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RESEARCH ARTICLE

The effect of sodium polymethacrylate on the rheology of the positive paste and performance of the lead-acid battery

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Abstract

Due to its rheological properties, positive lead-acid battery paste can be difficult to spread on lead current collectors accurately and efficiently under industry machinery and setting. Sodium polymethacrylate dispersant was studied as an effective positive paste additive that could lower the yield stress of the paste without affecting paste density and battery performance. Under a four-blade vane rheometer setup, stress growth and oscillatory amplitude strain sweep experiments evaluated the rheological properties of positive paste with the addition of varying amounts of sodium polymethacrylate. Further, the electrochemical effects of sodium polymethacrylate were also evaluated in 2V batteries by testing positive active material utilization and cycle life.

KEYWORDS

additive, dispersant, lead-acid battery, rheology, paste, sodium polymethacrylate

1 | INTRODUCTION

Lead-acid batteries make up about 78% of the world's battery power.¹ They are still heavily used for SLI (starting, lighting, ignition) purposes in conventional, hybrid, and electric vehicles, and in uninterrupted battery supply and telecommunication applications.^{1,2} The strong appeal of the over 150-year-old battery technology lies in low cost, reliability, safety, and recyclability.²

The design origins of the modern lead-acid battery electrode can be traced back to Fauré's invention developed in 1881.³ In place of the original Planté battery that used lead metal sheets for the electrodes, Fauré proposed coating the lead sheets with a paste made of lead oxides, sulfuric acid, and water. The pasting invention greatly increased the capacity of the cell and enabled industrial production of lead-acid batteries.⁴ While the solid lead sheets are now perforated lead grids, to this day the pasting technique has remained an integral part of the lead-acid battery design.

The industrial pasting of these plates, however, has evolved significantly. New manufacturing technologies

and automations have increased the speed, consistency, and precision of the electrode pasting process. In the modern battery plant, the paste is mixed in a large reactor that controls the rate addition of the acid, temperature, and mixing speed. After preparation, the paste is released progressively into a hopper that rolls the paste further down to a high-speed belt-type pasting machine located underneath. The pasting machine spreads or presses paste onto the perforated lead grid sheets from the top and threads glass or cellulose pasting paper under the grids to physically support the applied paste from the bottom. After the system of conveyor belts transports the pasted grid and paper to pressing and cutting units, the pasted electrode plates are stacked and ready to be moved to the next technological process.

The paste mixing and pasting control operators are responsible for several parameters that play key roles in realizing the design specifications of the battery being produced. Among others these include paste density, paste plasticity, paste composition, pasted plate thickness, uniformity of the pasted plates, and the weight of applied

paste for each plate. The accuracy and precision of these quality factors cannot be overvalued, as they affect the subsequent curing, drying, formation processes, and ultimately the overall performance of the final battery.

In this study, the authors addressed one of the industrial challenges concerning the machine pasting of the positive paste. The positive paste is typically coined in industry as “hard” and “crunchy,” characteristically requiring large amounts of force to push the paste down and spread onto the grid. Typical remedies have been to slow the conveyor belt, allow for more over-paste, and to decrease the amount of tension on the grid. Additionally, the calibration and set up of the machinery for the positive paste is often lengthy, resulting in many of the initial pasted plates to be discarded. A paste additive approach was explored to mitigate the pasting challenges encountered in the lead-acid battery industry.

Commercial polymethacrylate-based dispersants are commonly used for the dispersion of ceramics and casting of slurries.^{5–7} A sodium polymethacrylate dispersant was found to increase the flow of the positive paste and make it easier to spread. Small amounts were effective, an important parameter as to not affect the wet paste density. To the authors’ best knowledge, the use of such a dispersant was never reported for the lead-acid battery or other pastes before. The electrochemical stability and reversibility were tested using sample 2V lead-acid batteries and measuring capacity and cycle performance. The effect of the amount of dispersant on the rheology of the positive paste was shown using a cylinder and four-blade vane geometry, under stress growth and oscillatory strain experiments.

2 | EXPERIMENTAL

2.1 | Lead-acid positive paste

The positive lead-acid paste is a multiphase system consisting of predominately $3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O}$ (3BS) with lesser amounts of Pb, (α , β)-PbO, and PbSO_4 . The paste ingredients were vigorously mixed in a closed container. More details of this process can be found in Ref. (8). Various amounts of commercial dispersant sodium polymethacrylate –Darvan®–7N (DN7) (R. T. Vanderbilt Company, Norwalk, CT) were mixed at the very end. DN7 is a commercial solution composed of 25 wt.% polymer and 75 wt.% water. Then, the wet paste density was determined by packing the paste inside a known cylindrical volume of 8.76 ml and weighing. It was determined this method had a $0.25\text{ g}\cdot\text{ml}^{-1}$ standard deviation. The amounts of DN7 and its effect on paste density are shown in Table 1. Up to 0.12 wt.% (w.r.t

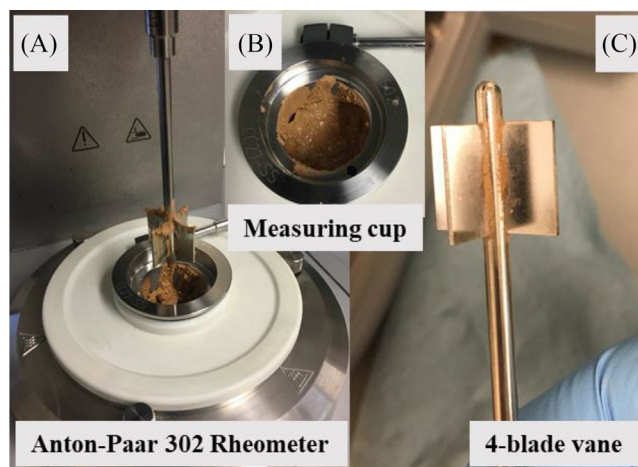


FIGURE 1 Experimental set-up of the rheometer (A), sandblasted measuring cup (B), and four-blade vane (C) used to measure rheological properties of the positive battery paste

leady oxide) of DN7, the wet paste density of the paste was not affected.

Qualitatively, it was observed that progressive addition of DN7 noticeably affected the texture and flowability of the positive paste. Cracks on the surface of the paste merged, and detached pieces of paste came together into one smooth body. These texture signs that the paste became smoother and better flowing. Also, less force was required to paste manually by hand. Stress growth and oscillatory amplitude strain sweep experiments were conducted to analyze rheological properties of the paste and the effect of dispersants.

2.2 | Rheological measurements

Rheological measurements were performed using a concentric four-blade vane and sandblasted cylinder geometry in an Anton Paar 302 rheometer at a constant temperature of 20°C (Figure 1). The use of the vane is a convenient and direct method for measuring yield stresses of pastes and has been successful in other highly concentrated systems such as soils, clays, and muds.⁹ Drying of the paste was not a factor, because the measuring configuration allowed about a 25 mm layer of paste to exceed the top of the stirrer (Figure 1B). Two different experiments were employed to measure the effect of DN7 on the flow of the positive battery paste - a stress growth test by applying a constant shear rate of 0.1 s^{-1} for 200 s and an oscillatory strain amplitude sweep from $1 \times 10^{-4}\%$ to $1 \times 10^3\%$ at a rate of 1 decade per 3 min and oscillation frequency of 1 Hz. Each presented curve is an average of five trials. Oscillatory tests were performed with an increasing strain ramp to avoid the consequence at low strain values of a preferential shear plane

TABLE 1 Positive paste recipe⁸ and the various amounts of DN7 added to the positive paste and their effects on wet paste density

Order	Paste ingredient	Amount (g)	Density (g·cm ⁻³)
1	Glass microfiber	0.50	
2	Deionized water	13.80	
3	Lead oxide	100.00	
4	Sulfuric acid solution (1.40 g·cm ⁻³)	6.10 (in 0.7 increments)	
		Wt.% (w.r.t. lead oxide)	
5	Darvan® 7-N (<i>R.T. Vanderbilt Company, Norwalk, CT</i>)	0.00	4.17 ± 0.25
		0.02	4.17
		0.12	4.21

near the blade edge, formed at high strain values. For the same reason, viscosity measurements were deemed unreliable, as the material lost homogeneity under large shear rates.

2.3 | 2V battery testing

Two amounts of DN7 were used inside the positive paste—0.02 and 0.12 wt.%—to test its compatibility as a dispersant for the lead-acid battery. Battery plates were hand pasted. Test 2V cells were built according to a positive material limited design (2 negatives, 1 positive) with excess volume of filling acid completely absorbed into six glass separator mats (AGM). Two mats were placed on both the bottom and top of the cell stack, and two single mats separated the cathode from the anodes. Polystyrene Petri dishes were used as the battery case, assuring about a 23% compression by height. The batteries were sealed airtight, and a check valve was used with 3.45 kPa cracking pressure.

After acid filling, batteries were soaked for a fixed duration in acid before the formation current was initiated. Two constant currents (0.002, 0.02 A) were used for a jar formation procedure, followed by a C/10 initial cycle, and 25 shallow C-rate conditioning cycles. Only after this was the battery final capacity measured, under various discharge rates C/20, C/10, C, 2C, 4C, and 8C. More details about the battery design and building procedure can be found in a previous study.⁸

Following the capacity measurements, the cycle life was tested under 2C discharge conditions. The cycling protocol consisted of discharging at 0.25 h and charging at C/3.5 rate for 1 h. The end-of-life was determined when the sample's end-of-discharge voltage falls below 1.70 V. To track the capacity degradation of the samples, every 200-cycle interval, the batteries were fully discharged to 1.80 V at the C/10 rate and to 1.70 V at the C rate.

3 | RESULTS AND DISCUSSION

3.1 | Rheological properties of paste with DN7 dispersant

3.1.1 | Stress growth measurements

To quantify the effects of various amounts of DN7 on paste flow, the shear stress of the paste was measured as a function of time at a constant applied shear rate of 0.1 s⁻¹ (Figure 2A and B). The maximum stress at which first evidence of plastic flow occurred was interpreted as the yield stress.^{9,10} DN7 lowered the yield stress of the positive paste; as the amounts of DN7 increased from 0.02, 0.06, and 0.10 wt.%, the yield stress was lowered to about 10 000, 8000, and 6000 Pa, respectively, compared to the yield stress of the control paste of about 12 000 Pa. The time and strain at which the yield stress occurred remained unchanged at about 40 s or 400%.

3.1.2 | Oscillatory strain sweep measurements

Oscillatory shear-strain amplitude sweep experiments are useful in characterizing the viscoelastic behavior of various pastes and gels. By oscillating the vane at a constant frequency, the complex shear modulus (G), calculated as the ratio of the resulting stress to the applied strain, can be separated into its storage (G') and loss (G'') components.¹¹ The linear viscoelastic region (LVE) can be defined as the region with a constant G' value and indicates the range of strain in which the structure of the paste remains intact. The shear stress at which the linearity of the LVE starts to deviate can be defined as the yield point.¹¹ After reaching the yield point, both G' and G'' decrease with a further increase in strain, indicating changes in the structure of the paste. As G' is still larger than G'' , the behavior is still predominantly elastic. The crossover point, at which $G' = G''$ indicates the transition from predominantly elastic to predominantly viscous behavior. Due to the suspected

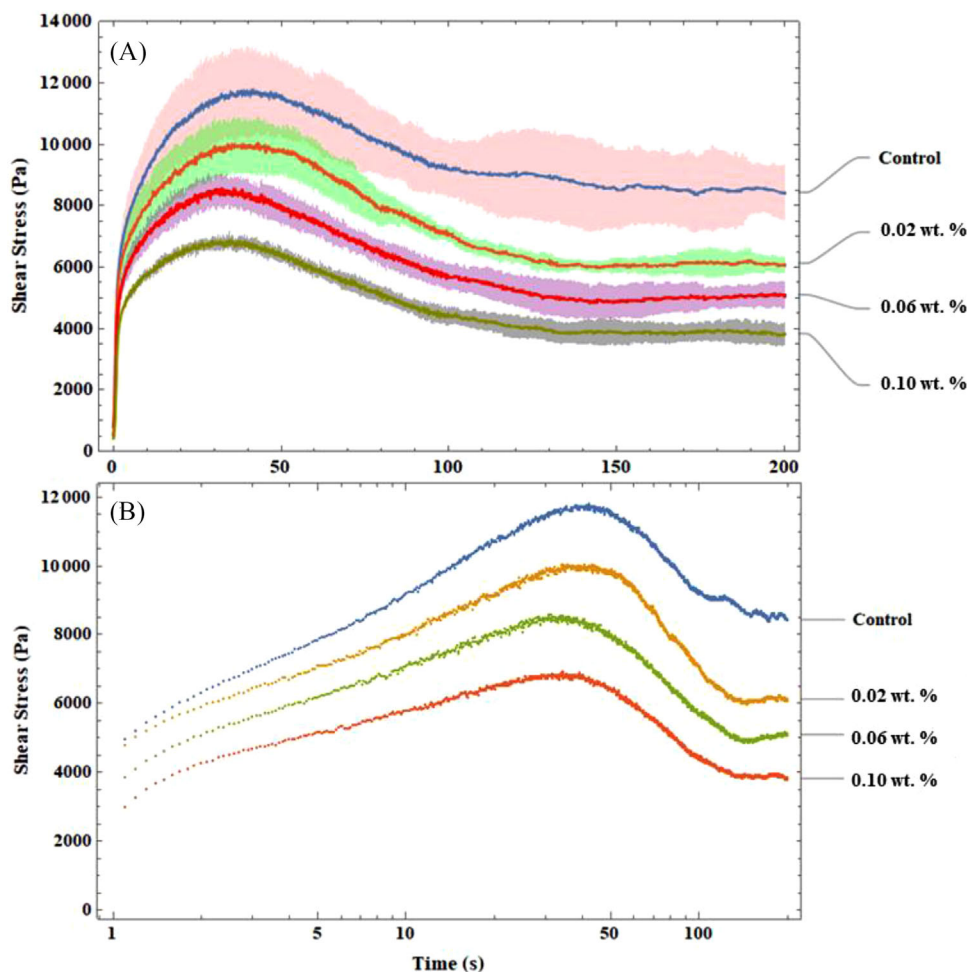


FIGURE 2 The average of five stress-time curves (bold) with corresponding 95% confidence interval (highlighted) at constant shear rate of 0.1 s^{-1} applied for 200 s for various amounts of DN7 in the positive battery paste (A). Time (s) in log scale (B)

formation of a shear plane beyond the yield stress, the data beyond the crossover point are not deemed reliable.

As marked in Figure 3A, the LVE region shortens, and the paste network begins to fracture at lower strain values with an increased dosage of DN7. In effect, 0.10 wt.% of DN7 lowers the yield point of the paste from approximately 853 to 448 Pa (Figure 3B). About a 50% amplitude strain marked the flow point of the paste for all DN7 amounts, and the total shear stress was lowered from 2100 to 1150 Pa at the moduli crossover. Oscillatory strain amplitude sweep showed the effects of DN7 on shortening the LVE strain region and lowering the yield point stress values.

3.1.3 | Discussion of rheological results

The vane geometry was a simple and highly reproducible method for measuring rheological properties of the positive lead-acid battery paste. Using the vane method to measure the effects of varying amounts of DN7 dispersant, the yield stress was measured under constant shear rate;

the yield and flow points were measured under oscillatory shear strain amplitude sweeps. In both techniques, DN7 lowered the shear stress values necessary for the paste to break structure and flow; although, a constant shear rate is more analogous to the pasting process in industry. Uncovering the result differences between the methods was outside the scope of this paper.

The paste was likely dispersed by an electrosteric stabilization mechanism, involving the adsorption of the anionic polyelectrolyte (DN7) onto the positively charged particle surfaces and repulsion between their stretched negatively charged polymer chains. The adsorption and degrees of disassociation of the polymer chains are dependent on the pH of the dispersion medium.⁵ The pH of the paste surface solution was measured to be about 8–10, based on a quick litmus paper test, and was in accordance with previous $\text{PbO}/\text{H}_2\text{SO}_4$ mixture studies.¹² Similarly, ammonium polymethacrylate was shown to disassociate and stretch most effectively in basic aqueous solutions.⁵

Since Pavlov et al.,¹³ a fundamental study on the rheological properties of the lead-acid battery pastes has not

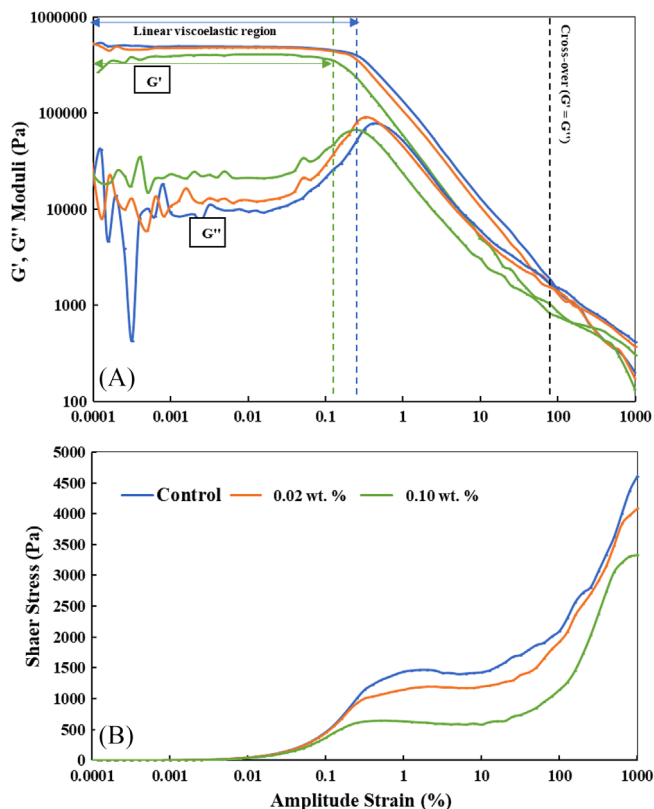


FIGURE 3 The storage (G') and loss moduli (G'') for positive pastes with various amounts of DN7 measured from the oscillatory amplitude strain sweep (A). The corresponding total shear stress for the amplitude sweep (B)

been undertaken. Moreover, benchmark tests for the material have been determined by relative means such as a penetrometer. This study demonstrates a more quantitative experimental technique to evaluate yielding characteristics of the paste. Further rheological studies using the vane method are encouraged to evaluate and understand the processing variables of the lead-acid battery paste more accurately and quantitatively.

3.2 | Battery performance

3.2.1 | Effect of DN7 on PAM utilization

For DN7 dispersant to be suitable as a positive paste additive, the material must demonstrate compatibility with the PAM discharge reaction. The 2V batteries were discharged in a wide range of low to high current rates, to evaluate the effects of DN7 on the PAM utilization in different discharge conditions. PAM utilization is represented as a percentage of the actual discharged capacity from the theoretical capacity based on active material weight.

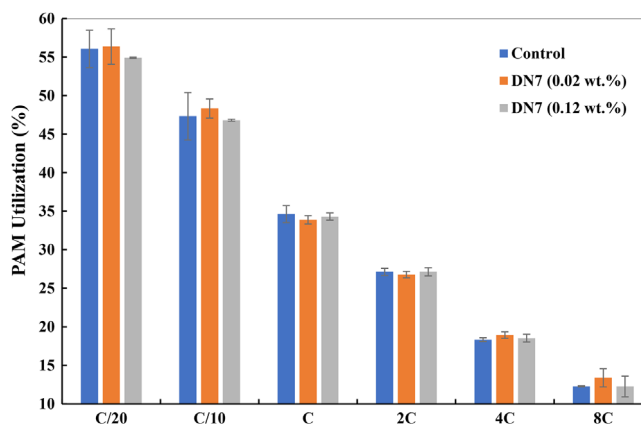
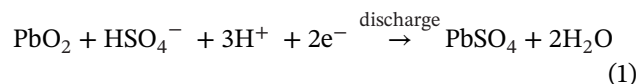


FIGURE 4 Comparison of PAM utilization (%) as a function of discharge rate for different amounts of DN7 additive and the control sample

The 2V battery capacities are designed to be limited by the discharge mechanism of the positive electrode. The basic electrochemical reaction of the positive electrode is shown below:⁴



The utilization of the PAM has two main controlling mechanisms: (1) electrolyte transport through the macro-pore system of the PAM structure and the PbSO_4 layer that inherently forms during discharge and (2) effective electronic conductivity of the PbO_2 and the surrounding PbSO_4 discharge product.^{14,15}

The PAM utilization results demonstrated in Figure 4 that 0.02 and 0.12 wt.% of DN7 had no noticeable effects on the PAM discharge mechanism. Thus, neither the electrolyte transport within the electrode structure nor the effective conductivity of the PAM were lowered with the addition of DN7. The results signify that DN7 addition does not affect lead-acid battery discharge performance, while being a successful flow-enhancing additive for the wet paste.

3.2.2 | Effect of DN7 on cycle life

The cycle life of the battery is limited by the mechanical integrity of the PAM (cracks between the PbO_2 clusters and spallation at the grid interface).^{16,17} As the PAM discharges to PbSO_4 , the molar volume increase by nearly 50%.⁴ The expansion of the PAM during discharge isolates unreacted PbO_2 as well as inhibits supply of acid to inner parts of the plates. In addition to mechanical considerations, the high oxidizing properties of PbO_2 , H_2SO_4 , and operational

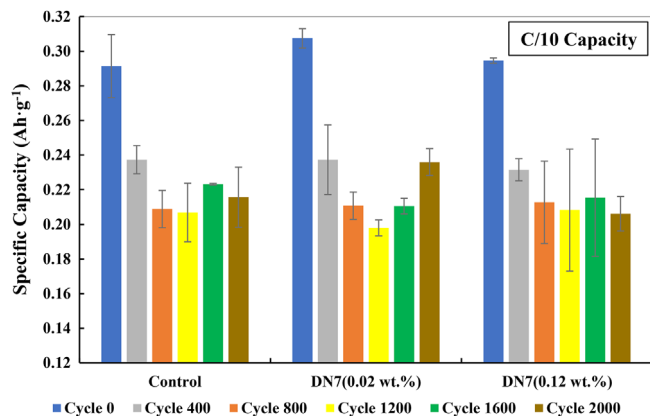


FIGURE 5 The evolution of C/10-rate-specific capacity with 2C cycling protocol

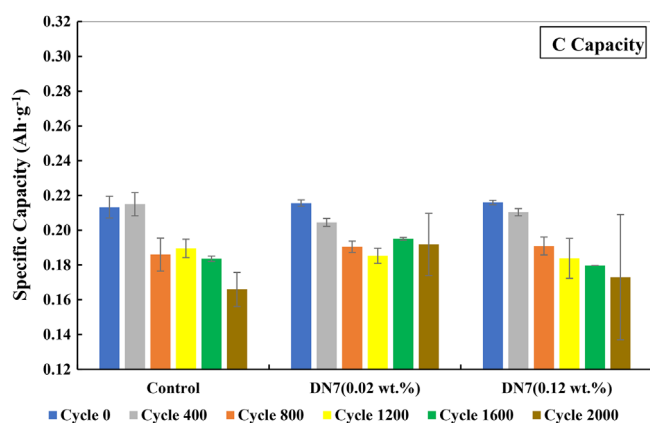


FIGURE 6 The evolution of C-rate-specific capacity with 2C cycling protocol

potentials of the PAM also place strict restrictions on the purity and stability of possible PAM additives.^{4,15,18}

To assess the reversibility and sustainability of the PAM processed with the DN7 dispersant in the PAM, the 2V batteries were cycled at a 2C constant discharge-charge current. The capacity performance was evaluated every 200-cycle interval, as shown in Figure 5 for C/10- and Figure 6 for C-specific capacities. The capacity degradation of the batteries was tracked with the number of total cycles.

After 2000 cycles (over 5-month testing period), both control and DN7 samples have not yet reached their fully discharged state condition. Thus far, the samples are degrading at a similar rate. The C/10 rate-specific capacities have decreased from about 0.29 to 0.22 Ah·g⁻¹; the C rate have decreased from 0.21 to 0.17 Ah·g⁻¹. The addition of DN7 to the positive paste to improve flow did not alter the cycle life or rate of battery degradation.

4 | SUMMARY

The four-blade vane rheometer method proved to be a reproducible method in measuring the yielding character-

istics of the lead-acid battery paste. Sodium polymethacrylate dispersant from 0.02 to 0.10 wt.% lowered the yield stress of the paste by 20% to 50%, respectively. Oscillatory amplitude strain sweep analysis confirmed similar effects, as the sodium polymethacrylate lowered the yield and flow points of the positive paste. Thus, never reported before rheological measurements conducted on lead-acid battery paste reaffirmed and quantified the qualitative observations of smooth texture and increased flowability during the pasting process. Moreover, the sodium polymethacrylate dispersant effectively lowers the yield stress for the positive lead-acid battery paste, without affecting the wet paste density. When added up to 0.12 wt.%, PAM utilization and battery cycle life were not affected. Sodium polymethacrylate was shown to be a successful dispersant additive for the positive lead-acid battery paste.

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REFERENCES

- Pillot C. The Rechargeable Battery Market and Main Trends 2016–2025, in Batteries 2017. Nice, France; Avicenne Energy; 2017.
- Lopes P, Stamenkovic V. Past, present, and future of lead-acid batteries. *Science* (New York, N.Y.). 2020;369:923–4.
- Faure CA. French Patent 141057. *A Construction of Secondary Galvanic Battery Couples*. 1881.
- Pavlov D Lead-Acid Batteries: Science and Technology. Elsevier Amsterdam. 2011. <https://doi.org/10.1016/C2009-0-16975-1>
- Cho J-M, Dogan F. Colloidal processing of lead lanthanum zirconate titanate ceramics. *J Mater Sci*. 2001;36(10):2397–403.
- Rueschhoff L, Rueschhoff L, Michie M, Youngblood J, Trice R. Additive manufacturing of dense ceramic parts via direct ink writing of aqueous alumina suspensions. *Int J Appl Ceram Technol*. 2016;13(5):821–30.
- Ighodaro OL, Okoli OI, Zhang M, Wang B. Ceramic preforms with 2D regular channels for fabrication of metal/ceramic-reinforced composites. *Int J Appl Ceram Technol*. 2012;9(2):421–30.
- Kosacki J, Dogan F. the effect of various graphite additives on positive active mass utilization of the lead-acid battery. *J Electrochem Soc*. 2021;168(3).
- Dzuy NQ, Boger DV. Yield stress measurement for concentrated suspensions. *J Rheol*. 1983;27(4): 321–49.
- Dzuy NQ, Boger DV. Direct yield stress measurement with the vane method. *J Rheol*. 1985;29(3):335–47.
- Mezger TG, Sprinz C & Green A Applied Rheology: With Joe Flow on Rheology Road. Anton Paar GmbH; 2018.
- Vallat-Joliveau F, Delahaye-Vidal A, Figlarz M, de Guibert A. Some structural and textural aspects of tribasic lead sulfate precipitation during the mixing of lead-acid battery positive paste. *J Electrochem Soc*. 1995;142(8):2710–6.
- Pavlov D, Papazov G. Dependence of the properties of the lead-acid battery positive plate paste on the processes occur-

- ring during its production. *J Appl Electrochem.* 1976;6(4):339–45.
14. Metzendorf H. The capacity limiting role of the electronic conductivity of the active material in lead—acid batteries during discharge. *J Power Sources.* 1982;7(3):281–91.
 15. Moseley PT. Positive plate additives. *J Power Sources.* 1997;64(1-2):47–50.
 16. Pavlov D, Bashtavelova E. Structural properties of the PbO active mass determining its capacity and the “breathing” of the positive plate during cycling. *J Electrochem Soc.* 1986;133(2):241–8.
 17. Bashtavelova E, Winsel A. PbO₂ active material as an electro-crystalline network. *J Power Sources.* 1993;46(2):219–30.
 18. Bullock KR, Dayton TC. Positive-Plate Additives to Enhance Formation and Battery Performance, in Valve-Regulated Lead-Acid Batteries. 2004. p. 109–34. Elsevier B.V. Amsterdam. <https://doi.org/10.1016/B978-0-444-50746-4.X5000-4>

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