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Q3 Effect of polyvinyl alcohol/nano-carbon colloid on the electrochemical performance of Q4 negative plates of lead acid battery

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ABSTRACT

Polyvinyl alcohol/nano-carbon colloid (PCC) was prepared through a simple physical mixture process. Both fully charge-discharge and insufficient charge tests were carried out to demonstrate the positive effects of PCC on the electrical storage capability of the negative electrode of lead acid battery. Cyclic voltammetry, steady polarization and electrochemical impedance spectroscopy were used to characterize the influences of PCC on the electrochemical behaviors of negative electrode in the lead acid battery. Experiment results demonstrate that PCC has positive effect on inhibiting PbSO_4 growth and increasing the HER overpotential, thus the lead acid battery with PCC shows the enhanced charge acceptance and stable discharge capacities under insufficient charge test. This paper opens a new way for enhancing the performance of lead acid battery without changing the traditional structure and design of lead acid battery.

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1. Introduction

Lead acid battery (LAB) has been a reliable energy storage device for more than 150 years since Plante invented LAB in 1859 [1–3]. Due to its characteristics of safety, reliable performance and mature manufacture, lead acid battery has been applied in various applications, such as start, light and ignition (SLI) batteries for automobiles [4], uninterruptable power supply (UPS) [5], electric vehicles (especially for electric bicycles and tricycles) [6] and the storage of electricity generated by renewable energies or pulse power source in hybrid electrical vehicles [7,8]. The applications of LAB can be classified into four user modes: (i) Infrequent discharge for UPS, in which condition, LAB is under fully charged condition at most time of its service life; (ii) Frequent, shallow depth of discharge for SLI applications; (iii) Deep charge-discharge duty in electric vehicles; (iv) The forth situations, probably the most rapid-developing application of LAB in 21st century, are the applications of LAB under partial state of charge (PSOC) duty, such as battery module in hybrid electric vehicles and the grid-scale energy storage of electricity generated by renewable energy.

For grid-scale energy storage, LABs works as an electrical load when renewable energy generates extra energy. When the requirement of load can't be satisfied by renewable energy, LABs release power. In

this case, LABs in renewable energy storage undergoes insufficient charge, which is also called PSOC conditions [9,10].

In PSOC duty, the negative active materials (NAM) of LAB faces sulfation, namely, the electrochemically active PbSO_4 with small particle size grows into non-electrochemically active PbSO_4 with large particle size which can be hardly charged into its active state of sponge Pb [11]. The sulfation of negative electrode is one of the main problems that shortens the cycle life of LAB, resulting in high electricity storage cost of renewable energy storage. It's of great necessity to enhance the service life of the negative electrode in LAB under PSOC operation.

Sulfation of negative electrode can be solved by inhibiting the growth of PbSO_4 particles. The addition of carbon materials into the NAM could reduce the sulfation problem [12–20]. Although, carbon materials greatly enhances the electrical double layer capacitance and the conductivity of negative plates at PSOC condition, the effect of carbon materials on the electrochemical process is thought mainly due to altering of the active surface which serves as nucleation sites for the deposition of Pb in negative electrode [15,16]. This role of carbon materials is just like the role of BaSO_4 , which reduces the particle size of PbSO_4 by severing as nucleation sites for the growth of PbSO_4 .

Despite of the positive effect of carbon materials, the production of lead-carbon composite electrode is somewhat technically difficult due to the change of the density of lead-oxide-based pastes, the lowered over-potential of hydrogen evolution reaction (HER), the instability of lead-carbon composite electrode and also the higher self-discharge rate [21].

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Fig. 1. (a) Stability test of nano-carbon in water, (b) PCC in water solution and (c) PCC added in sulfuric acid (s.g. 1.24) with a volume ratio of 2 v% after 8 months' storage.

Fig. 2. Schematic diagram of the charge-discharge protocol for the energy storage stability under insufficient charge conditions.

Another way to reduce the sulfation of negative electrode is to explore sulfation inhibitor in the electrolyte of LAB. The addition of sulfation inhibitor in the electrolyte is a facile method which can be adopted in industrial production easily [22–28]. Wang et al. designed a kind of polysiloxane-based gel electrolyte for LAB, the polysiloxane-based gel electrode possesses higher HER over-potential than traditional silica gel electrolyte [22]. Hence, the LAB based on the polysiloxane-based gel electrolyte exhibits higher capacity. Based on this case, the formation of gel electrolyte is very important for the PSoC operation of LAB [23]. Polyaspartic acid (PASP) seems to be an effective additive in the sulfuric electrolyte, especially in gel-based-electrolyte for LAB working under PSoC duty [24–26]. In 2006, Pavlov et al. reported that PASP controls the crystallization process of PbSO_4 and modifies the shape and size of PbSO_4 crystals [24]. In 2012, Pavlov

Fig. 3. (a) Dependence of discharge capacity on cycle numbers; (b) dependence of coulombic efficiency on cycle numbers; (c) the 10th charge-discharge curves of lead acid battery with and without PCC; (d) the 24th charge-discharge curves of lead acid battery with and without PCC.

further demonstrated the superior performance of PASP in electrolyte for a lead-carbon composite electrode [25]. In 2016, Tantavichet et al. discovered that the addition of 0.005 (w/v)% PASP in the gelled electrolyte could greatly enhance the performance of LAB in both 100% depth of discharge (DoD) and PSoC duty [26]. Notably, some other materials may be also suitable for both liquid electrolyte and gel-electrolyte. Deyab found the positive effect of L-serine on increasing the HER overpotential of negative electrode [27]. The electrolyte additives mentioned above reduce the particle size of PbSO_4 [28]. Subsequently, the electrochemically active PbSO_4 reduces polarization, which leads to low HER rate of negative electrodes and cyclic stability of LABs [16].

Since both organic additives and carbon materials [29–31] can be added to alter the electrochemical performance of negative electrode in LAB. In this paper, polyvinyl alcohol/nano-carbon colloid (PCC) was prepared through simple dissolution process. Experiment results demonstrate that PCC exhibits positive effect on suppressing the growth of PbSO_4 and improving the cyclic stability of LAB under insufficient charge condition. This paper proposes a new way for enhancing the performance of lead acid battery without changing the structure and design of LAB.

2. Experimental

2.1. Preparation of polyvinyl alcohol/nano-carbon colloid (PCC)

To synthesize the polyvinyl alcohol/nano-carbon colloid (PCC) additives, first, a kind of water-soluble polymer, polyvinyl alcohol (20 g), was dissolved in water (500 mL) at a fixed temperature of 95 °C with a stir stirring for 2 h, and then a kind of nano-sized carbon material, acetylene black (1 g), was added in the solution slowly with the help

of ultrasonic treatment for another 2 h. PCC was collected and preserved for use. As shown in Fig. 1, the nano-carbon precipitated in the water (Fig. 1), while, PCC has good stability in water (Fig. 1b). The concentration of PCC in sulfuric acid electrolyte (s.g. 1.24 g cm^{-3}) for container formation or electrochemical test was 2 v%, which is shown in Fig. 1c. The PCC added in sulfuric electrolyte also shows good stability.

2.2. Battery assembly and test

A 2 V battery with commercial negative plates and positive plates (obtained from Meineng group, Zhejiang province, China) was assembled. The unit 2 V battery was composed of 7 positive plates and 8 negative plates. Each plate has a geometric area of ca. 7 cm × 4 cm. H_2SO_4 solution with specific gravity of 1.24 g cm^{-3} was used as electrolyte in container formation process. The nominal 2-h capacity (C_2) of the assembled battery was 12 Ah. The charge-discharge test of LAB was carried on a battery tester (CT2001B, LANHE, China). The formation process was carried out in a standard industrial formation process, which was applied in our previous study [29]. After formation, the battery goes capacity test with a constant charge current of $0.2C_2$ to 2.45 V and a constant charge voltage of 2.45 V for 6 h, the discharge current is $0.5C_2$ with a cut-off voltage of 1.8 V. The test of insufficient charge of lead acid battery was shown in Fig. 2. After fully charged, the battery goes discharge and last for 120 h (5 days) at discharged state, then the battery goes three charge-discharge cycles, repeat the above process for 4 times.

2.3. Physical and electrochemical characterization

The morphologies of the negative plates were observed with a field emission scan electron microscope (SEM) (SU8020, Hitachi, Japan). For

Fig. 4. (a) Dependence of discharge capacity on cycle numbers under insufficient charge conditions; (b) dependence of coulombic efficiency on cycle numbers under insufficient charge conditions; (c) the 10th charge-discharge curves of lead acid battery with and without PCC; (d) the current-time curve during the constant voltage charge process of the 10th charge-discharge.

three-electrode electrochemical investigations, a pure lead electrode with geometric area of $2\text{ cm} \times 2\text{ cm}$ was applied. H_2SO_4 with specific gravity of 1.28 was used as electrolyte. The pretreatment of lead electrode was described in our previous work [16]. Cyclic voltammetry, steady polarization and electrochemical impedance spectroscopy (EIS) were tested on an electrochemical work station (Parstat 2273, Ametek, USA). Steady polarization was test with chronoamperometry method and the current response was collected after 1200 s when a certain potential was set. The EIS results were simulated via Zsimpwin software. In the three electrode measurement, all the potentials were quoted with respect to a mercurous sulfate electrode (MSE) ($\text{Hg}/\text{Hg}_2\text{SO}_4/\text{K}_2\text{SO}_4$ (saturated), 0.65 V vs. SHE).

3. Results and discussions

To demonstrate the positive effects of PCC towards lead acid battery, two parallel experiments (PCC1 and PCC2) were carried out. As shown in Fig. 3a, LAB with PCC added in the electrolyte has a relatively smaller capacity than the control battery at initial 10 cycles. However, higher capacity of LAB with PCC was observed from 18 to 24 cycles. The coulombic efficiency of LAB usually is higher than 90% due to the high HER overpotential on Pb electrode and high oxygen evolution overpotential on PbO_2 electrode. The coulombic efficiency of the control battery and LAB with PCC was displayed in Fig. 3b. Owing to the addition of PCC in the electrolyte in LAB, the LAB with PCC has a much higher coulombic efficiency than the control battery, which can be seen from the 10th (Fig. 3c) and 24th (Fig. 3d) charge-discharge curves.

As shown in Fig. 4a, the capacity of the control battery is relatively lower than the LAB with PCC within the 12 cycles under insufficient charge condition. Great difference has been seen in the coulombic efficiency (Fig. 4b), the LAB with PCC has a much higher coulombic

efficiency than the control battery. The control battery only has a coulombic efficiency of 83.65% after exposed at discharged condition for 120 h. With the accumulation of time at discharged condition for 480 h, the control battery only has a coulombic efficiency of 79.81%, much lower than LAB with PCC (90%–95%). This result is due to the lowered charge acceptance of lead negative electrode, since sulfation of negative electrode occurs when LAB was exposed at discharged condition for long time [9]. The subsequent reaction is the HER reaction on Pb negative electrode, which decreases the coulombic efficiency. Although the coulombic efficiency of LAB with PCC lowers after 120 h exposed at discharged condition, the coulombic efficiency of LAB with PCC was much higher than the control battery. Within 12 charge-discharge cycles, LAB with PCC always has a coulombic efficiency above 90%. The above results demonstrated that, PCC can improve the charge acceptance of negative electrode under insufficient charge conditions. The charge-discharge curves of LAB with PCC and control battery (Fig. 4c) reveals the much better charge acceptance of LAB with PCC than the control battery. Current-time curve at the constant voltage charge process reveals that the hydrogen evolution rate of LAB with PCC was lower than the control battery (Fig. 4d). Namely, the side-reaction of HER was lowered by adding PCC in electrolyte, which is the reason for the enhanced charge acceptance of LAB with PCC additive.

Large PbSO_4 particle size will make Pb electrode less electrochemically active, hence the HER on the sulfated negative electrode will be more preferential than the non-sulfated one. The preferential HER on sulfated lead negative electrode is the reason for the lowered coulombic efficiency. The sulfation of negative electrode will thus result in the subsequent loss of water and the failure of LAB to store electricity. SEM was used to observe the PbSO_4 accumulated on the surface of the negative

Fig. 5. SEM images of the surface of negative plate after insufficient charge test (a) with PCC and (b) without PCC.

Fig. 6. (a) Cyclic voltammograms of lead with continuous test before and after the addition of PCC; (b) steady polarization curve of lead with and without PCC added in electrolyte.

plates of LAB, as can be seen, the LAB with PCC in electrolytes has smaller PbSO_4 particle size (Fig. 5a) accumulated on the surface of negative plates of LAB than the control battery (Fig. 5b). The PCC used in electrolyte reduces the particle size of PbSO_4 effectively.

Electrochemical experiments were carried out to study the influence of PCC on the electrochemical behavior of Pb electrode. Cyclic voltammograms from -1.4 V to -0.7 V (Fig. 6a) were carried out to study the electrochemical behavior of Pb in 5 M H_2SO_4 , the oxidation peak tends to increase due to the activation of surface. After the activation of Pb surface, the oxidation peak tends to be steady. The nano-carbon materials in the colloids do not show clear effect on the reversibility of Pb/PbSO₄ redox couple, probably because of the unabsorbed state of

Table 1

Simulated values of each element in the equivalent circuit of Pb electrode with or without the addition of PCC.

Potential V	Electrolyte	R_s Ω	Q_{dl} $\Omega^{-1} \text{ s}^n$	n	R_{ct} Ω	χ^2
–1.0	Without	0.336	1.674×10^{-4}	0.8961	169.3	2.64×10^{-3}
	With PCC	0.341	1.471×10^{-4}	0.8924	219.2	4.54×10^{-3}
–1.1	Without	0.348	1.007×10^{-4}	0.9200	57.15	3.19×10^{-3}
	With PCC	0.356	9.081×10^{-5}	0.9155	71.51	2.92×10^{-3}
–1.2	Without	0.387	6.585×10^{-5}	0.9455	19.22	1.34×10^{-2}
	With PCC	0.373	7.278×10^{-5}	0.9226	25.76	4.49×10^{-3}

Fig. 7. Electrochemical impedance spectra (Nyquist plot) measured on Pb electrode with PCC or without PCC in electrolyte at (a) -1.0 V, (b) -1.1 V, (c) -1.2 V vs. MSE, respectively. The inset of (c) is the equivalent circuit of Pb electrode.

nano-carbon materials in the electrochemical test cell. However, in a compressed LAB, especially a valve-regulated LAB, the nano-carbon materials absorb on the surface of negative plate, because the internal oxygen combination reaction pushes the nano-carbon onto the surface of Pb plates. Nano-carbon on the surface of negative plates thus can work as the electrochemical active sites for the deposition of Pb in the charge process [32]. The hydrogen evolution behavior has been greatly influenced by the addition of PCC in electrolyte. The Pb electrode has a higher overpotential of HER, which is caused by the polyvinyl alcohol in PCC. The HER rate has been lowered by the addition of PCC which can be seen from the lower current response after the addition of PCC in electrolyte. Steady polarization (Fig. 6b) also demonstrated the lowered HER rate after the addition of PCC in electrolyte. The lowered HER rate of Pb electrode with PCC added in the electrolyte will endow LAB a high charge acceptance.

Electrochemical impedance spectroscopy (EIS) (Fig. 7) was used to study the electrode/electrolyte interface of Pb/ H_2SO_4 system. The as prepared Pb electrode was polarized at -1.2 V for 20 min to eliminate the oxides on the surface of Pb. The EIS was measured at -1.0 V, -1.1 V and -1.2 V respectively. Clear tendency can be observed that the impedance of Pb electrode with PCC in electrolyte was much higher than the Pb without PCC in electrolyte. The Nyquist plot shows a charge-transfer dominated behavior. Hence a classical R(QR) equivalent circuit was used to simulate the electrical behavior. In the equivalent circuit, R_s stands for the ohm resistance, Q_{dl} represents the non-ideal electrical double layer capacitor behavior and R_{ct} is the charge transfer resistance of HER on Pb electrode. The simulated results of the electrical elements are listed in Table 1. As shown in Table 1, the clear tendency was seen that the R_{ct} of Pb with PCC in electrolyte was much higher than Pb electrode without PCC. As an example, at -1.0 V the charge transfer resistance of Pb with PCC is 219.2 Ω , which is higher than Pb without PCC in electrolyte (169.3 Ω). At -1.2 V, the charge transfer resistance of Pb with PCC is 25.76 Ω , which is higher than Pb without PCC in electrolyte (19.22 Ω). The increased charge transfer resistance of Pb electrode with PCC in electrolyte demonstrated the HER inhibitor effect of PCC on Pb electrode during the charge process of LAB.

Fig. 8. Schematic diagram of the mechanism of PCC on Pb electrode.

4. Conclusion

In summary, the PCC added in the electrolyte of LAB has the following function (shown as schematic diagram shown in Fig. 8): (i) PCC can reduce the particle size of PbSO_4 on Pb electrode when Pb electrode is under insufficient charge condition, the reduced particle size of PbSO_4 makes it more electrochemically active; (ii) polyvinyl alcohol in PCC works as HER inhibitor altering the Pb/HSO_4 interface, and thus inhibiting the HER rate on Pb surface; (iii) carbon in the PCC may be absorbed on the surface on Pb electrode, thus increasing the electrochemical active surface during the charge process of Pb/PbSO_4 electrode. Since polyvinyl alcohol and acetylene black are very common, and the preparation of PCC is rather simple, PCC holds great potential to be used in the present lead acid battery industry.

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