



Short communication

Lead-acid batteries for partial-state-of-charge applications

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ABSTRACT

2 V/40 Ah valve-regulated lead-acid (VRLA) cells have been constructed with negative plates employing carbon black as well as an admixture of carbon black + fumed silica as additives in negative active material for partial-state-of-charge (PSoC) applications. Electrical performance of such cells is compared with conventional 2 V/40 Ah VRLA cells for PSoC operation. Active material utilization has been found to be higher for carbon-black + fumed-silica mixed negative plates while formation is faster for cells with carbon-black mixed negative plates. Both faradaic efficiency and percentage capacity delivered have been found to be higher for cells with carbon-black + fumed-silica mixed negative plates. However, a high self-discharge rate is observed for cells with carbon-black + fumed-silica mixed negative plates.

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1. Introduction

During the discharge of a lead-acid battery, semi-conducting lead dioxide at the positive plate and metallic lead at the negative plate react with sulfuric acid to form non-conducting lead sulfate with concomitant volume increase of 92% and 164%, respectively [1]. The build-up of PbSO₄ at the negative plate during the repeated charge–discharge of the valve-regulated lead-acid (VRLA) battery is deleterious to its operational life due to decreased electronic conductivity and reduced porosity of the active mass as well as local acid concentration.

At present, major R&D efforts on lead-acid batteries are directed to achieving maximum discharge capacity and, where deep-discharge duty is required, to sustain the battery capacity through as many discharge–charge cycles as possible. The technical challenge to be met in maximizing discharge capacity involves facilitating the access of all the reactants to the reaction site. For this purpose, it is desirable to provide: (a) high surface-area for the solid reactants, (b) high flux for species in solution, e.g. short diffusion-lengths, and (c) low resistance to sustain the electric current [2]. It is noteworthy that negative plate sulfation is the life-limiting factor in

valve-regulated lead-acid (VRLA) batteries under high-rate-partial-state-of-charge (HRPSoC) operational conditions.

In the literature, several additives, such as graphitic carbon, expanded carbon, Al₂O₃, TiO₂, etc., to the negative active-material have been employed to mitigate the sulfate accumulation during HRPSoC operation of VRLA batteries; among these carbon is the most promising additive [2–11]. Various grid-designs have also been employed in the literature to reduce sulfation [12,13]. It is also documented that silica forms a three-dimensional framework with H₂SO₄ having capability to retain copious amounts of H₂SO₄ [14].

The present study is an attempt to optimize both conductivity of the active mass and plate porosity while ameliorating local-acid concentration by using both carbon-black (hereafter to be referred as carbon) and fumed-silica (hereafter to be referred as silica) as additives to the negative-active-material paste.

2. Experimental

Carbon and silica additives employed in this study were procured from Infra Chemical Industries, Bangalore, India and Cabot Sanmar Ltd., Chennai, India, respectively. AGM separator was obtained from Nippon Sheet Glass Co., Japan.

Powder X-ray diffraction (XRD) data for the carbon, silica and carbon + silica mixture were obtained on a Panalytical X'Pert PRO Diffractometer. Surface morphologies of carbon, silica and carbon + silica mixture, and EDAX data for carbon + silica mixture were

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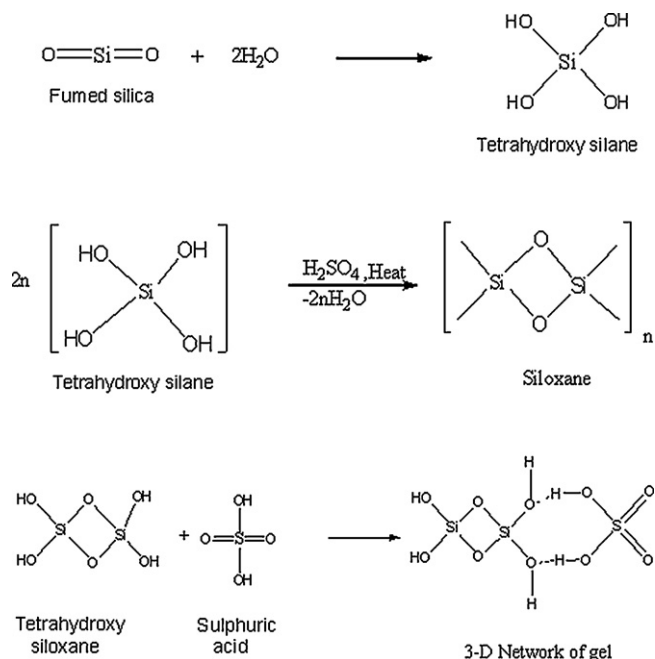


Fig. 1. Schematics of gel formation.

obtained on FEI-SIRION. BET surface areas for the samples were obtained on a Quantachrome Corporation NOVA 1000 High-Speed Gas Sorption Analyzer. Charge–discharge tests were conducted using a Bitrode LCN 100-12 voltage/current source (Bitrode Corporation, US) interfaced to a data acquisition system. Electrochemical

impedance measurements on the cells were obtained employing an AUTOLAB PGSTAT 30 instrument (EcoChemie BV, The Netherlands). The impedance spectra were analyzed using a non-linear least-square fitting program [15].

Both positive and negative plates of the cells and batteries were prepared by following an established industrial protocol [16]. Negative plates were prepared with and without additives. Negative plates with additives employed carbon (2 wt.%) and carbon (2 wt.%) + silica (0.5 wt.%). 2 V/40 Ah negative-limited VRLA cells were assembled by stacking four positive plates and three negative plates. Positive and negative plates in these cells were separated by placing 2 mm AGM separator in between them. The plates were strapped with polythene bands and connected to their respective lugs.

Sulfuric acid used for formation of cells was of sp. gr. 1.23. Prior to their formation, respective cells were filled with required amount of sulfuric acid and kept for 2 h for electrolyte soaking. The cells were formed by charging them galvanostatically at C/100 (1/2 h), C/50 (1/2 h), C/20 (1 h) and C/10 rate for 46 h followed by their discharge at C/5 rate. Subsequent to their formation, the cells were charged galvanostatically at C/10 rate (charge input = 110%) and discharged at C/5 rate until they attained a stable capacity.

The porosity of the negative pasted plates was estimated by the water evaporation method. In brief, the fully-saturated plates with no excess water on their surface were accurately weighed and subsequently dried in an air oven at 65 °C for 24 h. The dried plates were weighed to obtain the plate porosity from the following relationship [17]:

$$\% \text{ plate porosity} = \frac{\text{weight of the water removed}}{\text{initial weight of the pasted plate}} \times 100$$

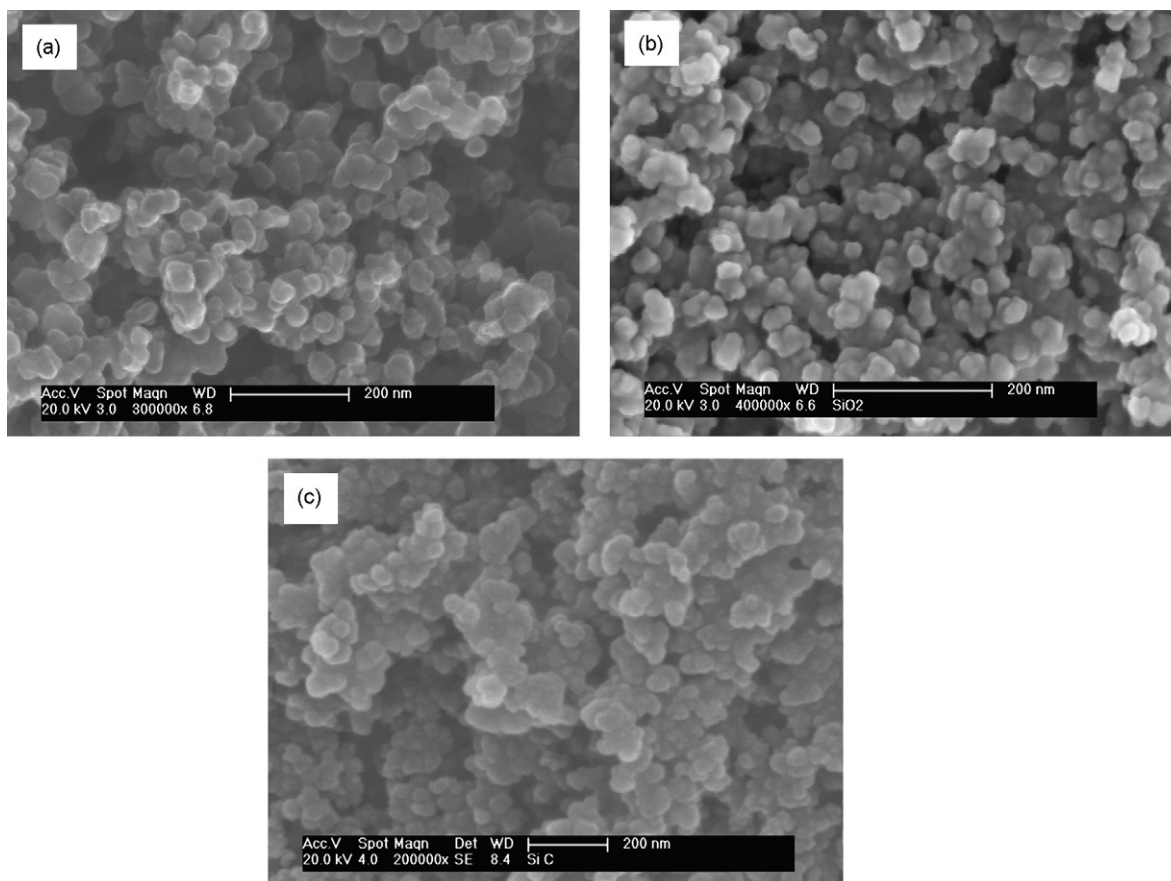


Fig. 2. Morphologies for (a) carbon, (b) silica and (c) carbon + silica mixture.

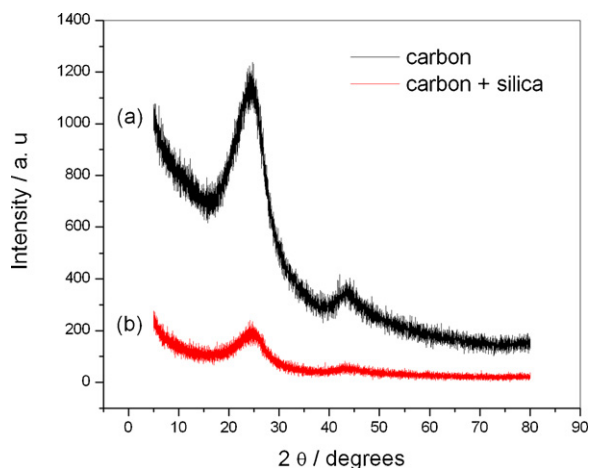


Fig. 3. Powder XRD patterns for (a) carbon and (b) carbon + silica mixture.

The cells were charged and discharged under PSoC condition at 2C rate in the state-of-charge (SoC) range between 0.6 and 0.4, i.e. 5 min charging followed by 5 min discharge, till the cells reached the cut-off value of 1.75 V. Electrochemical impedance measurements on the cells were conducted prior and after PSoC charge–discharge cycles at varying SoC values at 25 °C.

3. Results and discussion

Fumed silica with concentrated sulfuric acid forms thixotropic gel. A thixotropic gel is a semi-rigid solid in which the solvent is contained in a framework of material; it maintains a shape of its own until it is subjected to a shearing (lateral) force or some other disturbance such as shaking. It then behaves as a sol (a semi-fluid colloid) and flows freely. The schematic of the gel formation is shown in Fig. 1. In brief, silica hydrolyses with the atmospheric moisture to form tetra-hydroxy silane. Since tetra-hydroxy silane is thermodynamically unstable, it undergoes inter-molecular dehydration to form tetra-hydroxy siloxane. Subsequently, the residual hydroxyl groups form hydrogen bonds with sulfuric acid yielding a three-dimensional network of the thixotropic gel.

Carbon + silica mixture for XRD, EDAX and SEM analyses are prepared by thoroughly mixing and grinding carbon and silica. Surface areas for carbon and silica samples employed in the study are 80

and 200 m² g⁻¹, respectively, with the particle size values ranging between 20 and 40 nm (Fig. 2). Pristine carbon and silica are seen to be spherical and uniformly distributed. By contrast, the constituent particles seemingly aggregate on grinding in the carbon + silica mixture resulting in a non-uniform morphology. Powder XRD pattern for carbon + silica mixture exhibits lesser intensity peaks in relation to the pristine carbon primarily due to the reduced amount of carbon in the former (Fig. 3). It is also evident that there is no solid solution formation in the carbon + silica sample. Since amorphous silica is hard to detect in the carbon + silica mixture, EDAX analysis with adequate care was conducted on the sample to ascertain the presence of silica in it (Fig. 4). The EDAX analysis indicates the presence of the following elements in the mixture: C = 83.27 at. wt.%, O = 9.64 at. wt.%, and Si = 7.09 at. wt.%.

Paste density values for pristine, carbon mixed, and carbon + silica mixed negative active materials are 4.2, 3.8 and 3.44 g cm⁻³, respectively. Plate porosities for cured negative plates with pristine, carbon mixed, and carbon + silica mixed active materials are 38%, 40% and 42%, respectively, while the respective porosities for formed-plate are found to be 45%, 60% and 70%. By controlling the active-material paste density, it is possible to achieve nearly equal plate porosity values. However, we have attempted to study the effect of varying porosity.

Active material utilization values for pristine, carbon mixed, and carbon + silica mixed plates happen to be 40%, 50% and 65%, respectively. As expected, the paste densities for pristine, carbon and carbon + silica added negative plates decrease monotonically. Although the cured plate porosities for all the plates are identical, a substantial change in porosity values is observed for the plates after their formation. Interestingly, active material utilization is highest for the cell with negative plate added with carbon + silica. This suggests an improved electrically conductive path with higher amount of acid present in the vicinity of the active-material particles. It is noteworthy that the physical parameters relating to paste densities and plate porosities discussed above are not yet fully-optimized and further improvements are highly likely. For example, by optimizing the active material paste density, the plate porosity can be tailored to the desired value.

Charge acceptance for VRLA cells with carbon + silica mixed negative plates is found to be similar to the cells with carbon-mixed negative plates due to optimized ionic and electronic pathways in the plates that facilitate efficient formation (Fig. 5). Faradaic efficiencies for the negative plates with pristine, carbon mixed, and carbon + silica mixed active materials are found to be 87%, 90% and

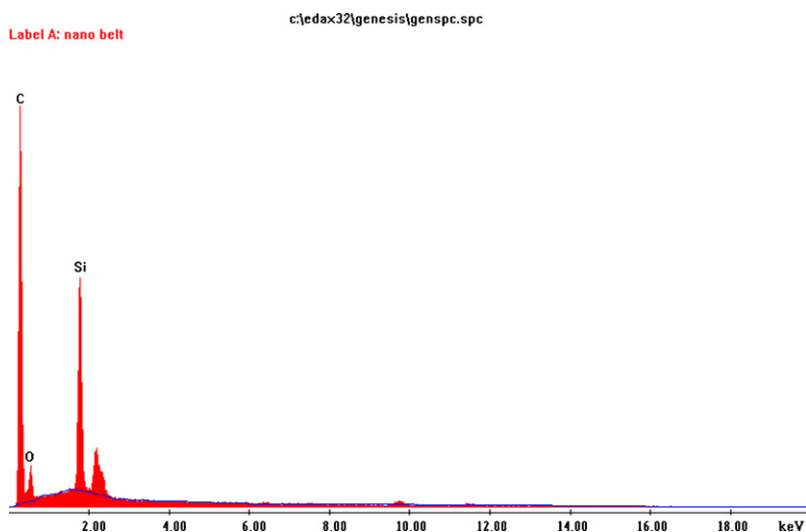


Fig. 4. EDAX data for carbon + silica mixture.

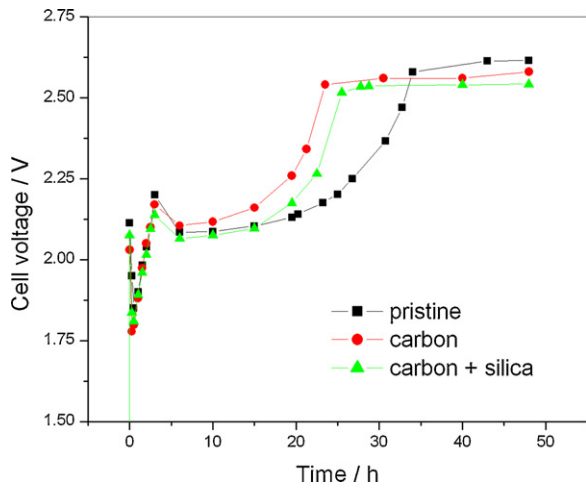


Fig. 5. Comparative formation-charge data for cells with pristine, carbon-mixed and carbon + silica mixed negative plates.

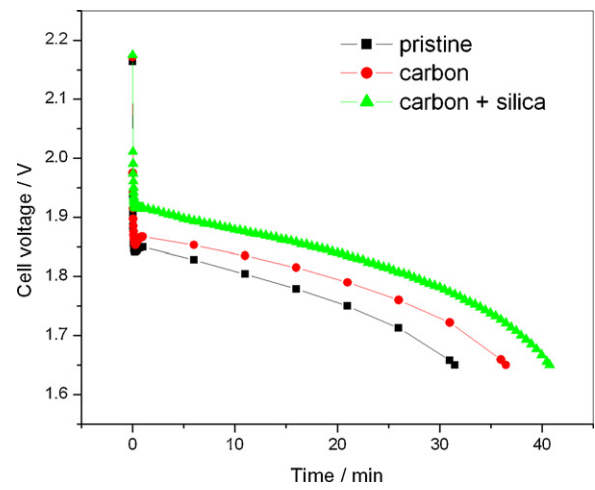


Fig. 7. Discharge data for cells at 2C-rate at 25 °C.

93%, respectively (Fig. 6). Percentage capacity values at 2C-rate at 25 °C for the cells with negative plates of pristine, carbon mixed, and carbon + silica mixed negative plates are found to be 53%, 61% and 68%, respectively (Fig. 7).

Under high-rate partial-state-of-charge (HRPSoC) operations at 2C-rate at 25 °C with SoC window between 0.6 and 0.4, cells with carbon-mixed negative plates could be subjected to 450 charge–discharge cycles prior to attaining cut-off voltage value of 1.75 V while pristine cells lasted only 120 cycles. By contrast, cells with carbon + silica mixed negative plates could be cycled beyond 600 cycles (Fig. 8). Interestingly, end-of-discharge voltage values for cells with carbon + silica mixed negative plates stabilized beyond 400 charge–discharge cycles suggesting minimal changes in the negative plate morphologies beyond 400 cycles. Accordingly, cells with carbon + silica mixed negative plates look promising for developing lead-acid cells for PSoc applications.

Electronic conductivity for carbon-mixed plates are higher than pristine plates as the carbon additive employed is more conductive. By contrast, silica is electrically insulating. In silica + carbon mixed plates, silica is only 0.5 wt.% as against 2 wt.% of carbon; therefore, the overall conductivity of carbon + silica mixed plates will be higher than pristine plates and, accordingly, ohmic resistance values at varying SoC values for cells with and without additives

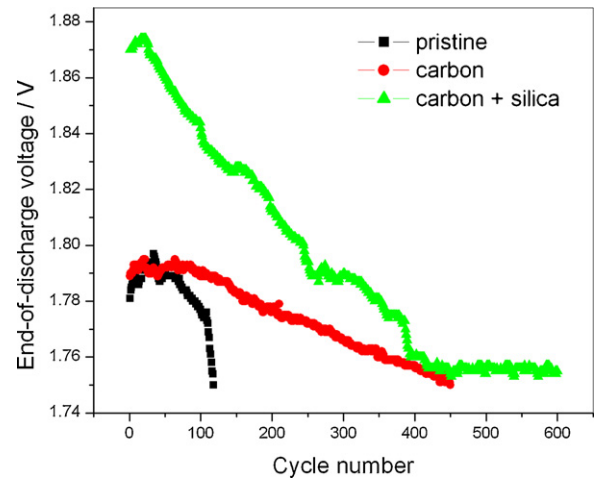


Fig. 8. End-of-discharge voltage values for cells during the HRPSoC operation.

in negative plates are found to be: carbon < carbon-silica < pristine (Fig. 9). Impedance measurements are conducted on respective cells before and after HRPSoC operations at SoC=0.4 at 25 °C and impedance data are analyzed using a non-linear least-square fitting

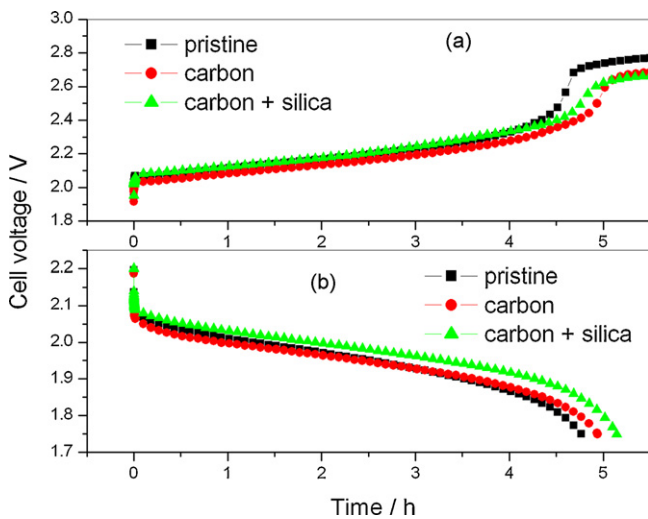


Fig. 6. Typical (a) charge and (b) discharge curves at C/5 rate at 25 °C for cells with pristine, carbon-added and carbon + silica added negative plates.

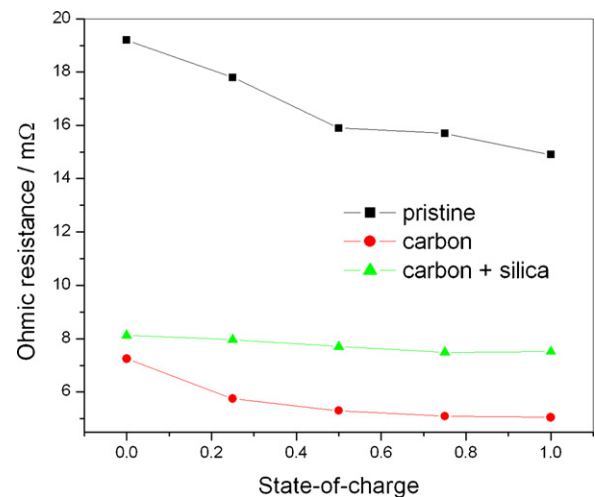


Fig. 9. Ohmic resistance data at varying SoC values for cells with and without additives in negative plates.

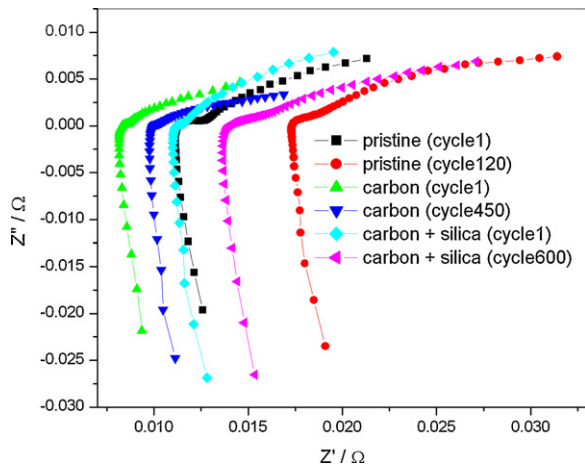


Fig. 10. Electrochemical impedance spectra for cells with pristine, carbon-mixed and carbon + silica mixed negative plates before and after the HRPSoC operation.

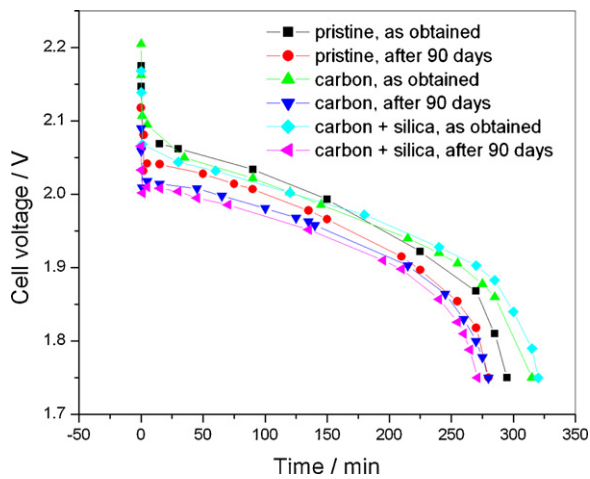


Fig. 11. Comparative self-discharge data for cells with pristine, carbon-mixed and carbon + silica mixed negative plates at 25 °C after storage for 90 days.

program. It has been possible to fit the impedance plots to a $R_{\Omega}(R_1Q_1)(R_2Q_2)$ equivalent circuit where R_{Ω} is the ohmic resistance, R_1 and Q_1 are the respective values for resistance and constant phase element (CPE) corresponding to the high-frequency semicircle, and R_2 and Q_2 are the respective values for resistance and CPE corresponding to the low-frequency semicircle. The impedance data indicate the internal resistance values for the pristine, carbon-

added and carbon + silica added negative plate cells after 120, 450 and 600 cycles to increase by 6, 2 and 3 m Ω , respectively, as shown in Fig. 10. This data also supports the higher conducting nature of carbon-mixed plates. Self-discharge values for cells with conventional, carbon mixed, and carbon + silica mixed negative plates after 90 days of storage at 25 °C are 5%, 11% and 15%, respectively (Fig. 11). Higher self-discharge data for carbon and carbon + silica mixed plates as compared to pristine plates are due to an increase in plate porosity as higher porosity of a plate helps retaining higher quantity of electrolyte within the active material of the plate. Accordingly, cells with carbon + silica mixed negative plates exhibit higher self-discharge. Interestingly, higher plate porosities (~70%) have little effect on cycle life and mechanical integrity of the plates.

4. Conclusion

The study demonstrates that addition of carbon + silica to negative paste ameliorates the performance of the lead-acid cells during PSoC operations albeit at a higher self-discharge.

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