Raman Spectroscopy for Lead acid Battery Analysis.

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INTRODUCTION

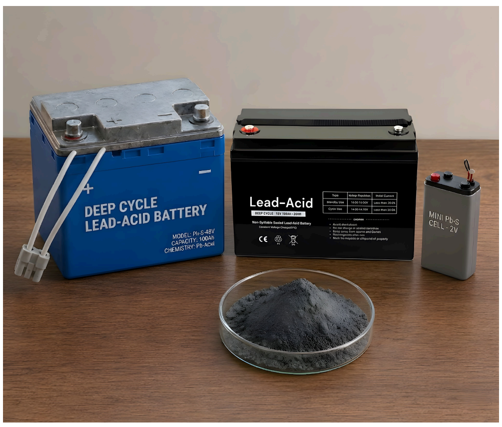
Lead-acid batteries remain a cornerstone of energy storage technology, valued for their reliability, low cost, and high recyclability, particularly in automotive and stationary applications. Despite their maturity, these batteries face performance limitations and degradation mechanisms such as negative 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.

MATERIAL AND METHODS

Raman spectra were acquired using TechnoS IndiRAM^{TM} CTR-300 Raman spectrometer, designed to provide high spectral resolution, wavelength stability, and excellent SNR 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: $BaSO_4$ (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:

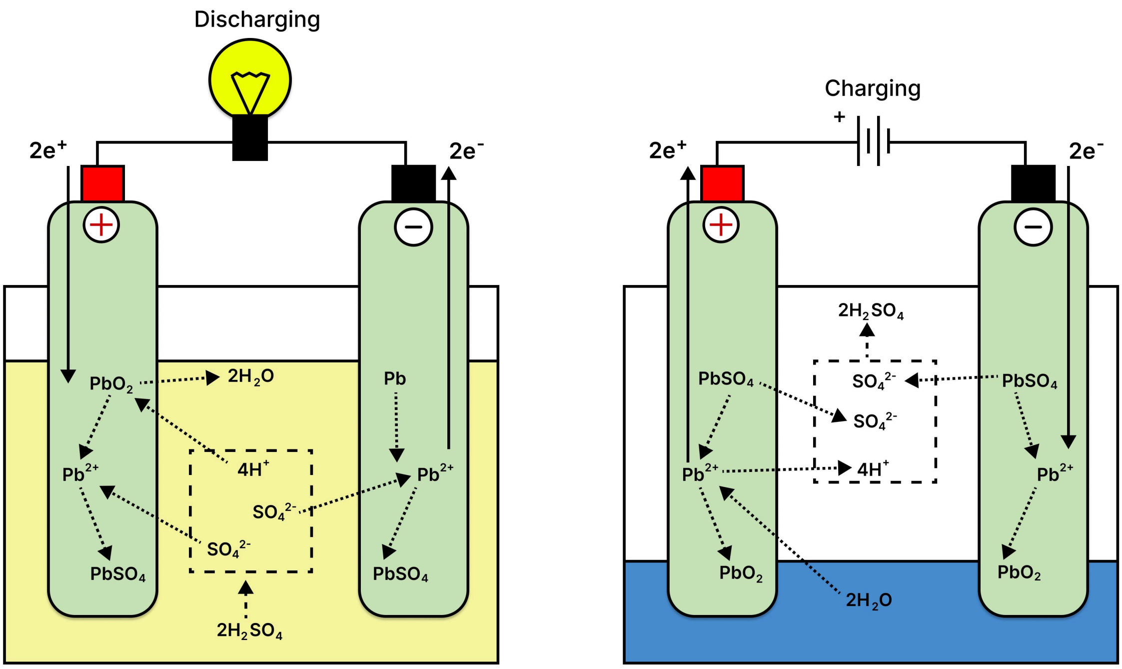
Product at both electrode : $PbSO_4$

- *Cathode reaction:*
  $PbO_2 + 3H^+ + HSO_4^- \rightarrow PbSO_4 + 2H_2O$
- *Anode reaction:*
  $Pb + HSO_4^- \rightarrow PbSO_4 + H^+ + 2e^-$

(ii) Charging state:

Cathode: PbO_2, Anode: Pb

- *Cathode reaction:*
  $PbSO_4 + 2H_2O \rightarrow PbO_2 + 3H^+ + HSO_4^-$
- *Anode reaction:*
  $PbSO_4 + H^+ + 2e^- \rightarrow Pb + HSO_4^-$



Raman mode of lead sulphate ($PbSO_4$), lead oxide (PbO_2) and barium sulphate ($BaSO_4$)

1. Raman mode of Anglesite (Pure $PbSO_4$)

- 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 $(SO_4)^{-2}$: [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}

2. Raman mode of lead oxides

- PbO_2 :
  eg : 424 cm^{-1} , a1g: 515 cm^{-1}
  and b2g :653 cm^{-1} [*ref 3*]
- PbO: 117, 139, 270, 314, 500, 533
- Pb_3O_4: 122, 148, 540-550

3. Raman mode of Barite (Pure $BaSO_4$: *ref 4*)

- Symmetry bend vibration at ~ 450 cm^{-1}
- Asymmetry bend vibration v4(F2) at ~ 620 cm^{-1}
- Symmetric stretching of $[SO_4]^{-2}$ at ~ 988-1000 cm^{-1}
- Asymmetric stretching at ~1080, 1150, 1167 cm^{-1}

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 .

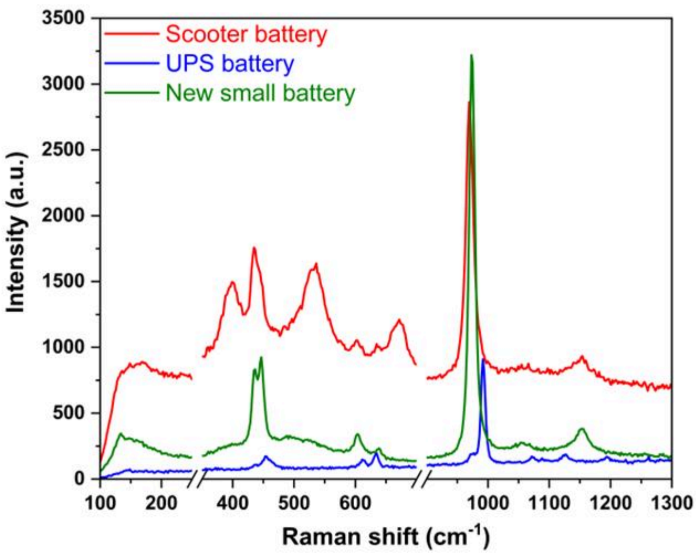


fig 1

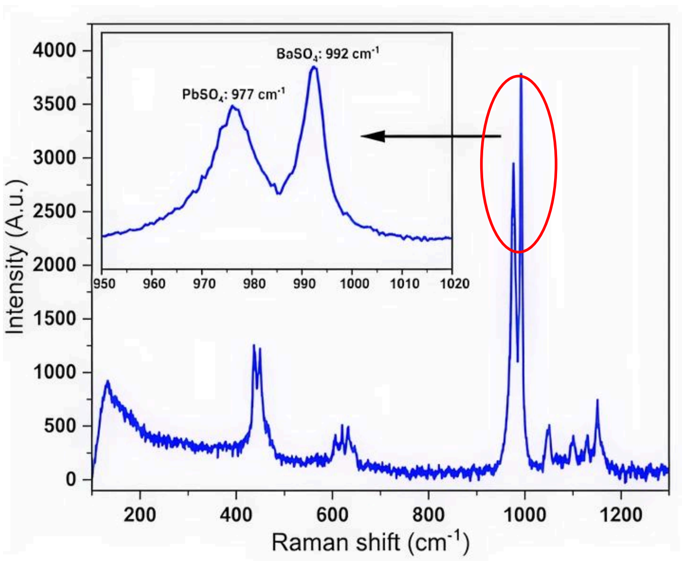


fig 2

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

High resolution:

The grating of 1800/mm was used for separating out peak of $BaSO_4$ and $PbSO_4$ clearly in fig. 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_8O_{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 battey. The distinct spectral signatures of impurity of BaSO4 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. (Since BaSO4 is used ~ 0.8-1% by weight relative to the leady oxide.)

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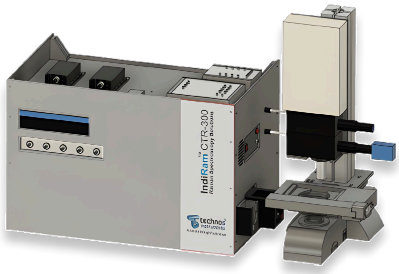

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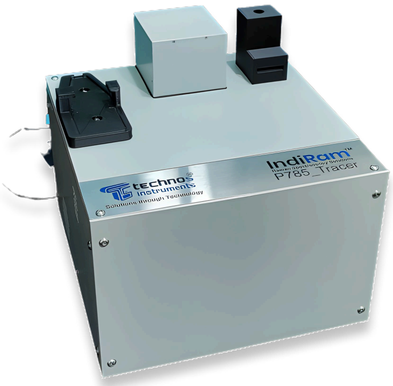

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