



Short communication

Diphenylamine: A safety electrolyte additive for reversible overcharge protection of 3.6 V-class lithium ion batteries

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ABSTRACT

A polymerizable monomer, diphenylamine (DPAn), is reported to act as a safety electrolyte additive for overcharge protection of 3.6 V-class lithium ion batteries. The experimental results demonstrated that the DPAn monomer could be electro-polymerized to form a conductive polymer bridging between the cathode and anode of the battery, and to produce an internal current bypass to prevent the batteries from voltage runaway during overcharge. The charge–discharge tests of practical LiFePO₄/C batteries indicated that the DPAn additive could clamp the cell's voltage at the safe value less than 3.7 V even at the high rate overcharge of 3 C current, meanwhile, this monomer molecule has no significant impact on the charge–discharge performance of the batteries at normal charge–discharge condition.

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1. Introduction

The voltage of the aqueous secondary batteries is generally limited to a value below 2.0 V by the decomposition of water solvent. At the same time, the overcharge protection of this type of secondary batteries can be easily provided by the decomposition of water at one electrode and recombination of gaseous products at the other electrode, such as in sealed lead/acid, Ni–Cd and Ni/MH. In contrast, lithium ion batteries (LIBs) using organic electrolytes lack of a spontaneous intrinsic limitation for their voltage rise during overcharging, because the organic solvents commonly used in LIBs are not capable of being reversibly oxidized or reduced. When overcharged, the voltage of the battery would uncontrollably climb up and then, a number of exothermic reactions would take place inside the cell [1–7], such as decomposition of the cathode material, oxidation of organic electrolyte at oxidizing cathode, thermal decomposition of the solid electrolyte interphase (SEI), and reduction of the electrolyte on the highly reactive anode. These reactions produce excessive heat and flammable gas, and finally lead to a thermal runaway, causing cell cracking, fire or even explosion. Therefore, the safety concerns of LIBs at overcharging conditions are considered to be a main obstacle to their high rate or large capacity applications, such as electric vehicles and stationary energy storage systems.

To avoid the voltage runaway at overcharging, great efforts have been focused in recent years, on developments of internal and self-actuating overcharge protection mechanisms for LIBs. Well-known approaches include various types of electrolyte additives [8–21] and electro-active polymer separators [22–25]. Comparatively, the electrolyte additives seem to be a more attractive means because of its simplicity and convenience for the practical battery applications. The electrolyte additives for the overcharge protection can be classified as redox shuttle additives [8–14] and polymerizable additives [15–21]. The former can protect the cell from overcharge by locking the potential of the positive electrode at the oxidation potential of the shuttle molecules, but until now, the most of shuttle molecules reported so far can only provide a limited shuttling current and therefore fail to function even at normal operating current due to their poor solubility in non-aqueous electrolytes. In addition, the electrochemical stability of shuttle molecules on a long-term operation is also an issue for their practical applications, because without few exception, almost all the shuttle additives with high oxidation potentials ≥ 3.5 V (vs. Li⁺/Li) reported in the previous studies belong to aromatic compounds, such as 1,4-dimethoxybenzene derivatives [10–13] and 1,2-dimethoxybenzene derivatives [10,14], which have a tendency of being electro-polymerized at the high positive potentials of the cathode and then, lose their shuttling functions gradually. The use of polymerizable additives for overcharge protection of LIBs is based on the consideration that at high overcharge potentials, the additive molecules polymerize at cathode to release gaseous products, which in turn activate the current interruption devices,

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while the resulting polymers close down the cathode surface and thus prevent the cathode from further overcharging [15,18]. In the past few years, many aromatic compounds have been found to be capable of using as polymerizable additives for overcharge protection of LIBs, such as biphenyl [16,17], xylene [18], cyclohexylbenzene [19], 2,2-diphenylpropane [20,21], phenyl-R-phenyl compounds (R=aliphatic hydrocarbon, fluorine substituted) and 3-thiopheneacetonitrile [21]. Unluckily, these polymerizable additives actually should belong to shutdown additives because they can only provide overcharge protection just once for batteries. Once the protection occurs, the cell operation will be terminated permanently.

Recently, we found that polymerizable monomer of diphenylamine (DPAn) could be used as an electrolyte additive to provide a reversible overcharge protection for practical LiFePO_4 -based Li-ion batteries. The experimental results showed that this reversible overcharge protection results from the formation of a polymer bridge between the cathode and the anode, which is created by in situ polymerization of DPAn additive during overcharging. Since this polymer bridge is composed of the electro-active polydiphenylamine (PDPAn) [26], which can be p-doped at high oxidation potential into an electronically conductive phase and de-doped at normal operating voltage into an electronically isolating state, it functions as a potential switch to control the batteries voltages at safety region. In this paper, the preliminary results of our experimental studies are presented.

2. Experimental

Diphenylamine ($\geq 99.0\%$ purity, Sinopharm Chemical Regent Co., Ltd., Shanghai, China) was used as received without further purification. The electrolyte used in this study was 1 M LiPF_6 in a 1:1:1 mixture (by vol.) of ethylene carbonate (EC), dimethyl carbonate (DMC) and ethyl-methyl carbonate (EMC) purchased from Zhangjiagang Guotai-Huarong New Chemical Materials Co., Ltd. (Zhangjiagang, China). The test batteries used in this study were prismatic LiFePO_4 -graphite batteries with a nominal capacity of 620 mAh, provided by the Fenghua Lithium battery Co., Ltd. (Zhaoqing, China).

The electro-oxidative polymerization of DPAn monomer and the electrochemical behaviors of the polymerized product of PDPAn were studied with cyclic voltammetry (CV) at a platinum microdisc electrode (diameter = 100 μm). The voltammograms were recorded on a two-electrode cell using a large lithium sheet as both counter electrode and reference electrode on a CHI 600 C electrochemical workstation (Shanghai, China).

The effects of the electrolyte additive on the overcharge behaviors of the batteries were investigated by comparing the charge-discharge performance of the prismatic LiFePO_4/C batteries using the electrolytes with and without DPAn additive. The charge and discharge measurements were carried out using a programmable computer-controlled battery charger (BTS-55 Neware Battery Testing System, Shenzhen, China). To reveal the working mechanism of the electrolyte additive for overcharge protection, the morphological changes of the separators after overcharge were examined using a Quanta 200 Scanning Electron Microscope (FEI Company, Netherlands).

3. Results and discussion

The key criterion for choosing a monomer as a polymerizable safety additive is the ability of the monomer to be electro-polymerized into a conductive polymer in the battery electrolyte, at the right potential slightly higher than the terminating potential of the completely charged cathode and considerably lower than the

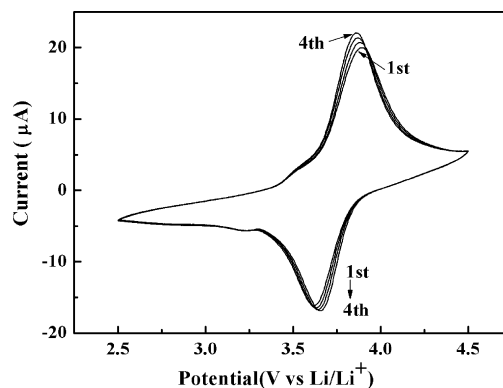


Fig. 1. CV curves of a Pt microelectrode in 1 M $\text{LiPF}_6/\text{EC}+\text{DMC}+\text{EMC}$ electrolyte containing 5 wt.% DPAn, sweep rate = 10 mV s^{-1} .

decomposition potential of the electrolyte. For LiFePO_4 -based LIBs, the potential of fully charged cathode is ca. 3.6 V.

Fig. 1 shows the CV curves of a Pt microelectrode in 1 M $\text{LiPF}_6/\text{EC}+\text{DMC}+\text{EMC}$ electrolyte containing 5 wt.% DPAn with a scan rate of 10 mV s^{-1} . On the first positive scan, a small shoulder-like oxidation peak appears at 3.4–3.6 V, indicating the electro-oxidative polymerization of DPAn additive on Pt surface. When the potential is extended to a more positive region, a strong oxidation current appears with a peak position at 3.75 V, characteristic of the electrochemical p-doping process of the electro-polymerized PDPAn. On the reversed scan, there is a strong reductive current peak appearing in the potential range of 3.5–3.8 V, corresponding to the de-doping process of p-doped PDPAn. In the successive scans, the magnitudes of these current peaks progressively increase, suggesting the continuous build-up of electro-active PDPAn on the electrode. In addition, it is also can be seen that the current peaks of both the p-doping and de-doping processes are very symmetric with a small peak spacing of 0.18 V and almost equivalent peak areas, indicating the very reversible and rapid electrochemical oxidation-reduction of the resulting polymer. These CV features suggest that DPAn additive can be electro-polymerized into an electro-active polymer and the resulting polymer is highly reversible for p-doping and de-doping at an oxidation potential $\geq 3.6\text{ V}$, which is suitable to use for overcharge protection of LiFePO_4 -based LIBs.

Fig. 2 shows the charge-discharge curves of the prismatic LiFePO_4/C batteries with addition of 5 wt.% DPAn in electrolyte at 1 C rate. In order to ensure the complete electro-polymerization of DPAn additive, the test cell was activated by cycling at 2.0–3.55 V for two cycles at 30 mA before overcharge experiments. It is clearly shown in the figure that once overcharged, the charging voltage

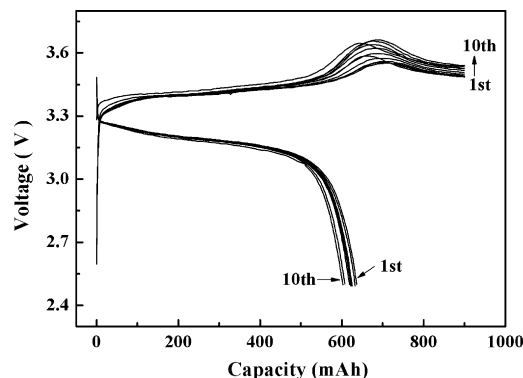


Fig. 2. The charge-discharge curves of the prismatic LiFePO_4/C batteries using an electrolyte containing 5 wt.% DPAn additive at 1 C rate.

of the battery rose up steeply at first at the onset of overcharge and then gradually dropped to produce a voltage plateau at 3.58 V, showing an effective control of the charging voltage. This phenomenon could be well explained that in the prior activating process, DPAn monomer had been electro-polymerized to form a polymer bridge (PDPAn) in-between the cathode and anode. At the beginning of overcharge, the electrochemical p-doping of the PDPAn polymer cannot proceed so quickly that the polymer bridge is not entirely conductive, showing an ohmic polarization to cause the charging voltage higher than expected. As the overcharge proceeds, the polymer bridge becomes sufficiently conductive, which leads to a decrease in the ohmic polarization and the charge voltage. Once the polymer bridge turns into a completely conductive state, the charging voltage is stabilized at the p-doping potential of PDPAn, showing a stable voltage plateau as observed. It can also be seen in Fig. 2 that the test batteries can deliver a capacity of 620 mAh at following discharge even subjected to a 50% overcharge of its nominal capacity, showing no negative impact of the DPAn additive on the discharge performance of the batteries. These experiment results demonstrated that the DPAn monomer is capable of acting as an electrolyte additive for reversible overcharge protection of LiFePO₄-based LIBs.

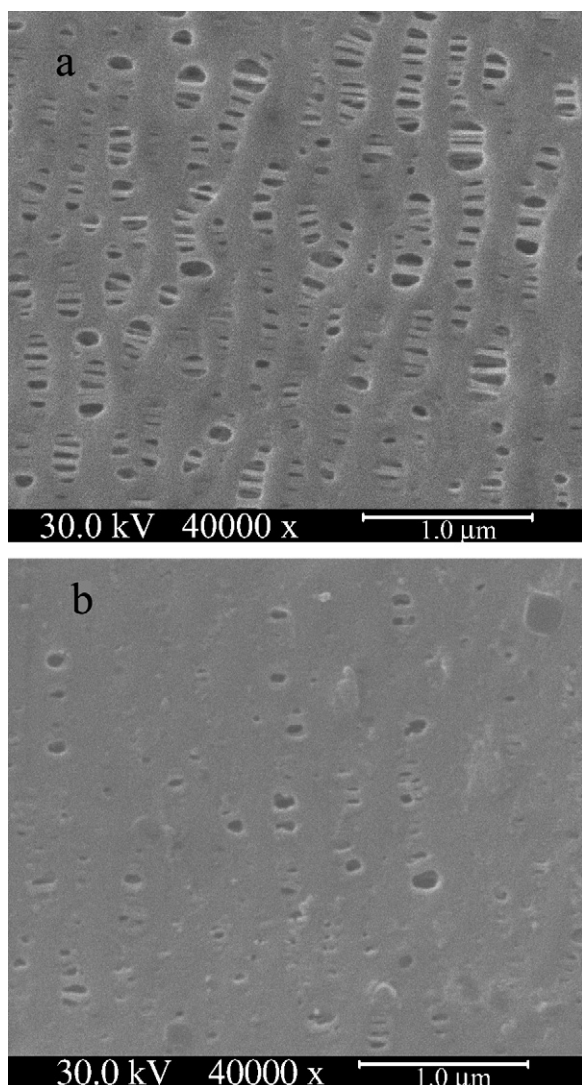


Fig. 3. SEM photographs of the separators from the prismatic LiFePO₄/C batteries after overcharge using electrolyte containing (a) 0 wt.% and (b) 5 wt.% DPAn.

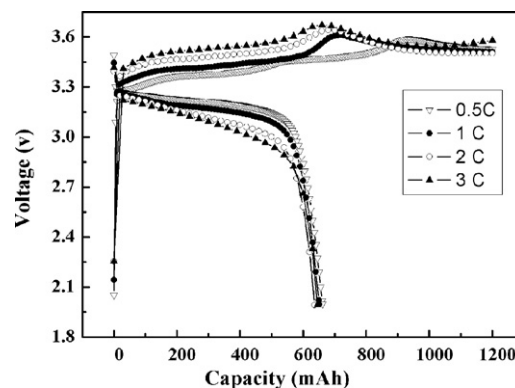


Fig. 4. The charge–discharge curves of the prismatic LiFePO₄/C battery using an electrolyte with 5 wt.% DPAn additive at various charge and discharge rates.

To confirm the working mechanism of the DPAn additive, the morphological changes of the battery separators after overcharge were examined by SEM. Fig. 3 compares the SEM images of the separators taken from the overcharged cells with or without the DPAn additive in the electrolyte. As can be seen, the separator in blank electrolyte has a clear surface and uniform pore distribution. In contrast, the separator in the electrolyte containing DPAn additive shows a vague image and a blocked pore structure. These phenomena evidence the fact that the growth of the polymeric product not only occurs on the cathodic electrode, but also extends to the separator and even penetrates through the porous separator to reach the anodic surface, electronically wiring the cathode and the anode.

An important factor determining the feasibility of the polymerizable additive is its sustainable current at charge and discharge. Fig. 4 gives the charge–discharge curves of the prismatic LiFePO₄/C battery with 5 wt.% DPAn additive at various charge and discharge rates. It can be seen that although the charge rates are increased from 0.5 C to 3 C, the overcharge voltage plateaus of the test batteries are only slightly elevated and can all be controlled at the values below 3.7 V effectively. Even though the discharge rate is increased along with the charge rate to 3 C, this cell can still deliver a capacity of 620 mAh at discharge, showing an excellent high rate charge and discharge capability.

As an applicable safety additive, it is also very required that the additive monomer cannot only provide an effective voltage control at overcharge, but also have no significant impacts on the normal charge–discharge performances of the batteries. To evaluate the influence of DPAn additive on the cycling performance of the batteries, the prismatic LiFePO₄/C batteries with 5 wt.% DPAn additive were prior activated by cycling at 2.0–3.55 V for two cycles at 30 mA and then, were cycled at normal operating voltage of 2.0–3.5 V at

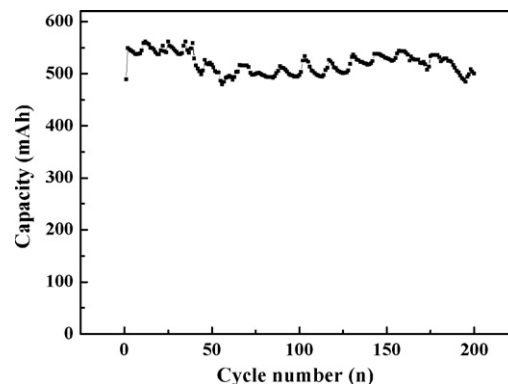


Fig. 5. The cycling performance of the LiFePO₄/C battery with 5 wt.% DPAn additive at normal charge–discharge voltage interval of 2.0–3.5 V at 1 C rate.

1 C rate. The typical cycling performance of these batteries is shown in Fig. 5. It can be found that after 200 cycles, the discharge capacity of the battery is still kept at 500 mAh, showing a good cycling performance.

4. Conclusion

In summary, a polymerizable monomer of diphenylamine was tested as a safety additive for overcharge protection of 3.6 V-class lithium ion batteries. The experimental results demonstrated that the DPAn additive could polymerize to form a conductive polymer bridging between the cathode and anode during overcharging, producing an internal current bypass to prevent the battery from voltage runaway. In addition, the electrolyte additive has no significant influence on the charge–discharge performances of lithium ion batteries at normal charge–discharge condition, showing a great prospect for practical application in 3.6 V-class lithium ion batteries.

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References

- [1] S. Tobishima, J. Yamaki, *J. Power Sources* 81/82 (1999) 882–886.
- [2] K. Kumai, H. Miyashiro, Y. Kobayashi, K. Takei, R. Ishikawa, *J. Power Sources* 81/82 (1999) 715–719.
- [3] D.D. MacNeil, J.R. Dahn, *J. Electrochem. Soc.* 149 (2002) A912–A919.
- [4] R. Imhof, P. Novak, *J. Electrochem. Soc.* 146 (1999) 1702–1706.
- [5] J.R. Dahn, E.W. Fuller, M. Obrovac, U. von Sacken, *Solid State Ionics* 69 (1994) 265–270.
- [6] Z. Zhang, D. Fouchard, J.R. Rea, *J. Power Sources* 70 (1998) 16–20.
- [7] Ph. Biensan, B. Simon, J.P. Pèrès, A. de Guibert, M. Brousely, J.M. Bodet, F. Pertont, *J. Power Sources* 81/82 (1999) 906–912.
- [8] C.S. Cha, X.P. Ai, H.X. Yang, *J. Power Sources* 54 (1995) 255–258.
- [9] Z. Chen, K. Amine, *Electrochem. Commun.* 9 (2007) 703–707.
- [10] L.M. Moshchak, M. Bulinski, W.M. Lamanna, R.L. Wang, J.R. Dahn, *Electrochem. Commun.* 9 (2007) 1497–1501.
- [11] C. Buhrmester, J. Chen, L. Moshurchak, J. Jiang, R.L. Wang, J.R. Dahn, *J. Electrochem. Soc.* 152 (2005) A2390–A2399.
- [12] J.R. Dahn, J. Jiang, L.M. Moshurchak, M.D. Fleischauer, C. Buhrmester, L.J. Krause, *J. Electrochem. Soc.* 152 (2005) A1283–A1289.
- [13] J. Chen, C. Buhrmester, J.R. Dahn, *Electrochem. Solid-State Lett.* 8 (2005) A59–A62.
- [14] J.K. Feng, X.P. Ai, Y.L. Cao, H.X. Yang, *Electrochem. Commun.* 9 (2007) 25–30.
- [15] H. Mao, U. von Sacken, US Patent 5,776,627 (1998).
- [16] L.F. Xiao, X.P. Ai, Y.L. Cao, H.X. Yang, *Electrochim. Acta* 49 (2004) 4189–4196.
- [17] H. Mao, D.S. Wainwright, US Patent 6,074,776 (2000).
- [18] X.M. Feng, X.P. Ai, H.X. Yang, *J. Appl. Electrochem.* 34 (2004) 1199–1203.
- [19] Y.S. Kim, H.J. Kim, H.Y. Cha, H.C. Lee, US Patent 0,263,696 (2006).
- [20] H. Mao, U. von Sacken, US Patent 6,033,797 (2000).
- [21] J.N. Reimers, B.M. Way, US Patent 6,074,777 (2000).
- [22] G. Chen, T.J. Richardson, *Electrochem. Solid-State Lett.* 7 (2004) A23–A26.
- [23] L.F. Xiao, X.P. Ai, Y.L. Cao, Y.D. Wang, H.X. Yang, *Electrochem. Commun.* 7 (2005) 589–592.
- [24] G. Chen, T.J. Richardson, *Electrochem. Solid-State Lett.* 9 (2006) A24–A26.
- [25] J.K. Feng, X.P. Ai, Y.L. Cao, H.X. Yang, *J. Power Sources* 161 (2006) 545–549.
- [26] R. Hirai, I. Maruyama, Y. Sakon, Patent JP 6,120,6170 (1986).