



Short communication

Enhancing the performance of lead–acid batteries with carbon – In pursuit of an understanding

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HIGHLIGHTS

- Conflicting notions of the beneficial effect of carbon are reconciled.
- The evidence underpinning mechanisms is reviewed and rationalised.
- A combination of different forms of carbon offers maximum benefit.

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ABSTRACT

The inherently poor dynamic charge-acceptance of the lead–acid battery can be greatly improved by the incorporation of additional carbon to the negative plate. An analysis is undertaken of the various ways by which the carbon may be introduced, and of the proposed mechanisms whereby its presence proves to be beneficial. It is intended that such an investigation should provide a guide to the selection of the optimum carbon inventory.

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1. The challenge of high-rate partial state-of-charge (HRPSoC) duty

The emerging application of lead–acid batteries for the storage of energy from regenerative braking in various types of electric vehicle requires the best possible recovery of charge during high-rate partial-state-of-charge (HRPSoC) duty.

Micro-hybrid vehicles, which are fitted with stop–start features both to improve fuel economy and to reduce emissions, employ batteries that operate under PSoC conditions and are charged by energy recuperation from the regenerative braking system. The schedule is a micro-cycle of short bursts of discharge and charge, each at a high rate, with the charge from regenerative braking supplementing that from the generator. The PSoC amplitude is just

a few percent. The current accepted by the battery during the charge periods should be sufficient, when efficiently used, to convert discharge product to the active state and thereby ensure availability of stop–start and other essential functions. This charge current has been defined [1] as the ‘dynamic charge-acceptance’, DCA, and is the average current over the initial charging period, which is usually between 3 and 20 s. The parameter is quoted in terms of amperes (A) per ampere-hour (Ah) of battery capacity, i.e., $A\text{ Ah}^{-1}$. Standardized industry specifications are in the course of preparation (CENELEC Standard EN50342-6: Lead–acid Starter Batteries for Micro-cycle Applications).

The DCA of new lead–acid batteries generally lies between 0.5 and 1.5 A Ah^{-1} , although some applications may require higher values. For effective fuel savings and low-emission features, this value should be sustained. After relatively short service under PSoC conditions, however, recent work [2,3] has found the DCA to decrease to around 0.1 A Ah^{-1} and, after brief periods of parking, to even lower levels. Resolution of this problem is essential if the

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intended benefits are to be achieved. Factors that influence these inconsistencies in battery performance have been investigated, namely: local current distribution, state-of-charge, temperature, and variable acid strength due to stratification [4]. The progressive decrease in DCA can be attributed to rate-limiting processes that include the accumulation of lead sulfate in the negative plates with subsequent effects on concentration and potential gradients within the porous matrix.

New lead–acid batteries can be recharged effectively at high rates of charge because the freshly-discharged product, lead sulfate, has a small crystallite size which facilitates rapid dissolution — a requirement that is fundamental to subsequent recharge via the so-called ‘solution–precipitation’ mechanism (reaction [3] in Fig. 1). On the other hand, if the battery is left at a PSoC for a significant length of time after discharge from top-of-charge, the lead sulfate crystals have the opportunity to grow progressively via the ‘Ostwald Ripening’ process. Consequently, the charge-acceptance of the battery declines, particularly at the negative plate which offers less surface-area ($0.5\text{--}1\text{ m}^2\text{ g}^{-1}$) than the positive ($4\text{--}5\text{ m}^2\text{ g}^{-1}$).

The immediate history of the battery affects the charge-acceptance quite markedly when micro-cycling is performed over a narrow range of PSoC, with no excursions to top-of-charge [5,6]. A small discharge produces some new (small) lead sulfate crystals, which can support a high rate of recharge so that a relatively healthy DCA can be achieved. Immediately after a charge event, however, the small crystals of lead sulfate will have been consumed so that only material of low surface-area remains and poor DCA is observed.

Lacking a construction that is purpose-designed for HRPSoC duty, valve-regulated lead–acid (VRLA) batteries typically lose at least 50% of their initial capacity after operating in a simulated hybrid electric vehicle (HEV) mode for a relatively short time. The loss of capacity has been attributed to a progressive build-up of lead sulfate on the negative plate, especially at the bottom. Since the battery is not brought to a full state-of-charge in PSoC duty, there is no routine method available to remove this lead sulfate.

On charging a lead–acid cell, the fundamental reaction at the positive electrode may be accompanied by oxygen evolution and that at the negative by hydrogen evolution. All four reactions are independent. The only requirement is that the currents at the two electrodes are equal. The end-point of a completed charge is always water electrolysis during which gas evolution predominates. The

rates of other possible side-reactions, such as grid corrosion, ozone formation and the decomposition of organic additives, are low and usually neglected. With new freshly-formed cells, negative electrodes can be charged efficiently over a range of current densities and temperatures with little gas evolution, whereas under similar conditions positive electrodes evolve oxygen from the outset [7].

At high rates of charge, it becomes difficult to sustain the mass and charge balances that are necessary for the solution–precipitation charging mechanism to proceed. While the lead sulfate crystals are small, the fluxes of ions to the reaction sites may be rate-determining [8]. With increasing crystallite size, however, the discharge product may become resistant to the charging and, as a consequence, the potential rises and charge current is diverted to the parasitic reaction of hydrogen evolution. Ultimate battery failure occurs when the negative plate remains in the discharged state. It has been found [9] that some forms of carbon, when present in or on the negative active-material, can be very beneficial in minimizing the irreversible formation of lead sulfate.

2. Previous notions about the function of carbon

It is standard practice in the manufacture of lead–acid batteries to add to the negative plate a combination of barium sulfate, an organic extract of wood, and carbon. Collectively known as ‘expanders’ and usually in total comprising less than 1 wt.% of the negative mass, the additives not only increase the available capacity (especially when cells are discharged at high current densities and low temperatures) but also reduce capacity loss during cycling. The mechanism by which expanders prove effective was studied extensively during the last century [10–14]. Barium sulfate is considered to act as a seed for the precipitation of lead sulfate due to the isomorphous structure of the two salts. The organic additives — usually sulfonated derivatives of lignin (a natural product extracted from wood pulp) — are surfactants that absorb both on the surface of lead and on the lead sulfate crystals as they are formed during discharge. This action inhibits crystal growth during the dissolution–precipitation reaction and thereby helps to maintain a high surface-area by preventing contraction and solidification of the ‘spongy’ lead active-material.

The function of carbon additions to the negative active-material has been the subject of much debate. At one time, the presence of finely-divided amorphous carbon, otherwise known as ‘lampblack’

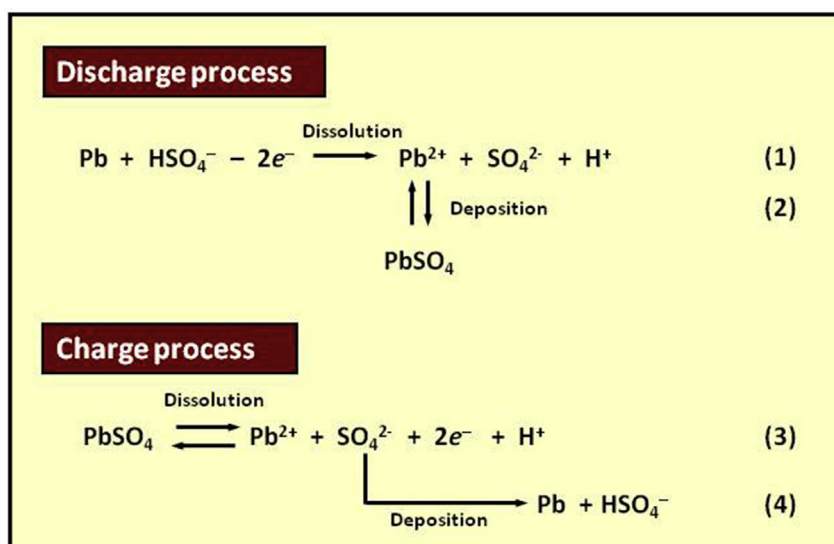


Fig. 1. Discharge and charge reactions at the negative plate of a lead–acid cell.

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