

A comparison of the reactivity of cathode/electrolyte pairs depending on the salt type

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The thermal behavior of lithium-ion batteries depend on a number of factors, including electrolyte (salt and solvent), electrode, and amount of electrolyte present, all of which combine to give the overall thermal stability of the cell. We have previously shown how the thermal stability of $\text{Li}_{0.5}\text{CoO}_2$ and LiMn_2O_4 , charged to 4.2V, is affected by the concentration of LiPF_6 in EC/DEC [1,2]. The thermal stability of LiCoO_2 was found to increase as the concentration of LiPF_6 increased, whereas the thermal stability of LiMn_2O_4 decreased as concentration increased.

Recent studies have shown a large change in the thermal behavior of graphitic anode materials with a change in the electrolyte salt [3]. Here, the change in thermal behavior of $\text{Li}_{0.5}\text{CoO}_2$ and LiMn_2O_4 , charged to 4.2V, as a result of changing the electrolyte salt material will be presented. Four different salts have been used and these include LiPF_6 , LiBF_4 , $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ (HQ), and $\text{LiN}(\text{CF}_3\text{CF}_2\text{SO}_2)_2$ (BETI). For $\text{Li}_{0.5}\text{CoO}_2$, it was found that the thermal stability followed the following order $\text{LiPF}_6 > \text{LiBF}_4 > \text{LiN}(\text{CF}_3\text{SO}_2)_2 = \text{LiN}(\text{CF}_3\text{CF}_2\text{SO}_2)_2$, where LiPF_6 had the largest thermal stability. It has been shown previously that the reaction of $\text{Li}_{0.5}\text{CoO}_2$ in the presence of just solvent (EC/DEC) shows the most thermal instability [1]. In fact, when $\text{Li}_{0.5}\text{CoO}_2$ is reacted in the presence of $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ or $\text{LiN}(\text{CF}_3\text{CF}_2\text{SO}_2)_2$ the reactivity of the sample is very similar to that of $\text{Li}_{0.5}\text{CoO}_2$ in the presence of just solvent. This indicates that, at least for $\text{Li}_{0.5}\text{CoO}_2$, the presence of $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ or $\text{LiN}(\text{CF}_3\text{CF}_2\text{SO}_2)_2$ does not provide any protective coating on the cathode to increase thermal stability.

The thermal response of a variety of potential cathode materials for lithium-ion batteries was investigated in EC/DEC (33/67) using LiPF_6 (1M). The selected cathodes consist of LiNiO_2 , $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$, LiCoO_2 , $\text{LiNi}_{0.7}\text{Co}_{0.2}\text{Ti}_{0.05}\text{Mg}_{0.05}\text{O}_2$, and LiMn_2O_4 . These materials were analyzed in an Accelerating Rate Calorimeter (ARC) and a Differential Scanning Calorimeter (DSC). Typical DSC profiles are shown in Figure 3, and similar profiles (both ARC and DSC), will be shown for each cathode.

References

- [1].D.D. MacNeil, paper 77 presented at 198th Meeting of the Electrochemical Society, Phoenix Az, Oct. 2000.
- [2].D.D. MacNeil, paper 66 presented at 198th Meeting of the Electrochemical Society, Phoenix Az, Oct. 2000.
- [3]. D.D. MacNeil, D. Larcher, J.R. Dahn, *Journal of the Electrochemical Society*, 146 (10), 3596-3602 (1999).

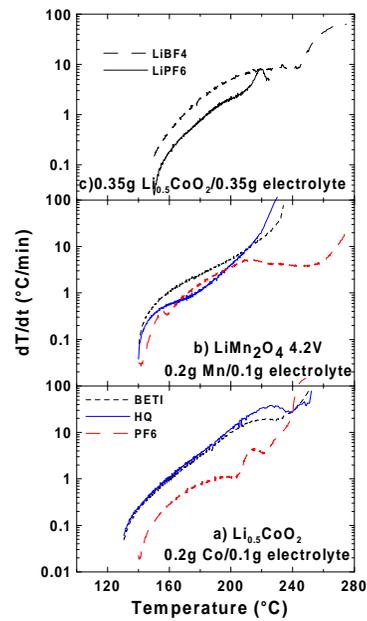


Figure 1. Comparison of the self-heating rates of a) $\text{Li}_{0.5}\text{CoO}_2$ and b) LiMn_2O_4 , charged to 4.2V, to a change in salt type for 1M EC/DEC (33/67) electrolyte. c) Comparison of 1M LiBF_4 (dashed) and 1M LiPF_6 (solid) for 0.35g of $\text{Li}_{0.5}\text{CoO}_2$ in 0.35g of electrolyte.

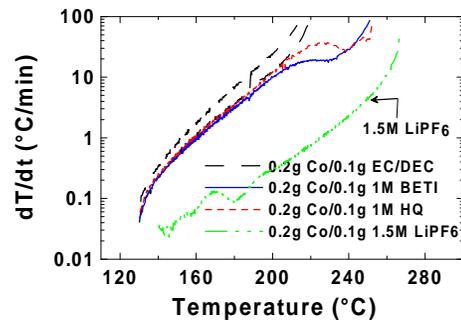


Figure 2. Comparison of the self-heating of $\text{Li}_{0.5}\text{CoO}_2$ in solvent (EC/DEC, 33/67), in 1M electrolyte in EC/DEC (33/67) (both BETI and HQ salts) and in 1.5M LiPF_6 in EC/DEC (33/67).

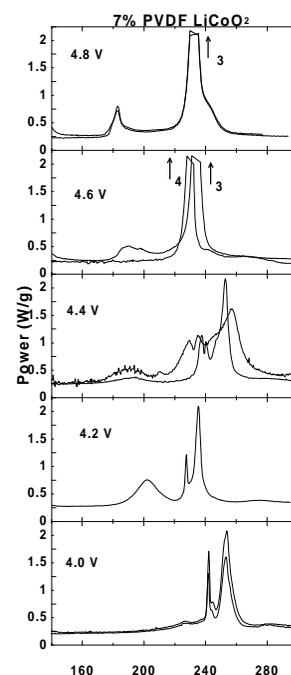


Figure 3. DSC profiles at $2^\circ\text{C}/\text{min}$ of $\text{Li}_{0.5}\text{CoO}_2$ charged to indicated voltages.