

Investigation to a high performance electrolyte additive on solid electrolyte interface formation in lithium ion batteries

Chin-Shu Cheng¹, Fu-Ming Wang^{1,2*}

¹Sustainable Energy Center, National Taiwan University of Science and Technology, Taipei, Taiwan

²Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, Taipei, Taiwan

Correspondence: mccabe@mail.ntust.edu.tw

Introduction

It is important to have high-performance SEI on anode surface by electrochemical reactions in applications of lithium ion batteries. Characteristics such as thickness, composition and stability at high temperature all affect battery performance. Based on the information presented in our research, we discovered a novel additive (E/A), to be the primary additive. A new method was developed by directly using water as a secondary additive in lithium ion batteries that subverted most of the traditional notions that H₂O cannot be existed.¹⁻² This binary additive system (E/A/H₂O) was conceptually used here in a novel approach to lithium ion battery production that the moisture curing reaction proceeded to solve problems such as performance loss and additional humidity control cost. However, the weight of SEI is difficult to observe due to the infinitesimal variation after the electrochemical reaction. We investigated the multiple interactions and mechanisms among additive, H₂O, lithium salts and SEI properties of anode materials by Electrochemical Quartz Crystal Microbalance (EQCM) measurements.

Experimental

The graphite anode material consisted of 93wt% mesocarbon microbead (MCMB), 3 wt% KS-6 as a conductive additive and 4 wt% PVDF as a binder. Graphene nanosheets (GNS) were synthesized by modified Hummers' method.³ After the brown graphene oxide (GO) powder was obtained, it was subsequently reduced at 300°C for 2 hours under a reducing atmosphere of 15% H₂/85% N₂. GNS-300 was obtained for electrochemical tests. Working electrode was made of graphene-based material, Super P and binder with weight ratio of 89/ 1/ 10. The electrolyte was 1.1 M lithium hexafluorophosphate (LiPF₆) in ethylene carbonate (EC)/ propylene carbonate (PC)/ diethyl carbonate (DEC) (3/2/5 v/v). We utilized the connections between quartz crystal analyzer (QCM, SEIKO EG&G, QCA 922) and electrochemical instrument (Biologic VMP3) to establish the unique design in the specific small glove box filled with high dried air. This QCM cell was consisted of the quartz flake as working electrode, platinum wire as counter electrode and one lithium foil as reference electrode. The container could be filled with electrolyte to do the linear sweep voltammogram (LSV) measurements. The electrochemical performance tests were conducted on a Maccor battery tester series 4000. The cycle ability of the batteries was measured in a 0.1C/0.1C cycle in the voltage range 0.005-3.5V.

Results and Discussion

The electrolytes with primary (E/A) and binary additives (E/A/ H₂O) result in the different rate of SEI formation. Regardless of the analytic voltage range, Figure 1 indicates

electrolyte with E/A/H₂O forms heavier passivation layer on the quartz electrode than that of pure electrolyte (E) and primary additive (E/A) by using EQCM measurement. The SEI weight of electrolyte with binary additive is partially reductive on the quartz electrode after the electrochemical reaction between 2.52 V and 2.45 V. Then, the portion of primary additive (E/A) is reacted with electrolyte and lithium salt in the range of 2.45 V to 2.39 V. Finally, the lithium based ligand formed by the combination reaction of residual additive, lithium salt, and H₂O results in the similar weight of SEI from 2.39 V to 2.26 V compared with the second range (2.45~2.39 V). Although the SEI formation of binary additive is 2.6 times the weight of primary additive, the SEI of lithium based ligand possesses high conductivity implying that the inner resistance of SEI decreases. These results are proved this innovative inner SEI increases the transport property of lithium ions and effectively maintains battery performance as the binary additive is used.

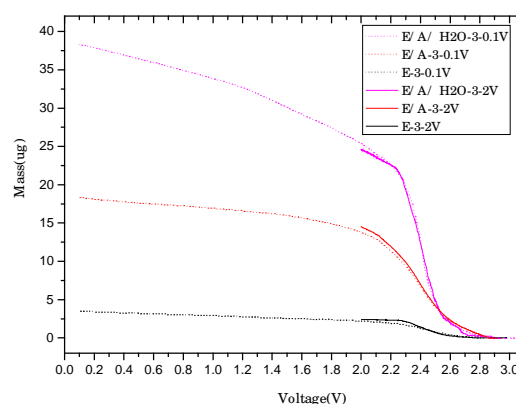


Figure 1 The effect of electrolytes w/wo primary (E/A) and binary additives (E/A/ H₂O) at weight variation vs. voltage by the EQCM analyses from 3 V to 0.1 V. Working electrode, quartz flake; counter electrode, platinum wire; reference electrode, lithium; scan rate 0.5 mV/s.

Conclusions

In conclusion, the experimental results provided not only the outstanding battery performance of binary additive (E/A/ H₂O) but the particular components of SEI films on anode materials by EQCM technique. We will understand the formation mechanism of SEI by a constant voltage scanning and represent the intercalation and de-intercalation of lithium ions rather than the mere electrochemical variations of electrolytes or additives.

Acknowledgements

The authors are grateful for the financial support from the National Science Council of Taiwan, R.O.C, under Grant NSC 100-2628-E-011-018-MY2, 100-2923-E-011-001-MY3 and 102-ET-E-011-003-ET.

References

1. F. M. Wang, C. S. Cheng, J. Rick, *MRS Comm.*, **2** (2012) 5
2. C. S. Cheng, F. M. Wang, J. Rick, *Int. J. Electrochem. Sci.*, **7** (2012) 8676
3. Hummers WS, Offeman RE, *J. AmChem. Soc.* 1958, **80**: 1339