

固态离子学的新应用

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固态离子学是研究固体中快离子输运规律及其应用的科学。它是上世纪 70 年代发展起来的一门新兴学科, 重点研究具有快离子传导特性的固体电解质材料以及具有离子/电子混合传导特性的电极材料。近年来, 固体离子及混合导电化合物在二次电池、燃料电池、传感器、超级电容器、电色器件、太阳能电池等方面的应用取得了突破性进展, 锂离子电池在各种电子器件中的大规模应用及其新材料体系的发现^[1-2]、钠硫电池在大规模储能应用中的领先地位、ZEBRA 电池在储能市场上的崛起、固体氧传感器在市场上的稳步发展以及 SOFC 逐步迈进市场成为固态离子学领域一个个闪光点, 极大地促进了新能源利用、电动汽车开发以及智能电网建设等重大任务的实施, 多领域的科学家和工程技术人员投身到固态离子学的研究中。

在众多的新能源技术研究方向中, 高比能量二次电池的研究是当前热点, 也是目前电动汽车开发和智能电网建设公认的瓶颈技术。近几年, 金属电极电池技术的发展使人们对二次电池的未来充满了信心。以金属为负极的二次电池得益于金属电极本身极高的比容量。金属负极主要以碱金属锂、钠和碱土金属镁为代表, 其中锂的重量和体积比容量分别高达 3860 mAh/g 和 2062 mAh/cm³, 远高于目前商业化的碳类负极材料, 成为未来高比能量二次电池的目标。近期, 以金属锂负极活性材料的锂硫电池和锂空气电池的研究在国内外如火如荼, 并不断取得进展。

这些电池不仅具有高比能量的特点, 更有价格低廉的绝对优势, 同时也存在尚需改进之处。(1)在锂硫电池方面, 美国 Sion Power 公司利用 PolyPlus 公司的锂负极保护膜技术, 有望实现锂硫电池能量密度 500 Wh/kg 及循环 500 次的目标^[3]。就在近期, 英国 Oxis Energy 公司报道其研制的 200 Wh/kg 的锂硫电池预计循环 1700~1800 次后的容量维持率仍达 80%, 该公司计划明年早些时候实现量产^[4], 这无疑是对锂硫电池的有力推动。国内有众多研究锂硫电池的机构, 如防化研究院、国防科技大学、北京理工大学、上海硅酸盐研究所、南开大学等均研制了软包装锂硫电池^[5]。上海硅酸盐研究所研制的硫电极在 2C 倍率下循环 500 次后比容量达到 900 mAh/g 以上。不过目前看来, 锂硫电池虽然前景良好, 但要在市场上展现其价值尚需开展很多工作。(2)在锂空气电池方面, 针对电解质隔膜、催化剂、载体等核心材料有大量的文献报道, 通过无碳电极设计以及基于 LATP 锂离子固体电解质的电池设计, 很好地改进了锂空气电池的基本性能^[6-8], 但离实际应用还差距甚远, 其电池反应机理方面尚存在争议, 电池技术还没有取得公认的突破。然而, 以锂空气电池为代表的金属空气电池由于其极高的比能量仍是未来电动汽车无法抗拒的追逐目标。

金属负极电池的开发在很大程度上取决于固体电解质新体系和新型电极材料的开发, 固态离子学成为高比能量二次电池研究与开发必须掌握的一门重要的科学, 无论是已经获得规模化应用的 LiCoO₂ 和 LiFePO₄ 等锂离子电池正极材料, Na-β/β'-Al₂O₃、ZrO₂ 等离子导体, 还是新近突破的 Li₁₀GeP₂S₁₂ 和 Li₇La₃Zr₂O₁₂^[1-2]等锂离子导体新体系, 都为实现锂金属电池新的突破以及锂电池的全固体化、从而从根本上解决锂离子电池的安全性问题奠定了坚实的基础。正因为如此, 锂离子电池的企业界也在大力拓展市场的同时, 不断关注新型二次电池以及固态离子学的进展, 仅以我国两年一届的全国固态离子学学术会议为例, 其规模也从 1980 年的数十人发展到 2012 年第 16 届全国会议的与会代表 400 余人, 其中近 20%代表来自电池与材料企业。可以说, 未来固态离子学将越来越发挥其重要作用, 为新能源技术的发展保驾护航。

New Applications of Solid State Ionics

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During the past four decades, Solid State Ionics (SSI) field has attracted numerous researchers and engineers to cultivate new technologies which plays important roles in the development of sustainable energy utilization and

clean transportation tools. The commercialization of lithium ion battery, sodium sulfur battery, sodium chloride battery, solid oxygen sensors have illustrated the success of SSI's theories and technologies. The discovery and successful applications of ionic or mixed conductive materials, such as LiCoO_2 and LiFePO_4 as active materials of lithium ion battery cathode, $\text{Na-}\beta/\beta''\text{-Al}_2\text{O}_3$ ceramics as solid electrolytes and separators for sodium based batteries, ZrO_2 as electrolytes for SOFC and oxygen sensors, and the newly developed $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ ^[1] and $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ ^[2] as lithium ion conductor, laid a solid foundation for the development of SSI technologies.

Recently, rechargeable lithium metal anode based batteries have become hot research topics in the field of SSI due to their extremely high specific capacity suitable for future generation of power sources in portable electronic devices, electric vehicles and energy storage systems. Among all the Li anode based batteries, Li-S and Li-air battery systems are the two most attractive candidates because of the low cost and abundance of sulfur and air as cathode active materials, especially the characteristics of easy access of active O_2 from the surrounding air for Li-air batteries.

Breakthroughs have been made recently with these batteries. SION Power's Li-S cells reached the highest practical specific energy as high as 350 Wh/kg, with a pack of 576 cells engineering the QinetiQ Zephyr Unmanned Aerial Vehicle (UAV) more than 336 h (14 d) of continuous flight, significantly surpassing the previous official record^[3]. Their energy densities are higher than 500 Wh/kg for more than 500 cycles^[3] and commercialization in the near future^[4] are expected. Many Chinese institutions successfully prepared soft package lithium sulfur batteries^[5]. The highest specific capacity of sulfur electrode over 900 mAh/g at 2C rate was realized by the Shanghai Institute of Ceramics, Chinese Academy of Sciences. Important advances in Li-air batteries were also made by designing carbon free air electrode^[6,7] and by the aid of LATP solid lithium electrolyte lately^[8]. However, the development of the rechargeable high energy lithium metal batteries are still hindered by the high reactivity of lithium metal with liquid electrolytes and the occurrence of dendrite growth during charge and discharge cycles. Moreover, the cycling stability of the batteries are still far away from the standard of practical applications of electric vehicle and electronic devices. Owing to the intrinsic highly resistive feature of the cathode materials, sulfur and lithium containing resultants with oxygen, structural and compositional designs of the cathode, the protection of lithium metal anode, and the control of the electrode/electrolyte interface are urgent matter to develop practical rechargeable lithium batteries.

SSI has been tackling the vital technical problems of high performance devices with solid ionic and mixed conductors as their key materials, which has great potential contribution to future energy and environmental needs of our society.

参考文献:

- [1] Kamaya N, Homma K, Yamakawa Y, *et al.* A lithium superionic conductor. *Nature Materials*, 2011, **10**: 682–686.
- [2] Murugan R, Thangadurai V, Weppner W. Fast lithium ion conduction in garnet-type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$. *Angew. Chem. Int. Ed.*, 2007, **46**(41): 7778–7781.
- [3] Technologyoverview[EB/OL]. <http://www.sionpower.com/technology.html>, 2013-08-22.
- [4] OXIS Jump-Starts First Commercialization Of Lithium-Sulfur Batteries[EB/OL]. <http://www.hybridcars.com/oxis-jump-starts-first-commercialization-of-lithium-sulfur-batteries/>, 2013-08-25.
- [5] HU Jing-Jing, LI Guo-Ran, GAO Xue-Ping. Current status, problems and challenges in lithium-sulfur batteries. *Journal of Inorganic Materials*, 2013, **28**(11): 1181–1186.
- [6] Peng Z Q, Freunberger S A, Chen Y H, *et al.* A reversible and higher-rate Li-O_2 battery. *Science*, 2012, **337**(6094): 563–566.
- [7] Cui Y M, Wen Z Y, Liu Y. A free-standing-type design for cathodes of rechargeable Li-O_2 batteries. *Energy Environ. Sci.*, 2011, **4**: 4727–4734.
- [8] Zhang T, Zhou H S. A reversible long-life lithium-air battery in ambient air. *Nature Communications*, 2013, **4**: 1817.



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