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Review

The role of carbon in valve-regulated lead–acid battery technology☆

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Abstract

The properties of different forms of carbon and their potential, as active mass additives, for influencing the performance of valve-regulated lead–acid batteries are reviewed. Carbon additives to the positive active-mass appear to benefit capacity, but are progressively lost due to oxidation. Some forms of carbon in the negative active-material are able to resist the tendency to sulfation during high-rate partial-state-of-charge operation to some considerable extent, but the mechanism of this benefit is not yet fully understood.
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Contents

1. Introduction

For many years, carbon has been favoured as an additive to the negative active-material in lead–acid batteries, despite the fact that there has never been universal agreement on the reasons for its use [1]. Now that the valve-regulated version of the battery (VRLA) is being exposed to high-rate partial-state-of-charge (HRPSoC) operation in various applications [2], evidence is emerging that demonstrates clearly the beneficial effects of carbon. In particular, increased levels of certain forms of carbon act to restrict the progress of plate sulfation, the process which ultimately terminates the useful life of the battery in HRPSoC duty. There has also been a report [3] that the addition of certain types of carbon to the positive active-material can improve battery capacity and life. In view of these developments, and the diverse range of chemical and physical properties that are observed in different forms of carbon, it is timely to review the mechanisms by which carbon additions could benefit VRLA batteries in various duty cycles, and to assess the forms of carbon that are likely to provide the greatest benefit.

2. Allotropes of carbon and their properties

Elemental carbon participates in two distinct types of covalent bonding. In the diamond structure, each atom is joined to

four neighbours, at a distance of 1.54 Å, by tetrahedrally oriented bonds that are formed by sp^3 hybrid orbitals. There is an energy gap of 5.3 eV between the σ and σ^* bands so that the material is an insulator [4]. In the graphite structure, the atoms are arranged in planar hexagonal networks (so-called 'graphene' layers) that are held together by strong sp^2 bonds, 1.42 Å in length. The bonding between these planar layers (van der Waals type) is relatively weak (bond length 3.35 Å). In graphite, which is the equilibrium phase under ambient conditions, π and π^* bands around the Fermi level fill the σ–σ^* gap, which renders the material semi-metallic. The structure leaves the conductivity highly anisotropic, however, with the in-plane conductivity two-to-three orders of magnitude greater than that in the direction perpendicular to the plane [5]. More recently discovered forms of carbon (fullerenes, nanotubes, etc.) consist of structures in which hexagonal networks of carbon atoms are curved into spherical or cylindrical shapes.

The diamond structure tends to exhibit a high degree of crystalline perfection, although isolated point defects can occur. The layered structure in graphite, however, allows a range of defect opportunities, that give rise to considerable variability in physical properties. The normal –AB– layer stacking sequence, in which the atoms of alternate layers in the crystallographic c-axis sequence are situated identically in the x–y plane, results in a hexagonal structure. The structure can, however, be re-ordered to construct a rhombohedral sequence –ABC– in which the atoms of every third layer in the c axis sequence are situated identically in the x–y plane. Such re-ordering can be partial or complete. Further, a fraction of the carbon atoms can be sp^3 rather than sp^2 hybridized, with the result that the graphene layers become buckled. Indeed, the concentration of sp^3 carbons can be quite high [4]. Disordered carbon systems with the same sp^2/sp^3 ratio show a variety of different electronic structures owing to the degree of clustering of sp^2 carbons into 'graphitic domains' [6]. A disordered distribution of sp^2 sites in an sp^2/sp^3 mixed system disrupts the conjugated π electron system even when the concentration of sp^3 carbons is rather low. This 'non-graphitic' disorder serves to reduce conductivity, but this can be restored by thermally induced migration of sp^3 defects at temperatures from 200 to 400 °C [4]. The degree of crystalline perfection is reduced to a minimum in the production of amorphous or glassy forms of carbon. The ultimate crystallite size for carbon materials can vary over a large range, from 0.001 to 100 μm [7]. Evidently, the specific surface area of such material can also vary widely.

Departures from the perfect structure of graphite, which can arise from the occurrence of stacking faults and/or the accommodation of sp^3 carbon atoms, cause the conductance of the material to be variable over a wide range [4]. The chemical reactivity of a given carbon material is influenced by the specific area and the composition of the surface. Each sp^3 carbon atom has one free bond that is not involved in holding the graphene layer together. Such bonds can accommodate a variety of chemical entities, e.g., carbonyl, carboxyl, lactone, quinone, phenol, and various sulfur and nitrogen species [7].

Two important factors affect the electrochemical behaviour of graphite, namely, the layered structure and an amphoteric disposition [8]. The layered structure of graphite, which involves strong bonds within the sheets of atoms lying perpendicular to the c axis and weak bonds between the sheets, allows a rich intercalation chemistry. A wide variety of species can be inserted between the graphene sheets and this increases the spacing between the sheets (Fig. 1) without disturbing the bonds that hold the sheets together. The earliest graphite intercalation compounds, which involved the incorporation of potassium, were reported over 160 years ago [9]. Intercalation into graphite host materials is classified in terms of 'n' stages. Stage-n is defined as the structure in which intercalates are accommodated regularly in every nth graphitic gallery. The structure in which intercalates occupy every graphite gallery is termed a stage-1 structure (as in Fig. 1). The process of intercalation can give rise to a large expansion in the c axis direction of the crystal structure as quite large ions and/or groups can be accommodated.

The amphoteric characteristic arises because graphite is a semi-metal (the valence and conduction bands overlap slightly [10]) in which both electrons and holes are always available to carry current. As a result, graphite can act as an oxidant towards an electron donor intercalate and as a reductant towards electron acceptor species such as acids. Pure graphite intercalation compounds can be synthesized with stages between 1 and, at least 12, depending on the nature of the intercalate and the synthesis route. Graphite intercalation compounds can exhibit remarkable properties. For example, the stage-1 lithium graphite intercala-
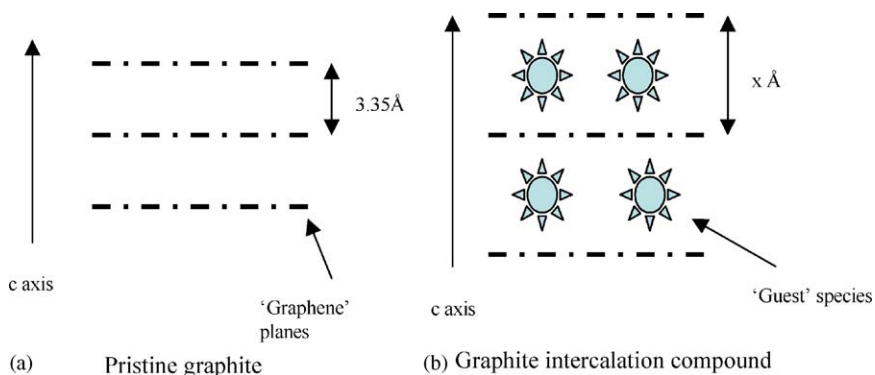

Fig. 1. Schematic of graphite intercalation. (a) An 'edge-on' view of the graphene planes in un-reacted graphite; (b) an edge-on view of a stage-1 graphite intercalation compound showing expansion of the interplanar spacing to accommodate the guest species. The dimension, x, can take values up to 9 Å or more without disrupting the long-range order of the crystal structure.