

Investigating ionic liquids for optimizing lithium metal anode

Author

Zhang, L, Al-Mamun, M

Published

2021

Journal Title

Green Energy and Environment

Version

Version of Record (VoR)

DOI

[10.1016/j.gee.2021.08.001](https://doi.org/10.1016/j.gee.2021.08.001)

Rights statement

© 2021, Institute of Process Engineering, Chinese Academy of Sciences. Publishing services by Elsevier B.V. on behalf of KeAi Communications Co., Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>), which permits unrestricted, non-commercial use, distribution and reproduction in any medium, providing that the work is properly cited.

Downloaded from

<http://hdl.handle.net/10072/407666>

Griffith Research Online

<https://research-repository.griffith.edu.au>



Research Highlights

Investigating ionic liquids for optimizing lithium metal anode

Lei Zhang*, Mohammad Al-Mamun

Centre for Clean Environment and Energy, Griffith University, Gold Coast Campus, Gold Coast, QLD 4222, Australia

Received 7 June 2021; revised 25 July 2021; accepted 3 August 2021

Available online ■ ■ ■

Abstract

Developing renewable energy technology is an effective way to address the global warming and air pollution problems derived from depleting fossil fuels. Due to the high theoretical capacity (3860 mAh/g) and low electrochemical potential of lithium metal anode, lithium metal batteries (LMBs) have attracted tremendous research attention with the scalable application and vigorous deployment of electric vehicles. Unfortunately, the further commercialization of Li metal anode is hindered by the random growth of Li dendrites during the lithium plating/stripping processes, leading to the continuous consumption of active Li and the puncture on the separator. Just recently, Ma's group proposed a new approach to systematically investigate the relationship between functional groups and Li dendrite generation during the Li plating/stripping processes. The proposed new approach could be of an effective tool to gain new insights into functional groups in the electrolyte additives and Li dendrites formation, highly valuable for the rational structural design of high-performance Li metal electrode materials.

© 2021, Institute of Process Engineering, Chinese Academy of Sciences. Publishing services by Elsevier B.V. on behalf of KeAi Communications Co., Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Keywords: Lithium dendrite; Ionic liquids; Lithium metal; Anode; Battery

Developing renewable energy technology is an effective way to address the global warming and air pollution problems derived from depleting fossil fuels [1–8]. Due to the high theoretical capacity (3860 mAh/g) and low electrochemical potential of lithium metal anode, lithium metal batteries (LMBs) have attracted tremendous research attention with the scalable application and vigorous deployment of electric vehicles [9,10]. Unfortunately, the further commercialization of Li metal anode is hindered by the random growth of Li dendrites during the lithium plating/stripping processes, leading to the continuous consumption of active Li and the puncture on the separator [11]. As a result, increasing amount of dead Li is generated during cycling and the safety of the cells is reduced, resulting in the poor Coulombic efficiency (CE) and cycling life. According to the previous study, the Li dendrites formation is highly determined by the components and quality of the solid electrolyte interphase (SEI) [12]. Therefore, it is promising to control and suppress the Li dendrite growth by

adjusting the composition and additives of the electrolyte. Recently, some additives, such as the LiNO₃, fluoroethylene carbonate (FEC), ethylene sulfate (DTD), vinylene carbonate (VC), and vinyl ethylene sulfite (VES), have demonstrated superior electrochemical performance for stabilizing Li anode [13–18]. However, little is known on the further detailed influencing mechanism of different organic groups from the additives and the real relationship between functional groups and Li dendrites growth.

Therefore, Ma's group proposed a new approach to systematically investigate the relationship between functional groups and Li dendrite generation during the Li plating/stripping processes [19]. They selected the imidazole-based ionic liquids (ILs) as the target additives, because various functional groups were included in the ILs, such as the anions, cationic substituent chain lengths and substituent groups, which provide an ideal model to conduct relevant studies. Fig. 1a–h show their energy values of the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO). The ethylene carbonate (EC) and dimethyl carbonate (DMC) show the higher LUMO values

* Corresponding author.

E-mail address: lei.zhang@griffith.edu.au (L. Zhang).

than all other ILs, demonstrating that ILs can be preferably reduced on the surface of Li anode, which contributes to the generation of inorganic component rich SEI with high ionic conductivity. To prove the ability of ILs for suppressing the Li dendrite random formation, the Li||Li symmetrical cells were assembled and electrochemically tested. As shown in Fig. 1i and j, all the symmetrical LMBs with IL-contained electrolytes showed enhanced cycling stability and reduced voltage polarization. Compared with the electrolytes with 1-n-butyl-3-methylimidazolium hexafluorophosphate ([BMIm]PF₆), 1,3-dimethylimidazolium ([DMIm]PF₆), and 1-octyl-3-methylimidazolium ([OMIm]PF₆) demonstrated the best battery performance. Among various anion-based IL-contained electrolytes, [OMIm]TFSI with the optimized concentration of 0.5 wt% exhibits the longest cycling life (~250 h) for Li||Li symmetric cell and the smallest voltage polarization.

SEM images in Fig. 1k and m show that the Li anode surface was coated with cross-linked Li dendrites in the blank electrolyte, demonstrating that the Li dendrite formation could not be well suppressed in the blank electrolyte. For the IL-contained electrolytes, solid Li metal was transferred to the

porous structure, indicating the unsuccessful protection on the Li anode. However, the smooth surface of Li anode can be formed after 10 cycles when ILs with efficient anions were used (Fig. 1l and n). Especially, the smooth Li surface could be obtained in [OMIm]TFSI-contained electrolyte, revealing the outstanding ability to inhibit Li dendrite growth. Furthermore, the ionic conductivity of the optimized half-cell was also significantly improved. As for the battery test, the cells with IL-contained electrolytes delivered better cycling performance. The Li||NMC622 full cell with [OMIm]TFSI-contained electrolyte showed the best cycling stability, and still obtain the capacity of 141.7 mAh/g after 200 cycles at 0.5C (Fig. 1o). By contrast, the rapid capacity decay for the cell with the blank electrolyte occurred after 100 cycles.

The work from Ma's group systematically investigated the electrochemical relationship between the battery performance and different functional group from the electrolyte additives. The proposed new approach could be of an effective tool to gain new insights into functional groups in the electrolyte additives and Li dendrites formation, highly valuable for the rational structural design of high-performance Li metal electrode materials.

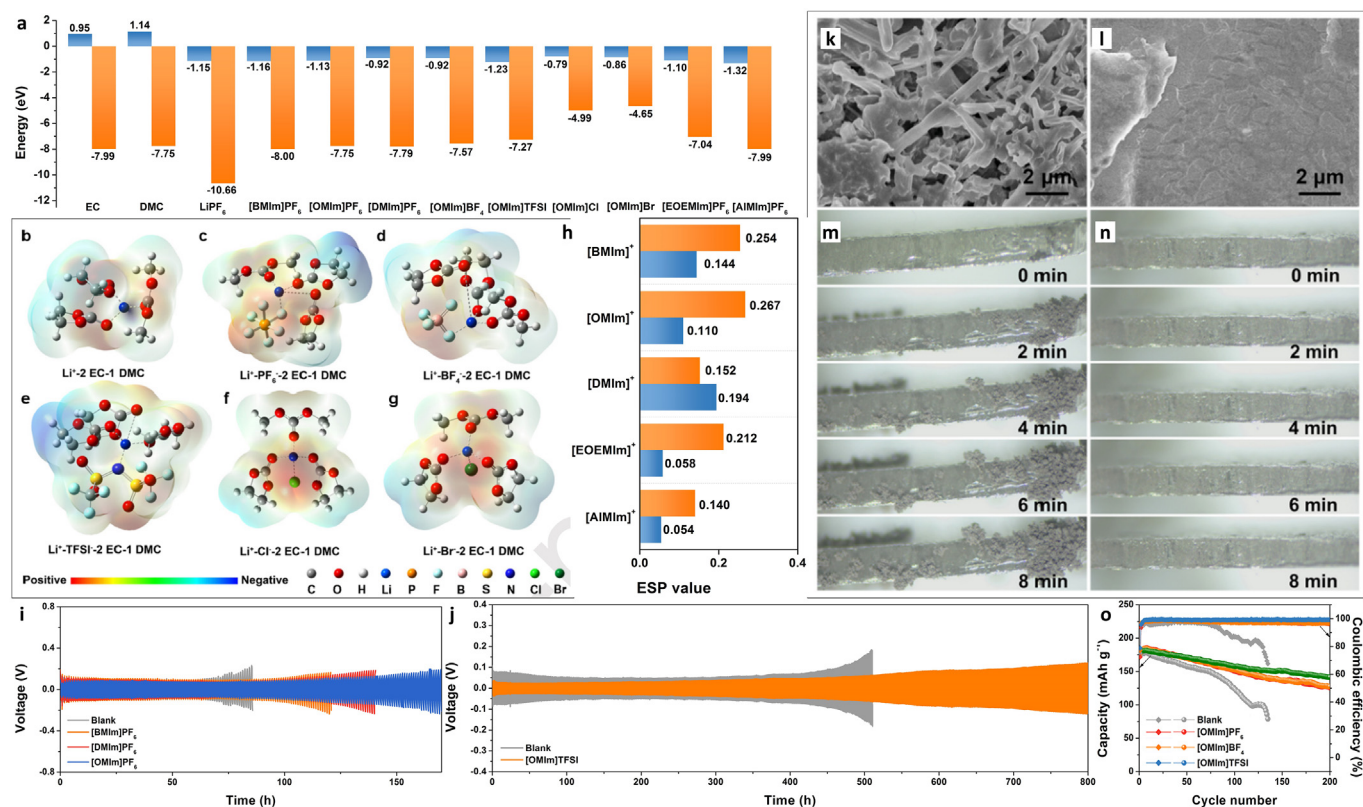


Fig. 1. **Theoretical calculation results of blank and IL-contained electrolytes.** (a) The HOMO and LUMO energy values of EC, DMC, LiPF₆ and the ILs used. Schematic illustration of the primary sheath structure of Li + solvation: (b) without any anion, (c) with PF₆⁻, (d) with BF₄⁻, (e) with TFSI⁻, (f) with Cl⁻, and (g) with Br⁻. (h) ESP charge distributions on the 1-N and 3-N of imidazole rings. **Electrochemical performance of Li||Li symmetrical cells with different electrolytes.** (i) Li deposition/stripping performance and (j) Li/stripping performance of symmetrical cells for selected cycles in the blank and [OMIm]TFSI-contained electrolytes at 0.5 mA/cm² with 0.25 mAh/cm [2]. **Morphology characterization of the Li anode cycled with the blank and [OMIm]TFSI contained electrolytes.** SEM images and *in situ* optical microscope observations of Li anode cycled with (k, l) blank electrolyte and (m, n) [OMIm]TFSI-contained electrolyte. XPS profiles of Li anodes cycled in the blank and various anion-based IL-contained electrolytes. **Electrochemical performance of Li||NMC622 full cells assembled with different electrolytes.** (o) The cycling performance of the full cells with various IL-contained electrolytes.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work is supported by Australian Research Council Discovery Projects (DP180103430, DP200100965) and 2020 Griffith University Postdoctoral Fellowship (CEE2550 LEZHA).

References

- [1] L. Zhang, B.W. Zhang, C.R. Wang, Y.H. Dou, Q. Zhang, Y.J. Liu, H. Gao, M. Al-Mamun, W.K. Pang, Z.P. Guo, S.X. Dou, H.K. Liu, *Nano Energy* 60 (2019) 432–439.
- [2] C.R. Wang, L. Zhang, M. Al-Mamun, Y.H. Dou, P.R. Liu, D.W. Su, G.X. Wang, S.Q. Zhang, D. Wang, H.J. Zhao, *Adv. Energy Mater.* 9 (2019).
- [3] L. Zhang, Y.H. Dou, H.P. Guo, B.W. Zhang, X.X. Liu, M. Wan, W.J. Li, X.L. Hu, S.X. Dou, Y.H. Huang, H.K. Liu, *J. Mater. Chem.* 5 (2017) 12073–12079.
- [4] L. Zhang, Y.H. Wang, G.W. Kan, Z.L. Zhang, C.G. Wang, Z.Y. Zhong, F.B. Su, *Rsc Adv.* 4 (2014) 43114–43120.
- [5] L. Zhang, B.W. Zhang, Y.H. Dou, Y.X. Wang, M. Al-Mamun, X.L. Hu, H.K. Liu, *ACS Appl. Mater. Inter.* 10 (2018) 20422–20428.
- [6] B.W. Zhang, W.H. Lai, T. Sheng, X.M. Qu, Y.X. Wang, L. Ren, L. Zhang, Y. Du, Y.X. Jiang, S.G. Sun, S.X. Dou, *J. Mater. Chem.* 7 (2019) 5214–5220.
- [7] Y. Wang, S.J. Fan, S.X. Wu, C. Wang, Z.G. Huang, L. Zhang, *ACS Appl. Mater. Inter.* 10 (2018) 42372–42379.
- [8] X.X. Liu, L. Zhang, X.W. Lan, X.L. Hu, *Electrochim. Acta* 274 (2018) 23–30.
- [9] G.R. Zheng, Y.X. Xiang, S.J. Chen, S. Ganapathy, T.W. Verhallen, M. Liu, G.M. Zhong, J.P. Zhu, X. Han, W.W. Wang, W.M. Zhao, M. Wagemaker, Y. Yang, *Energy Storage Mater.* 29 (2020) 377–385.
- [10] C. C. Fangyi Shi, Zheng Long Xu, *Adv. Fiber Mater.* (2021), <https://doi.org/10.1007/s42765-021-00070-2>.
- [11] L. Zhang, Q.W. Huang, X.Z. Liao, Y.H. Dou, P.R. Liu, M. Al-Mamun, Y. Wang, S.Q. Zhang, S.L. Zhao, D. Wang, G.W. Meng, H.J. Zhao, *Energy Environ. Sci.* (2021).
- [12] S. Li, Z. Luo, L. Li, J.G. Hu, G.Q. Zou, H.S. Hou, X.B. Ji, *Energy Storage Mater.* 32 (2020) 306–319.
- [13] X.Q. Zhang, X. Chen, X.B. Cheng, B.Q. Li, X. Shen, C. Yan, J.Q. Huang, Q. Zhang, *Angew. Chem. Int. Ed.* 57 (2018) 5301–5305.
- [14] X. Zhang, Y. Yang, Y. Zhou, *Chem. Soc. Rev.* 49 (2020) 3040–3071.
- [15] X. Wu, K. Pan, M. Jia, Y. Ren, H. He, L. Zhang, S. Zhang, *Green Energy Environ.* 4 (2019) 360–374.
- [16] Z. Luo, C. Liu, Y. Tian, Y. Zhang, Y. Jiang, J. Hu, H. Hou, G. Zou, X. Ji, *Energy Storage Mater.* 27 (2020) 124–132.
- [17] Z. Luo, S. Li, L. Yang, Y. Tian, L. Xu, G. Zou, H. Hou, W. Wei, L. Chen, J. Xiaobo, *Nano Energy* (2021) 106212.
- [18] Q.T. Ma, X.Y. Zhang, A.X. Wang, Y.Y. Xia, X.J. Liu, J.Y. Luo, *Adv. Funct. Mater.* 30 (2020).
- [19] J.L. Shihan Qi, Jian He, Huaping Wang, Mingguang Wu, Daxiong Wu, Junda Huang, Fang Li, Xin Li, Yurong Ren, Jianmin Ma, *J. Energy Chem.* (2021), <https://doi.org/10.1016/j.jechem.2021.05.040>.