

Electrochemical splitting of LiF: a new approach to lithium-ion battery materials

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Introduction

Lithium-ion batteries (LIB) are the electrochemical storage systems with the highest energy density, which is yet insufficient for many applications. State of the art cathodes applied in the modern LIB rely on intercalation type of electrochemical reactions. However, intercalation type materials have already reached maturity and further significant increase in their energy density is unlikely. On the other hand, Li binary compounds with high formation energies may offer another approach to the electrochemical energy storage. Table 1 compares the Gibbs free energies and the theoretical discharge capacities of several binary lithium compounds [1].

Both Li₂O and Li₂O₂ are considered in the Li-air technology. However, despite its higher energy density Li₂O cannot be split electrochemically [2, 3]. Recent study has evidenced electrochemical splitting of LiF and reversible Li⁺ extraction and insertion was observed of FeF₂ blended with LiF at the nanoscale [4]. This cathode is a mixture of lithium-ion host (LiF) and transition metal host (FeF₂). During the first charge, FeF₂+LiF mixture transforms into FeF₃. First discharge transforms it into LiFeF₃-like further undergoing reversible Li⁺ reinsertions. We have expanded this study and show that LiF can be split electrochemically in the presence of other redox hosts, able to act as F acceptors. In this case, we have used four manganese oxides as redox hosts; MnO, Mn₃O₄, Mn₂O₃, and MnO₂.

Experimental

MnO_x/LiF composite samples were prepared by means of high energy ball-milling. Samples were blended from mixtures of LiF and MnO, Mn₃O₄, and Mn₂O₃ respectively. Milling was performed in zirconia grinding bowls with φ 3mm zirconia balls. The balls:material weight ratio was set to 15. The composite was milled for 5 hours at 750 rpm under Ar. To increase the electronic conductivity, the composite was mixed with 25 wt% acetylene black (AB) and the mixture further milled for 5 hours at 350 rpm. The as prepared mixture was blended with polytetrafluoroethylene (PTFE) binder in a mortar to form pellets. The pellet content was 70 wt% LiF-MnO_x composite, 25 wt% AB, and 5 wt% PTFE, and pellet weights were around 30 mg. Composites were tested vs. Li/Li⁺ in 2032 coin cells. The electrolyte was 1 M LiPF₆ in (EC:DMC) 1:1 by volume, and the cells were tested by galvanostatic cycling at 7.5 mA g⁻¹ in the voltage window 1.5-4.8 V.

Results and discussion

Figure 1 shows the first and second voltage profiles of the MnO_x + yLiF blends. In all cases Li:Mn mole ratio is fixed to 1.5. Table 2 shows the composition of the blend, oxidation state of Mn in the corresponding oxide, the theoretical capacity, if all LiF is split into Li⁺ and F⁻. The quotients between the first charging capacity and the theoretical capacity were considered as the extracted Li

ratio by initial charge up to 4.8 V.

A plausible reaction mechanism during the first charge is: MO_x+yLiF→MO_xF_y + yLi⁺. Accordingly change of manganese oxidation states during the first charge were confirmed by XAFS and XPS. Further study is needed to improve the reversibility of these systems.

Table 1 Comparison of the Gibbs free energies and the theoretical discharge capacities of various binary Li compounds.

Binary Li compounds	Gibbs free energy [kJ g ⁻¹]	Theoretical capacity [Ah g ⁻¹]
Li ₂ O	- 22.7	1.03
LiF	-18.8	1.79
Li ₂ S	-9.56	1.17
Li ₃ N	-3.70	2.31

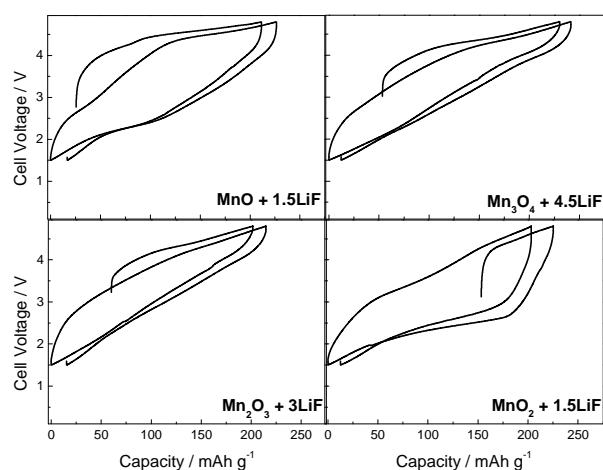


Fig. 1 Voltage profiles of MnO_x + yLiF blended cathodes, where Li:Mn=1.5.

Table 2 Performances of LiF+MnO_x blended cathodes.

Blended cathode	Mn valence state	Theoretical capacity	1 st charge capacity	Extracted Li
MnO+1.5LiF	Mn ²⁺	366 mAh/g	177 mAh/g	48.4%
Mn ₃ O ₄ +4.5LiF	Mn ^{2.67+}	349 mAh/g	141 mAh/g	40.4%
Mn ₂ O ₃ +3.0LiF	Mn ³⁺	341 mAh/g	186 mAh/g	54.5%
MnO ₂ +1.5LiF	Mn ⁴⁺	320 mAh/g	72 mAh/g	22.5%

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References

- [1] H. Li, P. Balaya, J. Maier, *J. Electrochem. Soc.*, **151**, A1878 (2004).
- [2] M.D. Radin, J.F. Rodriguez, F. Tian, D.J. Siegel, *J. Am. Chem. Soc.*, **134**, 1093-1103 (2012).
- [3] W. Xu, K. Xu, V. Viswanathan, S. Towne, J. Hardy, J. Xiao, Z. Nie, D. Hu, D. Wang, J.-G. Zhang, *J. Power Sources*, **196**, 9631 (2011).
- [4] S. Kim, K. Nam, D-H Seo, J. Hong, H. Kim, H. Gwon, K. Kang, *Nano Today*, **7**, 168 (2012).