 974, (1056, 1152): PbSO_4

(ii) 134, 150, 488 : PbO , PbO_2

Conclusion: Mainly PbSO_4 with small amount of PbO , PbO_2

Conclusion: Raman spectroscopy analysis revealed that the scooter battery sample was primarily composed of PbSO_4 , along with minor amounts of BaSO_4 , various lead oxides (PbO , PbO_2 , Pb_3O_4), chromium oxides (Cr_2O_3 , Cr_3O_{21}) and iron oxides (Fe_2O_3 , and Fe_3O_4). The UPS battery sample mainly contained BaSO_4 and PbSO_4 , whereas the small portable electronic battery sample was predominantly composed of PbSO_4 with trace amount of lead oxide (PbO and PbO_2). Raman spectroscopy provides a fast, non-destructive, and highly specific method for identifying Lead acid battery. The distinct spectral signatures of impurity of BaSO_4 and other products demonstrate Raman's effectiveness for Lead acid battery in exploration and energy application.

Using high-resolution IndiRAM CTR-300 Raman Spectrometer and with ongoing development of Portable Raman solutions, TechnoS Instruments enables accurate, Lead acid battery identification to support the growing demand for critical % Barium sulphate.

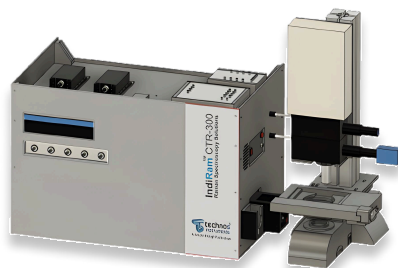
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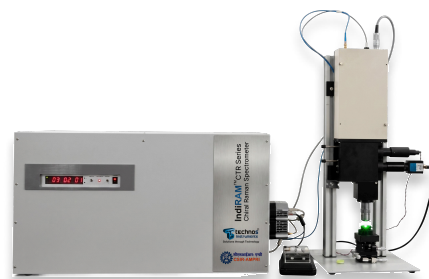
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