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Overcharge Self-Regulated Li-ion Battery Based on $LiFePO_4$ via a Solid State Combined Cathode

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ABSTRACT

Safety is one of the most crucial problems faced by the lithium-ion battery (LIBs) industry. In this work, we propose a strategy to avoid overcharging of a battery via the application of a solid-state combined cathode. The goal of this research is to produce LIBs with overcharge self-regulation capabilities. In order to achieve self-regulation functionality, 1,4-di-tert-butyl-2,5-dimethoxybenzene (DBB) is added to as-synthesized $LiFePO_4$, post synthesis. DBB has a trigger voltage of 3.9 V. When this voltage is reached, DBB forms a reduced ion that is released into the electrolyte from the cathode side. The DBB ion transfers to the anode side where it oxidizes and transfers back to the cathode side. This process forms a redox shuttle and consumes the extra charges keeping the voltage at a safe level (i.e. 3.9 V). The DBB redox shuttle protects the $LiFePO_4$-based LIBs with working voltage between 3.4 and 3.5 V. The cycleability of assembled batteries is tested using an Arbin Tester.

INTRODUCTION

Rechargeable lithium-ion batteries (LIBs) are a common power source for many portable electronic devices. Long battery lifetime, high specific capacity, and their compatibility with modern electronics have contributed to their widespread use [1]. Safety is a significant contemporary issue in LIBs research because abuse to the batteries can potentially cause serious safety issues.

In general, there are three types of abuse: 1) mechanical (e.g. crushing, dropping); 2) electrical (e.g. overcharging, overdischarging, and high current surge); and, 3) thermal (excessive heat exposure). These forms of abuse lead to exothermic reactions that may cause thermal decomposition of the electrolyte, reduction of the electrolyte by the anode, oxidation of the electrolyte by the cathode, and even thermal decomposition of the anode and cathode. Sometimes the melting of the separator can also be triggered. All of these situations can lead to critical battery failure and even to a dangerous event such as fire [2].

This research addresses electrical abuse, which can include overcharging, overdischarging, and high power surge. Among these, safety hazards caused by overcharging are most frequently reported in the literature. This is mainly because the positive electrode in a fully charged Li-ion cell contains a strong oxidizing transition metal oxide such as Ni, Co, or Mn. The negative electrode contains carbon, which is a very strong reducing material. Sandwiched between the positive electrode and the negative electrode is a non-aqueous electrolyte that uses an organic carbonate solvent and a lithium salt. In the cell, this solvent tends to be readily oxidized and reduced. Thus, the lithium-ion battery cell itself is thermodynamically unstable and the compatibility of the cell components is kinetically achieved by using passivation films on the surface of the electrodes.

Overcharging generally occurs during charging of a battery pack with multiple Li-ion cells connected in series [3]. When the battery pack is being charged, the charge controller continuously monitors the voltage of the battery pack to roughly estimate the state of charge (SOC). When the pack voltage is still lower than the target voltage, the charger will continue to charge the pack, and inadvertently overcharge the weakest cell. Therefore, having the ability to monitor individual voltages at the cell level is required to prevent overcharging. If monitoring and regulation of voltage at the cell level can be successfully done, then the requirements for a battery management system can be greatly reduced in a battery energy storage system.

This research investigates the possibilities for implementing voltage self-regulation at the cell level. To achieve this goal, a redox shuttle can be added to the electrolyte [4]. Redox shuttle additives are a group of materials that when overcharging occurs, transfer (back and forth) extra charges between the cathode and anode. Once the overcharging condition has ended, redox shuttle additives allow the cell to return to normal working conditions, effectively protecting the cell from overcharging. Redox shuttles have different trigger voltages [5][6]. In practice, the selected redox shuttle has a voltage that is 0.2 to 0.4 V higher than the working voltage of the battery cell. In this work, the redox shuttle is added into the cathode to form a solid-state combined cathode instead of adding it into the electrolyte [7]. This approach simplifies the battery fabrication process and allows for the addition of higher amounts of redox shuttle to the battery cell.

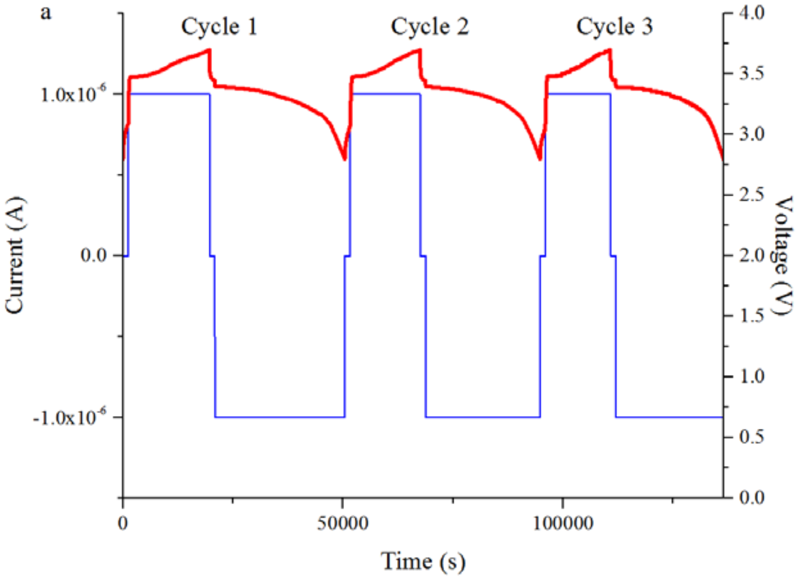
EXPERIMENT

1,4-di-tert-butyl-2,5-dimethoxybenzene (DBB) is applied as the redox shuttle material [4]. In order to make the solid state combined cathode, a mixture of $LiFePO_4$ with different ratios of DBB, are prepared (5 wt% 10 wt%, and 15 wt%). The prepared mixtures are dissolved into the binder solution, 10 wt% Polyvinylidene fluoride (PVDF) in N-Methyl-2-pyrrolidone (NMP), with a ratio of 1 g.:2.3 ml. [8]. The formed solutions are stirred at 1,200 rpm/min. under room temperature for 1 hour. The solutions are sonicated for 1 hour, vortexed for 30 seconds, and applied on an Al sheet by doctor blading. The applied films are dried on a hotplate at 120 ^{o}C for 12 hours. After drying, the Al sheets are cut into multiple circular cathodes, and the cathodes are assembled into testing coin-cells in a glove box. The cycling test and the continuous overcharging test are performed by an Arbin tester.

RESULTS AND DISCUSSION

Figure 1 shows the cycling test results for battery cells with 5 wt% DBB (a), 10 wt% DBB (b), and 15 wt% DBB (c). During the cycling test, the cell is charged and discharged between 3.7 V and 2.8 V, respectively. The current applied to all battery cells is 1.0 x 10-6 A. For each cell, three full charge/discharge cycles are shown. Since each cell has a different charging and discharging rate, the time period for a full charge/discharge cycle are different. It is observed that the battery cell with 5 wt% DBB has both a longer charging period (~20,000 s), and discharging time period (~30,000 s) compare to the battery cell with 10 wt% DBB (~10,000 s for charging, ~20,000 s for discharging), and 15 wt% DBB (~7,000 s for charging, ~1,000 s for discharging).

The battery cell with 5 wt% DBB has the largest charge and discharge capacity among all the battery cells. These results show that a higher DBB weight ratio inhibits battery performance. Also, it should be noticed in Figure 1a, the cell takes longer on discharging than charging. This is because lithium-ion batteries have a charging platform higher than the discharging platform [9]. Thus, the charging of the battery cell between 2.8 V and 3.7 V does not include the full charging platform. However, it does include the whole discharge platform (3.4 V to 3.2 V). Therefore, for a battery cell that works well, under this setting, it takes longer to discharge than to charge. On the other hand, Figure 1c shows a cell with very short discharging time under the same current conditions. In this case, the discharge platform is short and is hard to observe in the figure. This shows that a 10 wt% and 15 wt% DBB do have a significant impact on the electrochemical performance of the cells. DBB decreases the capacity of the cells and beyond a certain amount (e.g. threshold wt% DBB), it can even defunctionalize the battery cells. The amount of the DBB additive used is a critical parameter that needs further optimization.



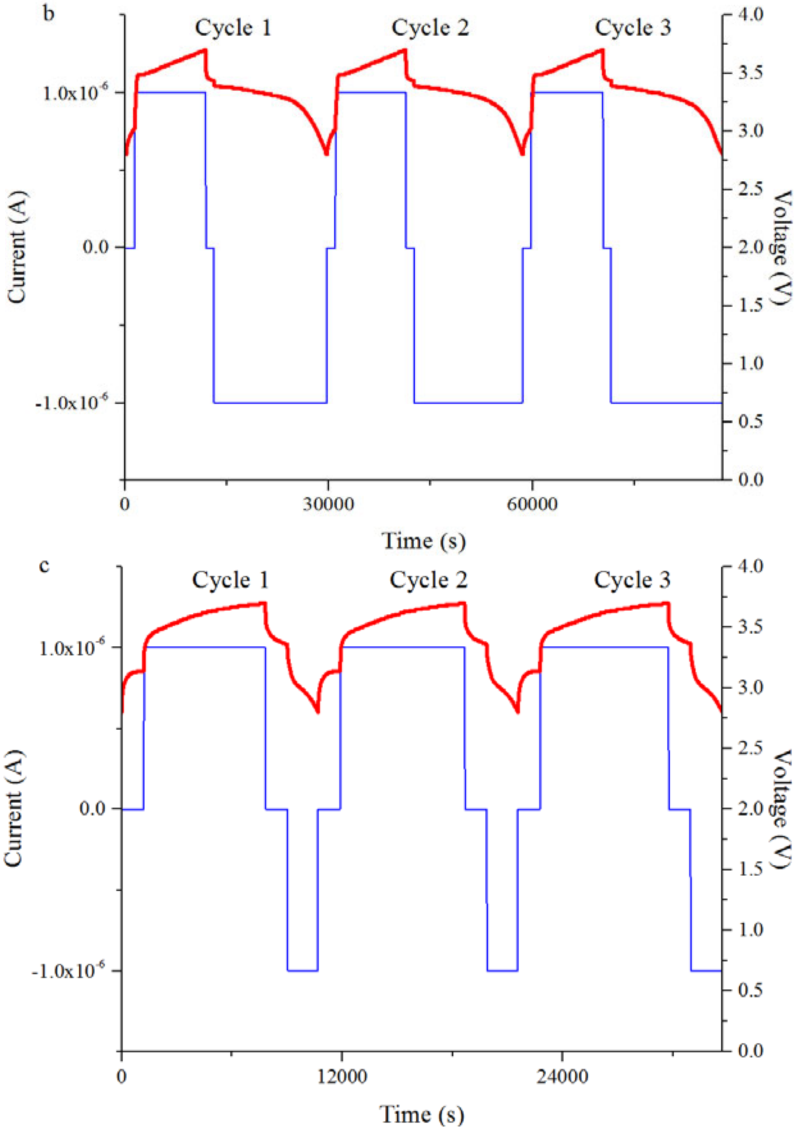


Figure 1. Cycling test for battery cells with a) 5 wt% DBB, b) 10 wt% DBB and c) 15 wt% DBB.

Figure 2 shows the results from the continuous overcharging of the battery cells with 5 wt% DBB, 10 wt% DBB, and 15 wt% DBB. The current applied to all battery cells is 1.0 x 10-6 A. As illustrated, the battery cell with 5 wt% shows almost no self-regulation capability, while the 10 wt% DBB shows some self-regulation behavior. Although it takes longer to overcharge the battery cell with 10 wt% DBB (40 hours), than the one with 5 wt% DBB (2 hours), it is not enough for providing over voltage protection. In both cases, the voltage of the battery cells with 5 wt% DBB and 10 wt% DBB kept increasing until reaching the target voltage of 4.5 V (which is set up as the shutdown voltage in the Arbin tester). Although the higher concentration of DBB enhances the ability to protect the cell from overcharging, it is not enough to fully protect the battery. On the other hand, the battery cell with 15 wt% DBB is charged over time until the voltage reaches 3.9 V, where it is maintained throughout the test. The trigger voltage of DBB is 3.9V, and at this voltage DBB: 1) oxidizes on the cathode side; 2) diffuses to the anode side; 3) reduces back to DBB; and, 4) diffuses back to the cathode side. This continuous cycle inside the electrolyte consumes the extra charges generated during overcharging, and allows the voltage of the cell to stabilize. The voltage is stabled at 3.9 V for a period of time longer than 70 hours, and the battery is effectively protected from overcharging.

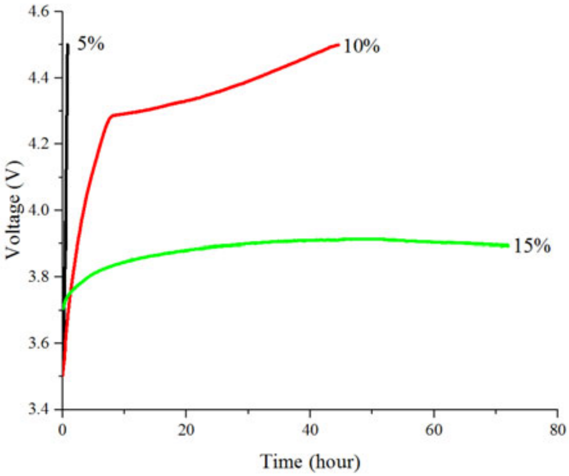


Figure 2. Continuous overcharge test for the battery cell with 5 wt% DBB, 10 wt% DBB and 15 wt% DBB.

CONCLUSION

In this work, a solid-state combined cathode with 5 wt%, 10 wt%, and 15 wt% DBB are fabricated and tested. The higher DBB weight ratio has a negative impact on the electrochemical performance of the battery cells. The battery cell with higher DBB ratio (15 wt%) shows a superior ability to regulate and maintain the battery cell voltage at 3.9 V, for more than 70 hours, but also shows the greater loss in charge and discharge capacity. Although DBB has the potential to protect the battery cell from overcharging, it also inhibits battery performance. In our future work, the amount of DBB applied, and the selected redox shuttle will be optimized to improve upon the self-regulation capability demonstrated in this work, while maintaining the electrochemical performance of battery cells.

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