

Impact of Electrolyte Additives on the Li⁺ Charge Transfer Kinetics in Li-ion Batteries

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Li-ion battery electrolytes containing an additive, or additives, are often called functional electrolytes [1], as the additives enhance and facilitate functions such as solid electrolyte interphase (SEI) formation on the anode, cycle life improvement for the cathode and safety. The introduction of additives that have their own redox stability limits also modifies the original redox chemistries on both anode and cathode and forms different SEI and cathode electrolyte interphases (CEI) [2]. Furthermore, the nature of the anode and cathodes also influences the properties of SEI and CEI on electrodes [3,4]. These changes significantly impact the Li⁺ charge transfer kinetics in the Li-ion cells.

Full cells made of graphite (Gr) anodes and lithium nickel cobalt aluminum oxide (NCA) cathodes in a baseline electrolyte of 1 M LiPF₆ in EC:EMC:MP (20:20:60 v/o), with or without additive, and a Li reference electrode inserted in between the two electrodes were used to measure the impedance across the Gr/electrolyte and NCA/electrolyte interfaces at the same time [5]. The Li⁺ charge transfer resistance, R_{ct}, was extracted from the impedance Nyquist plot by matching with an equivalent circuit. The activation energy, E_a, was derived from the R_{ct} values at different temperature using the relationship, $1/R_{ct} = A_0 e^{-E_a/RT}$, where A₀, R and T are a frequency factor, the gas constant and the temperature in Kelvin, respectively.

The additives studied included lithium bis(oxalato)borate (LiBOB), vinylene carbonate (VC), 1,3-propanesultone (PS), lithium difluoro(oxalato)borate (LiDFOB), and lithium bis(fluorosulfonyl)imide (LiFSI). The impact of LiBOB and LiFSI on the Li⁺ charge transfer kinetics are especially noteworthy. The presence of LiBOB results in a lower R_{ct} and E_a on the NCA cathode, but higher R_{ct} and E_a at the Gr anode compared to the baseline electrolyte. The presence of LiFSI results in a lower R_{ct} and E_a on NCA cathode and also lower R_{ct}, however, similar E_a on the Gr anode compared to the baseline electrolyte. The additive that is not ideal for the anode could benefit the cathode kinetics, such as LiBOB. The LiFSI could benefit both electrodes. The use of full cells with reference electrodes allows one to assess the full impact of an additive on both the anode and the cathode at the same time.

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References:

- [1] K. Abe, in: T. R. Jow, K. Xu, O. Borodin, M. Ue (Eds.), *Electrolytes for Lithium and Lithium-Ion Batteries*, Springer Series: Modern Aspects of Electrochemistry, Vol. 58, 2014, pp. 167-208.
- [2] S. A. Delp, O. Borodin, M. Olguin, C. G. Eisner, J. L. Allen, T. R. Jow, *Electrochimica Acta*, **209** (2016) 498.
- [3] T. R. Jow, M. B. Marx, J. L. Allen, *J. Electrochem. Soc.*, **159** (2012) A604.
- [4] J. Kasnatscheew, U. Rodehorst, B. Streipert, S. Wiemers-Meyer, R. Jakelski, R. Wagner, I. C. Laskovic, M. Winter, *J. Electrochem. Soc.*, **163** (2016) A2943.
- [5] J.-P. Jones, M. C. Smart, F. C. Krause, B. V. Ratnakumar, and E. J. Brandon, *ECS Trans.*, **75** (2017) 1.