

Positive plate additives

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Abstract

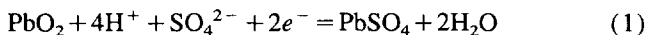
Approaches to the use of additives in pursuit of improved active material utilization in the positive plate of the lead/acid battery are reviewed. In order for the use of additives to lead to significant improvements in specific energy adequate provision must be made to support the stoichiometry of the discharge reaction and consideration must be given to the volume fraction occupied by candidate materials.

Keywords: Lead/acid batteries; Specific energy; Active material utilization; Additives

1. Introduction

A persistent frustration for developers of the lead/acid battery is that the utilization of active material, particularly in the positive plate, remains very low (typically around 30% at the $C_1/1$ rate) while strenuous efforts are being made to increase the specific energy of the system. The electric vehicle market in particular would certainly respond positively to the increase in specific energy that would result from a rise in active material utilization at the $C_1/1$ rate to even 60%.

The discharge capacity available from the battery, especially at high rates, is generally limited by the kinetics of supply of reactants in the discharge reaction [1]



At the site of the reaction — distributed over the surface area of the liquid/solid interface of the porous positive electrode — there must be an adequate supply of acid and of electrons to sustain the reaction at the required discharge rate. Simultaneously, the porous electrode structure must allow the diffusion of the reaction product (water) away from the reaction site and the accommodation of a solid reaction product (PbSO_4) with a greater molar volume than the solid reactant (PbO_2).

The supply of electronic charge is influenced by the electrical resistance of the material between the current collector grid member and the site of the reaction (see Fig. 1) via interparticle contacts, as in the so-called Kugelhaufen model [2]. The supply of acid from the reservoir outside the porous electrode is controlled by diffusion through the pores. The flux of acid is a product of the diffusion coefficient, D and the concentration gradient, $\delta m/\delta x$ of the diffusing species (here acid) according to Fick's first law

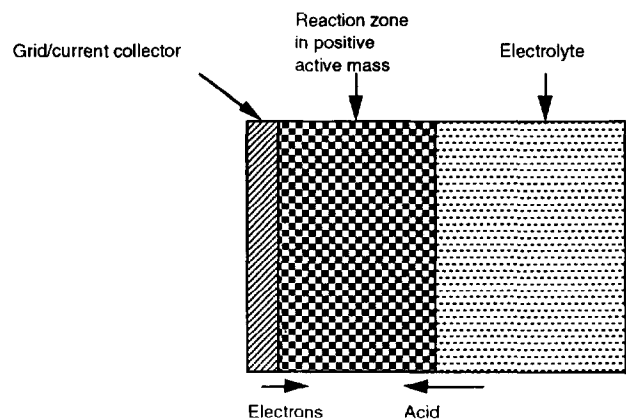


Fig. 1. Schematic of positive active mass shown bounded by current collector and electrolyte.

$$J = D \frac{\delta m}{\delta x} \quad (2)$$

Hence the overall flux of acid into the reaction sites can be increased and the utilization of the PbO_2 improved by decreasing the thickness of the active mass. However, unless the grid thickness is also reduced there will be a penalty in terms of a reduction in the active mass/grid weight ratio.

Utilization, and hence specific energy, is also strongly influenced by rate of discharge. For example, as shown in Fig. 2, a positive mass utilization of 60% at the 20-h rate falls to less than 40% at discharge rates that are of interest for electric vehicles [3].

It may be that at some discharge rates the limiting factor would be electronic conductivity while at other rates the limiting factor would be acid diffusion. Therefore, it is very important to take account of the rate at which the battery will

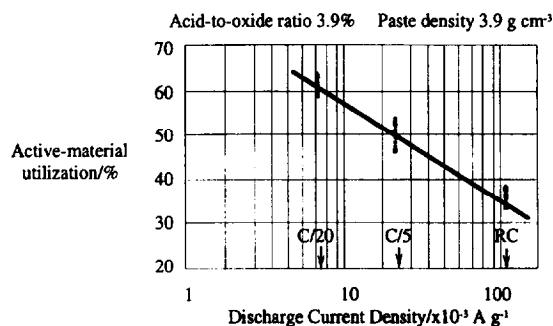


Fig. 2. Example of the effect of discharge current density on active material utilization taken from Ref. [3].

be discharged when seeking improvement by the use of additives to promote the discharge reaction.

In a similar way, the thickness of the active mass between the current collector and the bulk electrolyte also effects the degree of utilization and may dictate whether it is conductivity or diffusion that needs to be supported. This is because, at any particular temperature, the value of D in Eq. (2) remains constant so that acid flux depends directly on concentration gradient, $\delta m/\delta x$.

The motive behind much of the work on positive plate additives is the promotion of the supply of reactants to the site of the discharge reaction in pursuit of a higher active material utilization.

In all instances beneficial effects are sought with a minimum amount of additive since such materials do not themselves contribute to the discharge capacity. Materials proposed as additives for the positive active mass have been reviewed recently [4]. Issues that must be taken into consideration in the planned use of solid additives are taken up below.

2. Additives intended to enhance acid supply

There is ample evidence that acid supply is an important factor influencing discharge capacity of lead/acid cells. For example, available capacity has been shown to vary inversely with discharge time at low rates and with the square root of discharge time at high rates implying control by acid depletion and diffusion, respectively, in the two cases [5].

Attempts to aid acid supply are focused on providing additional porosity in order to enable enhanced diffusion from outside the active mass or to provide fine scale local reservoirs of acid within porous particles throughout the plate. The principle in this latter approach is to shorten the distance, x , in Eq. (2) and thus to enhance the flux. However, the stoichiometry of Eq. (1) indicates that the volume fraction ratio of the active mass would need to be around 10% oxide and 90% acid storage in order to provide for a complete discharge so that, in this case at least, the requirement for the additive to be a minority component is bound to be violated.

A third possibility is to induce bulk electrolyte movement in situ through assisted electro-osmosis [1]. This electrokinetic phenomenon describes the motion of liquid (e.g., battery electrolyte) through a membrane (e.g., porous lead dioxide structure) under the influence of an electric field (e.g., battery discharge). Under such action, there will be separation of electric charge between the solid and liquid phases and this is characterized by the zeta potential. The polarity of the zeta potential determines the direction of induced electrolyte flow, whilst the magnitude controls the flow rate. In battery-strength acid, the discharge product (lead sulfate) has a high positive zeta potential that tends to force acid out of the positive plate. The aim, therefore, is to develop robust electro-osmotic 'promoters' with substantially negative zeta potentials that, when incorporated in the positive action mass, will encourage electrolyte irrigation into the plate during battery discharge. Moreover, the ability of the promoter to keep pace with electrolyte demand is assisted by the fact that the rate of pumping is inversely proportional to electrolyte concentration and directly proportional to the current delivered by the battery. Thus, this is an attractive means of enhancing the irrigation of the plate since it is most effective for low concentrations of acid, i.e. when some assistance is most needed. However, the optimal deployment of the material within the porous electrode on the required scale is difficult.

Some of the materials that have been proposed as additives to enhance acid supply to the positive active mass are listed in Table 1.

Table 1
Materials proposed as additives to assist acid supply

Material	Loading (wt.%)	Mode of function	Refs.
Carboxymethyl cellulose	0.2–2.0	Porosity enhancement	[6], [7]
Hollow glass microspheres	1.1–6.6	Reduction in paste density	[8]
Carbon black	0.2–2.0	Porosity enhancement	[6], [7]
Silica gel	0.2	Acid reservoir	[4]
Synthetic fibers	0.2–2.0	Porosity enhancement	[6], [7]
Graphite ^a	0.1–2.0	Pore former	[9], [10]
	1–12	Electro-osmotic pumping agent	[1]

Other materials proposed in the patent literature are listed in Ref. [4].

^a Graphite may also act as a conductivity enhancer (see below).

Table 2
Materials proposed to enhance the conductivity of the positive active mass

Material	Loading (wt.%)	Conductivity at 300 K ($S\ m^{-1}$) ^a	Density ($Mg\ m^{-3}$)	Refs.
BaPbO ₃	~1	2×10^5	8.5	[13]
Ti ₄ O ₇	1–2	10^5	4.2	[14]
Ti ₅ O ₉	1–2	$\sim 10^2$	4.2	[15]
SnO ₂ (F)	2		6.9	[4]
SnO ₂ (Sb)	1–2	$10^2 - 10^4$	6.9	[16]
Graphite	0.5	10^5	2.2	[17]

Other transition metal oxides and a variety of forms of tin dioxide have been proposed in patents as reviewed in Ref. [4].

^a For comparison the electrical conductivities of α -, β -PbO₂ are 1.4×10^5 and $8 \times 10^5\ S\ m^{-1}$, respectively [18].

3. Additives intended to enhance conductivity

Attempts to assist the supply of electrons generally take cognizance of the progressive decrease of conductivity of the active mass associated with the conversion of a semi-conductor (PbO₂) to a resistive material (PbSO₄) and involve the addition of second phase materials with relatively high electronic conductivity. Thus, this type of additive is likely to be most effective in the later stages of discharge and in the latter stages of a plate's life when it is sulfated.

Some of the materials proposed to provide a constant conducting network over an adequate life are listed in Table 2. Issues in the development of these materials are resistance to corrosion and the deployment of the material with an appropriate aspect ratio. It has been suggested [11] that elongated fibrous additives will be most effective in providing a conducting network in the porous PbO₂ electrode.

Some of these materials have also been proposed as substitutes for lead alloys in the more substantial members of the current collecting system in the battery (the grid) [12]. Further some conducting additives are found to improve the efficiencies of the initial formation of the battery but the prime target for these studies, as with those that seek to promote acid supply, is an improved energy cycling performance of the battery.

4. Stability of additives

If an additive is to provide a capacity improvement through the working life of a battery then the material comprising it must be electrochemically inert in the acid environment and over the potential range of the positive electrode.

Several of the forms of conductive carbon employed as additives have been observed to oxidize during use and, although the porosity generated by the formation of CO₂ reaction product may be of some benefit the long term utility of carbon based additives appears to be questionable [4].

Some metal oxides may offer better prospects but it is important to bear in mind that it is generally necessary for a parent oxide to be invested with structural defects in order to achieve a useful electrical conductivity.

In the case of the Magnelli phases [4] the reduction of the parent oxide TiO₂ is accommodated by a crystallographic shear process in which two layers of the MO₆ octahedra of which the oxide is composed move closer together and eliminate a layer of oxygen ions. This systematically generates a number of Ti³⁺ ions that can contribute to the conductivity by donating electrons



Alternatively, donors may be generated in the parent oxide by the substitution of aliovalent ions. Examples would be the introduction of niobium onto the cationic sublattice of rutile, when donors would be generated by



or by fluorine substitution on the anionic sublattice of tin dioxide, when donors would be generated by



In any of these cases it will be necessary for the defect crystal structure containing shear planes or substitute ions to be stable in the conditions of the electrode throughout its life and some long-term testing will be essential.

5. Influence of stoichiometry

A factor that has not always been taken into account in the attempts to use additives to increase the rate of discharge of lead/acid cells is the influence of stoichiometry of the discharge reaction. Consideration of Eq. (1) indicates that there are three possible conditions to be taken into account:

1. If at a particular discharge rate the supply of reactants (acid and electronic charge) is in balance then an improved performance will only be achieved if the supply of both reactants is enhanced — improving acid access and electron conductivity — since both are limiting the reaction. Alternatively,
2. The electron supply alone may be limiting. This is probably the case at the end of a long slow discharge [3] when much of the material is already converted to insulating lead sulfate, or

3. Acid supply (diffusion) alone may be limiting. This tends to be the case earlier in the discharge, especially at high rates [19].

Thus, according to the stoichiometry of the discharge equation and starting from a balanced case, one would not expect the enhancement of the supply of electrons (depolarization) to make any difference to the utilization of active material without a concomitant increase in the acid supply.

The somewhat limited success of experiments with the additives shown in Tables 1 and 2 is perhaps not surprising since in most cases only one additive has been used at a time. Thus, even in those cases where the correct type of additive has been chosen, e.g. an acid supply enhancer where it is the acid supply that is limiting, the additive will only be effective until the other factor, in the example case the conductivity, becomes limiting. In cases where the supply of electronic charge and the supply of acid are in balance additives of either type will be ineffective because the other effect will immediately become limiting. Also, if the wrong type of additive is used — for example a conductor in a case when the acid supply is limiting — then again there will be no effect.

Instances of the successful use of additives to the positive active mass are consistent with these considerations. Thus, the addition of hollow glass microspheres [19] is most effective at highest rates, when it is most likely that acid supply will be limiting, but even then there is an optimum loading above which the measured utilization begins to fall as a result of the addition of insulating material and a switch back to a conductance limitation. Further, in the case of conducting flakes of tin oxide coated glass, the greatest improvement was found at the lowest paste density — a condition when acid supply is least likely to be limiting.

The logical conclusion that arises from an acknowledgement of the importance of monitoring stoichiometry in the use of additives is that either an additive must be found that will perform both functions — supporting acid supply and enhancing conductivity or additives must be used in pairs — one of each type.

Thus, it is interesting to note that instances where graphite additions have been reported to improve active material utilization [1,17] may be attributable to the material performing both a conductivity enhancement function and an acid supply

enhancement (by pore forming or electro-osmotic pumping) [1] simultaneously.

6. Conclusions

The pursuit of enhanced positive active mass utilization through the use of additives has a considerable history and there have been some positive results. The full promise has not yet been realized, possibly because insufficient attention has been paid to the stoichiometry requirements of the discharge reaction. Work on this topic will undoubtedly continue because the potential reward is highly significant.

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