

萜烯树脂/羧甲基纤维素复合水系粘结剂用于 锂离子电池石墨负极*

仲皓想¹, 卢继典², 何嘉荣^{1,3}, 李勇¹, 刘鹤筹⁴, 张灵芝^{1†}

(1. 中国科学院广州能源研究所, 广州 510640; 2. 广州力柏能源科技有限公司, 广州 510730;

3. 中国科学院大学, 北京 100049; 4. 澳大利亚新南威尔士大学, 悉尼 2052)

摘要: 萜烯是一类广泛存在于植物和海洋生物体内的天然碳氢化合物, 萜烯树脂 (TR) 经乳化得到萜烯树脂乳液 (ATRE)。本文采用 ATRE/羧甲基纤维素 (CMC) 作为锂离子电池石墨负极粘结剂。差示扫描量热 (DSC) 测试表明 ATRE/CMC 能够混溶。优化 TR/CMC 比例, 发现采用 TR/CMC (3:2, 质量比) 粘结剂制备的石墨电极在比容量和倍率性能优于目前商用丁苯橡胶 (SBR)/CMC 粘结剂。

关键词: 萜烯树脂; 水系粘结剂; 石墨负极; 锂离子电池

中图分类号: TK02

文献标志码: A

doi: 10.3969/j.issn.2095-560X.2017.04.001

Terpene Resin/ Carboxymethyl Cellulose as Novel Water Soluble Binder for Graphite Anode in Lithium Ion Battery

ZHONG Hao-xiang¹, LU Ji-dian², HE Jia-rong^{1,3}, LI Yong¹,
LIU He-chou⁴, ZHANG Ling-zhi^{1†}

(1. Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, China;

2. Guangzhou Lithium Force Energy Technology Co., Ltd, Guangzhou 510730, China;

3. University of Chinese Academy of Sciences, Beijing 100049, China; 4. University of New South Wales, Sydney NSW2052, Australia)

Abstract: Aquous terpene resin emulsion (ATRE) was prepared by the emulsification of natural terpene resins (TR) from many plants exudates and marine organisms. ATRE/carboxymethyl cellulose (CMC) were completely miscible by differential scanning calorimetry. ATRE/CMC composite was used as a binder for graphite electrode in Li-ion batteries in this paper. Optimized ratios of TR/CMC (3:2, by weight), the graphite electrode exhibits the higher specific capacity and better rate capability than that of the commercial styrene-butadiene rubber (SBR)/CMC binder.

Key words: terpene resin; water soluble binder; graphite anode; Li-ion batteries

0 Introduction

The binder has great influence on the electrochemical properties of the electrode as it binds together the active materials, conductive additives and current collector to form conductive network in the electrode^[1-2]. Currently, poly(vinylidene fluoride) (PVDF) was successfully used

as the binder for commercial Li-ion battery industry, but it still has some disadvantages^[3-4]. PVDF is generally dissolved in the volatile and flammable N-methyl-2-pyrrolidone (NMP), which is environmentally harmful. Besides, PVDF is relatively high cost. Therefore, it is essential to develop the greener and cheaper alternative binders^[5-6].

* 收稿日期: 2017-05-05 修订日期: 2017-07-10

基金项目: 王宽诚教育基金会; 国家自然科学基金 (21573239); 广东省科技项目 (2014TX01N014, 2014A050503050, 2015B010135008); 广州市科技项目 (201509010018); 广东省自然科学基金 (2015A030313721)

† 通信作者: 张灵芝, E-mail: lzzhang@ms.giec.ac.cn

* Received: 2017-05-05 Revisions received: 2017-07-10

Foundation Support by: K.C.Wong Education Foundation; Natural Science Foundation of China (21573239); Science & Technology Project of Guangdong Province (2014TX01N014, 2014A050503050, 2015B010135008); Guangzhou Municipal Project for Science & Technology (201509010018); Natural Science Foundation of Guangdong Province (2015A030313721)

† Corresponding author: Zhang Ling-zhi, E-mail: lzzhang@ms.giec.ac.cn

The water-soluble binders, such as, carboxymethyl cellulose (CMC)^[7-8], styrenebutadiene rubber (SBR)^[9], CCTS^[2,10-12], poly(acrylic acid) (PAA)^[13-14], alginate^[5], polyimide (PI)^[15-16] and guar gum (GG)^[17] have been explored as promising binders for use in Li-ion batteries. Currently, CMC/SBR binder for graphite anode has been commercially used in Li-ion batteries. However, it tends to form a thick solid electrolyte membrane, causing the high electrochemical impedance, which is unfavorable to the long-term cycle performance and rate capability of graphite anode^[18]. What's more, SBR, as a synthetic polymer, is an environment unfriendly product^[19].

Terpene widely exists in natural sources of hydrocarbons from many plants exudates and marine organisms. Terpene resins (TR) are prepared by polymerization of terpene monomers, and it has non-toxic, low cost, high adhesive property, good thermal stability, and good compatibility with other polymers^[20]. Aqueous terpene resin emulsion (ATRE) was obtained by direct emulsification of TR^[21]. Herein we report the use of the water-soluble bio-derivative TR/CMC as alternatives binder for graphite anode as compared with the commercial SBR/CMC system.

1 Experimental Section

1.1 Materials and Equipments

Graphite powder was obtained from Hunan Shanshan Advanced Materials Co. (China). Terpene resins was purchased from Guangzhou Songbao Chemical Co. (China). Aqueous terpene resin emulsion (ATRE) was prepared by the emulsification of natural terpene resins (TR). Styrene-butadiene rubber (SBR) in the form of an aqueous emulsion of 48wt% was purchased from Shanghai Gaoqiao BASF Dispersions Co. (China). PVDF (Solvay Solef ®6020) was purchased from Shenzhen Micro Electron Co. (China). Carboxymethyl cellulose (CMC) (Viscosity: 800 ~ 1200 mPa·s) was purchased from Changshu Wealthy Science and Technology Co. (China). The electrolyte of 1 M LiPF₆ in ethylene carbonate (EC, ≥99.9%)/diethylene carbonate (DEC, ≥99.9%)/dimethyl carbonate (DMC, ≥99.9%) (V/V/V = 1/1/1) was purchased from Zhangjiagang Guotai-Huarong New Chemical Materials Co. (China) (water content <10 ppm).

The morphology and microstructure of the experimental samples were observed by using a scanning electron microscope (SEM) (Hitachi S-4800, Japan) with an energy-dispersive detector (EDS). The coin half-cells (CR2025) were assembled to test the electrochemical performance of the obtained electrodes. The half-cells

were assembled in an Ar-filled glove-box, using 1 M LiPF₆ EC/DEC/DMC (V/V/V=1/1/1) as the electrolyte, Li foil as the counter electrode and Celgard 2400 as the separator. The cells were then galvanostatically charged and discharged on a Shenzhen Neware battery cycler (China) at different current density between cut-off voltages of 0.0 and 3.0 V (vs. Li/Li⁺). Adhesion strength of the polymer layers onto the Cu current collectors were tested using a 180° peel tester from Shenzhen Kaiqiangli testing instruments Co. (China). Thermal gravimetric analysis (TGA)/differential scanning calorimetry (DSC) measurements were conducted on a STA 409 C/PC-PFEIFFER VACUUMTGA-7 analyzer (NETZSCH-Gertebau GmbH, Germany) in an Ar atmosphere with a heating rate of 10°C/min from 30°C to 500°C. The particle distribution of active materials in the electrode slurry was measured (0 ~ 50 μm) by the grindometer (QXP, Tianjin, China).

1.2 Preparation of the slurry and electrode

Graphite powder was mixed with carbon black and the binder (TR/CMC) in a weight ratio of 90:5:5 in deionized water to form homogeneous slurry. As comparison, a PVDF-based electrode with 90wt% graphite, 5wt% carbon black, 5wt% PVDF and a SBR/CMC based electrode with 90wt% graphite, 5wt% carbon black, 5wt% binder (SBR/CMC in a weight ratio of 3:2) were prepared. The slurry was coated onto a 20-μm-thick aluminum foil and then dried at 100°C in a vacuum oven for 12 h to remove the solvent thoroughly. In similar method above, LTO electrode was prepared in this paper.

1.3 Characterization of electrochemical performance

Coin cells (CR2025) were assembled to test the electrochemical performances. Circular electrodes were punched out with an area of 1.54 cm². Lithium metal was employed as the anode. The cells were charged and discharged galvanostatically in a fixed potential range from 0.0 to 3.0 V at 25°C. Cyclic voltammetry (CV) was carried out on a Zennium/IM6 electrochemical workstation (Zahner, Germany) between 0.0 and 3.0 V (vs. Li/Li⁺) at a scanning rate of 0.2 mV/s. Electrochemical impedance spectroscopy (EIS) was also measured on a Zennium/IM6 electrochemical workstation by applying an alternating voltage of 5 mV over the frequency ranging from 10⁻² to 10⁶ Hz.

2 Results and Discussion

Chemical structure of terpene resins (TR) (softening point =100°C, $M_w = 1260$ g/mol) and SBR are illustrated in Fig. 1. Adhesion strength of TR/Cu current collector was measured by peel test and compared with

commercial SBR/Cu, and the results are shown in Fig. 2a. TR binder shows higher adhesion strength (0.17 N/cm) than SBR (0.15 N/cm). The higher adhesion strength of TR is closely related to its unique structure. Cyclic voltammetry (CV) from open circuit voltage (~ 3 V) to 0 V (vs. Li/Li⁺) was performed on TR coated Cu foils. An electrochemical cell consisting of Cu foil (working electrode) and lithium metal (counter electrode) was used to determine the electrochemical stability of TR (Fig. 2b). TR showed an electrochemically inactive between 0 and 3 V, indicated by the very weak oxidation-reduction current. Similar CV curves were observed in SBR coated Cu foils^[22]. Therefore, TR can be used as the binder for graphite electrode from 0 to 3 V.

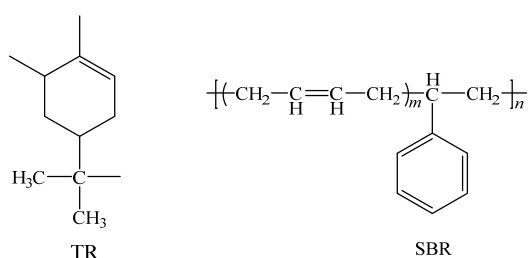


Fig. 1 Chemical structure of TR and SBR

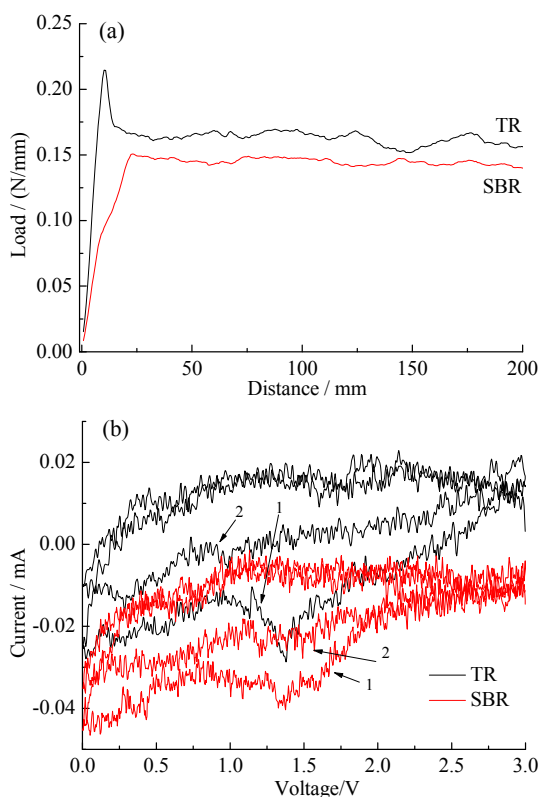


Fig. 2 Peel strength (a) and CV (b) of TR and SBR

TGA/DSC thermograms of TR, CMC, and TR/CMC are presented in Fig. 3. TR, CMC, TR/CMC starts

decomposition at about 270°C, 248°C, and 250°C with a maximum centered at 343°C, 281°C, and 265°C, respectively. TR/CMC is found slightly lower decomposition temperature than CMC and TR, but shows good compatibility between TR and CMC.

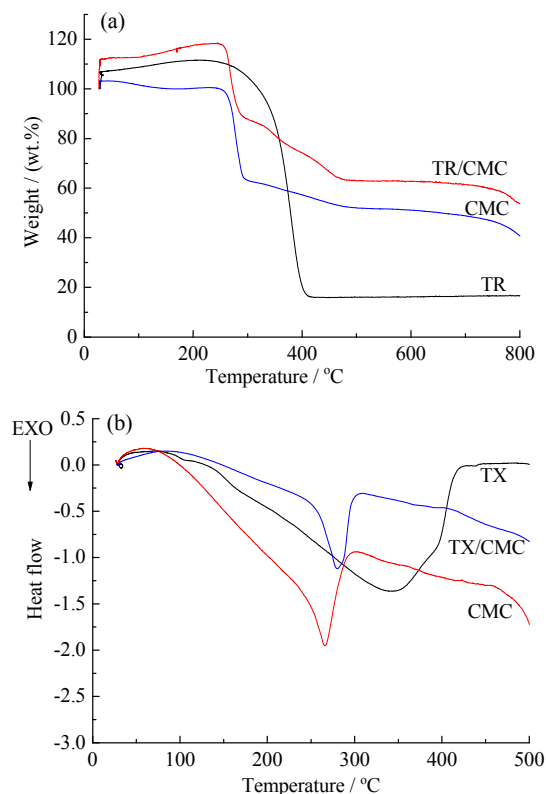


Fig. 3 TG (a) and DSC (b) of TR, CMC and TR/CMC

The cycling performance of graphite electrodes with TR/CMC binder was shown in Fig. 4a. At C/5 rate, graphite electrode with TR/CMC (1:1 and 3:2, by mass) binder delivers specific capacity of 318 mA·h/g, while 290 mA·h/g for TR/CMC (4:1) after 100 cycles. For TR/CMC (1:1 and 3:2), TR binder helps to form a conducting network in graphite electrode sheet, but excessive TR aggregates in a separate insulating phase. As a result, graphite electrode with TR/CMC (4:1) shows inferior cycle performance than that of TR (1:1, 3:2). In addition, graphite anodes with TR/CMC (1:1, 3:2) binder exhibited a comparable cycling performance to that of SBR/CMC binder. Fig. 4b showed the rate capability of graphite electrodes with TR/CMC and SBR/CMC, respectively. The rate was increased gradually from C/5 to 5 C and finally returned to C/5. At rates from C/5 to 0.5 C, graphite electrodes with TR/CMC (3:2) exhibited a similar rate performance with that of CMC/SBR, but far higher specific capacity than that of CMC/SBR at higher than 0.5 C rate. For example, at 1 C rate, graphite

electrodes with TR/CMC (3:2) delivered specific capacity of 281 mA·h/g, while only 270 mA·h/g for CMC/SBR. When the high-rate tests were completed and changed

back to C/5, the specific capacity of the two electrodes remained the same as before, which was confirmed that both of them performed well.

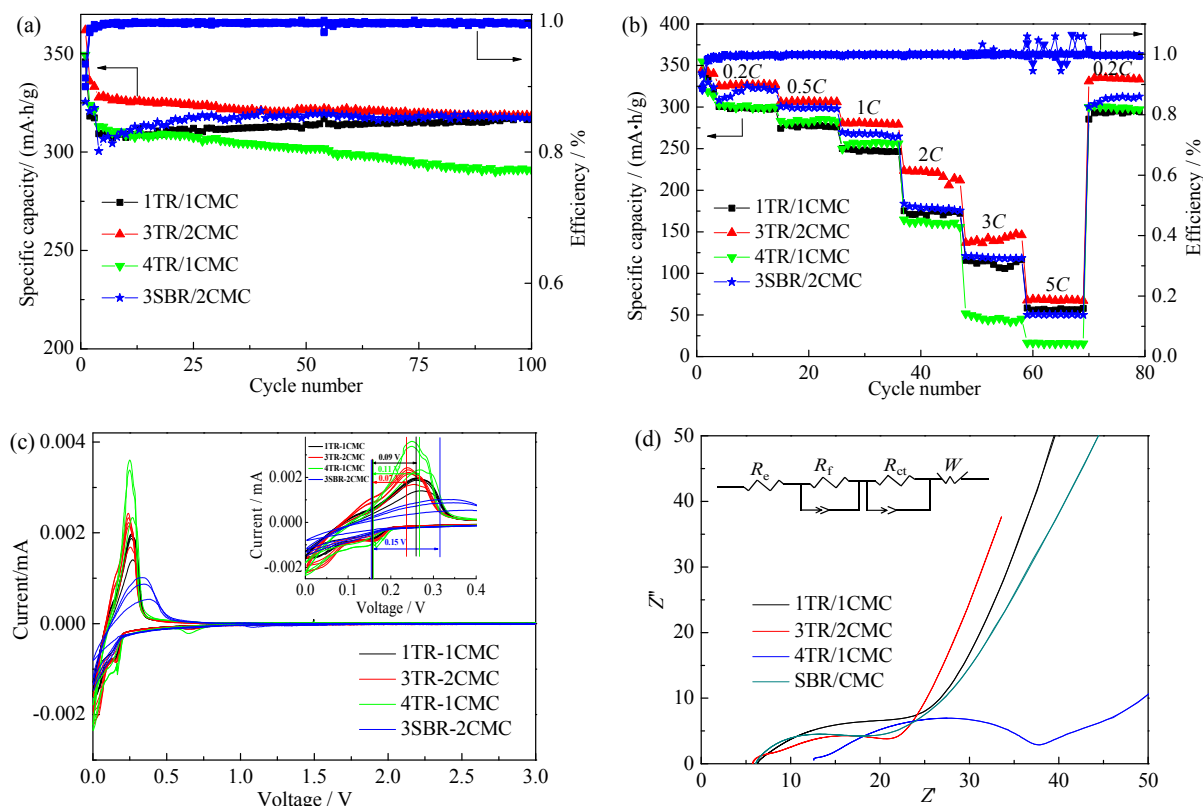


Fig. 4 (a) Cycle performances and (b) rate capabilities, (c-d) CV and EIS of the graphite anodes

Table 1 Fitting parameters for the Nyquist plots in Fig. 4d

Graphite Electrode	R_e/Ω	R_{ct}/Ω
Graphite with 1TR/1CMC	6.70	11.30
Graphite with 3TR/2CMC	5.77	10.16
Graphite with 4TR/1CMC	12.65	12.01
Graphite with SBR/CMC	6.12	11.44

CV was performed on graphite electrodes using TR/CMC binders with different ratios at a scan rate of 0.2 mV/s from 0 to 3.0 V in Fig. 4c. The oxidation and reduction peaks of graphite anodes with the two binders appeared at around 0 and 0.25 V, which was typically observed for graphite^[23]. The separation between redox peaks was 0.07 V, 0.09 V, 0.11 V, and 0.15 V for graphite with TR/CMC (3/2), TR/CMC (1/1), TR/CMC (4/1) and SBR/CMC, respectively. Graphite with TR/CMC binder showed comparable separation between redox peaks, lower than that of SBR/CMC, thus lower polarization. Fig. 4d displayed the Nyquist plots of graphite anodes

with TR/CMC, and SBR/CMC after 100 cycles. An equivalent circuit of graphite anodes (the insert of Fig. 4d) consists of an independent resistor, two resistors with constant phase elements (CPEs) in parallel and a Warburg diffusion element to account for electrolyte/electrode resistance (R_e), SEI film resistance (R_f) and charge-transfer resistance (R_{ct})^[24-25]. The values of the parameters obtained from the fitted impedance plots are summarized in Table 1. Graphite anode with TR/CMC (3:2) binder showed a smaller R_{ct} than that of TR/CMC (4:1, 1:1) and SBR/CMC, indicating an improved kinetic of electrode reactions (charge transfer and polarization) which is essential to facilitate the transportation of lithium ions in the bulk.

SEM images of graphite electrodes with different binders after 100 cycles were presented in Fig. 5. Graphite anodes with TR/CMC are both well preserved, thus TR/CMC could potentially be used as a water-soluble binder for graphite anodes in lithium ion battery.

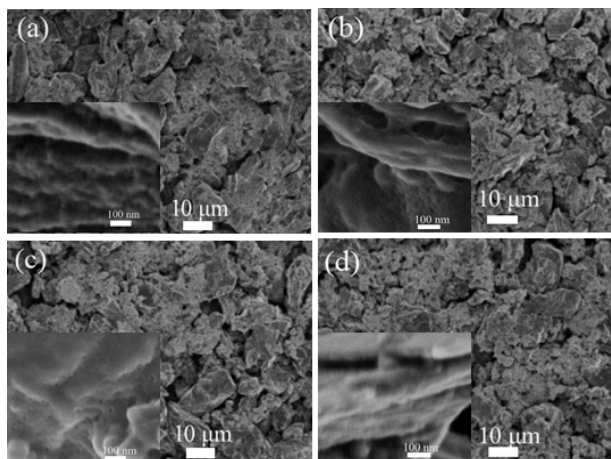


Fig. 5 SEM images of graphite anodes with different binder after 100 cycles, (a) TR/CMC (3:2), (b) TR/CMC (1:1), (c) TR/CMC (4:1), (d) SBR/CMC (3:2)

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) electrode with the TR/CMC (TR/CMC = 3:2, by weight) binder was shown in Fig. 6. LTO electrode shows capacity retention of 98.3% after 500 cycles at C/2 rate from 1.5 to 2.5 V, indicating TR/CMC binder could be also used for LTO electrode.

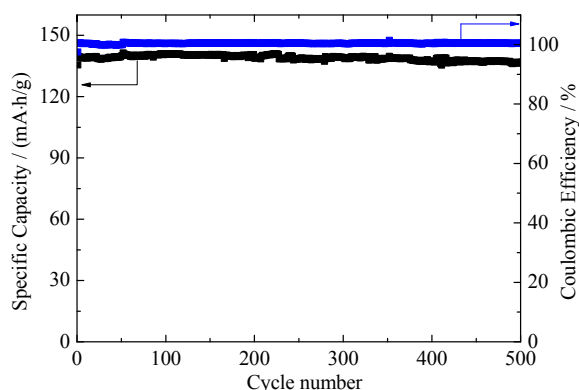


Fig. 6 The cycling performances of LTO electrode with TR/CMC binder

3 Conclusions

We have reported TR/CMC as a water-soluble composite binder for graphite anode in Li-ion batteries. With the optimized ratios of TR/CMC (TR/CMC = 3:2, by weight), graphite anode using the composite binder shows comparable cycling but better rate performances, and more favorable electrochemical kinetics than that of SBR/CMC. This strategy paves an avenue to develop the water-soluble bio-derivative TR/CMC binder systems for graphite anodes.

References:

[1] ZHAO H, WEI Y, QIAO R M, et al. Conductive polymer

binder for high-tap-density nanosilicon material for lithium-ion battery negative electrode application[J]. *Nano letters*, 2015, 15(2): 7927-7932. DOI: 10.1021/acs.nanolett.5b03003.

- [2] ZHONG H X, HE A Q, LU J D, et al. Carboxymethyl chitosan/conducting polymer as water-soluble composite binder for LiFePO_4 cathode in lithium ion batteries[J]. *Journal of power sources*, 2016, 336: 107-114. DOI: 10.1016/j.jpowsour.2016.10.041.
- [3] LEE S, OH E S. Performance enhancement of a lithium ion battery by incorporation of a graphene/polyvinylidene fluoride conductive adhesive layer between the current collector and the active material layer[J]. *Journal of power sources*, 2013, 244: 721-725. DOI: 10.1016/j.jpowsour.2012.11.079.
- [4] BIENSAN P, SIMON B, PÉRÈSA J P, et al. On safety of lithium-ion cells[J]. *Journal of power sources*, 1999, 81-82: 906-912. DOI: 10.1016/S0378-7753(99)00135-4.
- [5] KOVALENKO I, ZDYRKO B, MAGASINSKI A, et al. A major constituent of brown algae for use in high-capacity Li-ion batteries[J]. *Science*, 2011, 334(6052): 75-79. DOI: 10.1126/science.1209150.
- [6] SHAO D, ZHONG H X, ZHANG L Z. Water-soluble conductive composite binder containing PEDOT: PSS as conduction promoting agent for Si anode of lithium-ion batteries[J]. *Chemelectrochem*, 2014, 1(10): 1679-1687. DOI: 10.1002/celec.201402210.
- [7] DOBERDÒ I, LÖFFLER N, LASZCZYNSKI N, et al. Enabling aqueous binders for lithium battery cathodes-carbon coating of aluminum current collector[J]. *Journal of power sources*, 2014, 248: 1000-1006. DOI: 10.1016/j.jpowsour.2013.10.039.
- [8] WANG Z L, DUPRÉ N, GAILLOT A C, et al. CMC as a binder in $\text{LiNi}_{0.4}\text{Mn}_{1.6}\text{O}_4$ 5V cathodes and their electrochemical performance for Li-ion batteries[J]. *Electrochimica acta*, 2012, 62: 77-83. DOI: 10.1016/j.electacta.2011.11.094.
- [9] YABUUCHI N, KINOSHITA Y, MISAKI K, et al. Electrochemical properties of LiCoO_2 electrodes with latex binders on high-voltage exposure[J]. *Journal of the electrochemical society*, 2015, 162(4): A538-A544. DOI: 10.1149/2.0151504jes.
- [10] YUE L, ZHANG L Z, ZHONG H X. Carboxymethyl chitosan: a new water soluble binder for Si anode of Li-ion batteries[J]. *Journal of power sources*, 2014, 247: 327-331. DOI: 10.1016/j.jpowsour.2013.08.073.
- [11] SU M H, ZHONG H X, JIAO S R, et al. Investigation on carboxymethyl chitosan as new water soluble binder for LiFePO_4 cathode in li-ion batteries[J]. *Electrochimica acta*, 2014, 127: 239-244. DOI: 10.1016/j.electacta.2014.02.027.
- [12] ZHONG H X, ZHOU P, YUE L, et al. Micro/nano-structured SnS_2 negative electrodes using chitosan derivatives as water-soluble binders for Li-ion batteries[J]. *Journal of applied electrochemistry*, 2014, 44(1): 45-51. DOI: 10.1007/s10800-013-0590-x.
- [13] CHONG J, XUN S D, ZHENG H H, et al. A comparative study of polyacrylic acid and poly(vinylidene difluoride) binders for spherical natural graphite/ LiFePO_4 electrodes and cells[J]. *Journal of power sources*, 2011, 196(18): 7707-7714. DOI: 10.1016/j.jpowsour.2011.04.043.
- [14] HAN Z J, YABUUCHI N, SHIMOMURA K, et al. High-capacity Si-graphite composite electrodes with a

- self-formed porous structure by a partially neutralized polyacrylate for Li-ion batteries[J]. *Energy & environmental science*, 2012, 5(10): 9014-9020. DOI: 10.1039/c2ee22292b.
- [15] CHOI J, KIM K, JEONG J, et al. Highly adhesive and soluble copolyimide binder: improving the long-term cycle life of silicon anodes in lithium-ion batteries[J]. *ACS applied materials & interfaces*, 2015, 7(27): 14851-14858. DOI: 10.1021/acsami.5b03364.
- [16] YUAN Q F, ZHAO F G, ZHAO Y M, et al. Reason analysis for graphite-Si/SiO₂/C composite anode cycle fading and cycle improvement with PI binder[J]. *Journal of solid state electrochemistry*, 2014, 18(8): 2167-2174. DOI: 10.1007/s10008-014-2452-9.
- [17] ZHANG T, LI J T, LIU J, et al. Suppressing the voltage-fading of layered lithium-rich cathode materials via an aqueous binder for Li-ion batteries[J]. *Chemical communications*, 2016, 52(25): 4683-4686. DOI: 10.1039/C5CC10534J.
- [18] LG Chemical Co Ltd. The constitution of the dispersant in the preparation of the electrode active material slurry and the use of the dispersant: 200480008658.1[P]. 2006-05-03.
- [19] ISHALIN E R. Effect of type of emulsifier on the kinetics of copolymerization of Bd with St in emulsion[J]. *Khim tekhnol*, 1991, 34(6): 66-69.
- [20] HANARI N, YAMAMOTO H, KURODA K I. Comparison of terpenes in extracts from the resin and the bark of the resinous stem canker of *Chamaecyparis obtusa* and *Thujopsis dolabrata* var. *honda*[J]. *Journal of wood science*, 2002, 48(1): 56-63. DOI: 10.1007/BF00766239.
- [21] WU Z H, CHEN S P, LI A M, et al. Preparation of terpene-resin emulsions[J]. *Chemistry and industry of forest products*, 2005, 25(1): 102-104.
- [22] NGUYEN M H T, OH E S. Application of a new acrylonitrile/butylacrylate water-based binder for negative electrodes of lithium-ion batteries[J]. *Electrochemistry communications*, 2013, 35: 45-48. DOI: 10.1016/j.elecom.2013.07.042.
- [23] COURTEL F M, NIKETIC S, DUGUAY D, et al. Water-soluble binders for MCMB carbon anodes for lithium-ion batteries[J]. *Journal of power sources*, 2011, 196(4): 2128-2134. DOI: 10.1016/j.jpowsour.2010.10.025.
- [24] YUE L, WANG S Q, ZHAO X Y, et al. Nano-silicon composites using poly (3,4-ethylenedioxythiophene): poly (styrenesulfonate) as elastic polymer matrix and carbon source for lithium-ion battery anode[J]. *Journal of materials chemistry*, 2012, 22(3): 1094-1099. DOI: 10.1039/C1JM14568A.
- [25] MAHESH K C, MANJUNATHA H, VENKATESHA T V, et al. Study of lithium ion intercalation/de-intercalation into LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ in aqueous solution using electrochemical impedance spectroscopy[J]. *Journal of solid state electrochemistry*, 2012, 16(9): 3011-3025. DOI: 10.1007/s10008-012-1739-y.

作者简介:

仲皓想 (1976-), 女, 博士, 副研究员, 主要从事高容量电极材料及其高分子粘结剂研究。

张灵芝 (1969-), 男, 博士, 研究员, 博士生导师, 中国科学院“百人计划”引进国外杰出人才, 主要从事有机光电材料和纳米材料设计合成及其在各种能量储存转化器件应用研究。