

Novel gel polymer electrolyte with enhanced intrinsic safety

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Solid polymer electrolytes (SPEs) have been widely studied in the last decades for use in lithium-ion batteries because they display several advantages compared to liquid electrolytes. As in SPEs the lithium salt is dissolved by the polymer matrix without any solvent the risk of leakage is avoided. Furthermore, due to their solid character, the fabrication of flexible, all-solid state batteries in different shapes and sizes is possible. Though, their low room temperature conductivity, which is two to three orders of magnitude lower than that of liquid electrolytes, is the main reason why they have not yet been largely introduced to the market.

One approach to overcome this limitation is the use of gel polymer electrolytes (GPEs), where the polymer serves as matrix for the immobilization of a conventional liquid electrolyte. Therefore, the leakage of the liquid electrolyte is prevented, which leads to an increased safety of the system, while the ionic conductivity is close to that of pure liquid electrolytes.

Recently, our group has reported on a new GPE displaying high room temperature conductivity while having a sufficient mechanical stability to be used as separator.[1] The combination of these two different properties was achieved by the preparation of copolymers consisting of two monomers with different properties. This polymer host was able to retain a large amount of the liquid electrolyte 1 M LiPF₆ in EC:DMC (1:1 wt) without any leakage. The applicability of this electrolyte system in lithium-ion batteries was proven in full cells with industrial electrodes, which showed a stable cycling behavior over 200 cycles.

In the present work we focus on the study of a novel GPE comprising a high flash point liquid electrolyte. In order to further increase the intrinsic safety of the GPE the EC:DMC-based liquid electrolyte was substituted by an electrolyte based on EC and adiponitrile (ADN). This liquid electrolyte displays a flash point that is more than 110 °C higher than that of an electrolyte comprising linear carbonates.[2] Additionally, the vapor pressure of ADN at 20 °C is more than three orders of magnitude lower than that of DMC. TGA measurements revealed that in contrast to the EC:DMC-based GPE, which displayed a significant weight loss already at temperatures below 50 °C, the EC:ADN-containing GPE showed a negligible weight loss up to 100 °C.

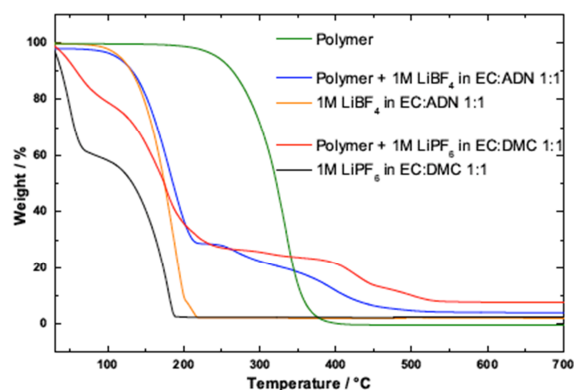


Fig. 1. TGA-curves of the polymer matrix, the liquid electrolytes 1 M LiBF₄ in EC:ADN 1:1 and 1 M LiPF₆ in EC:DMC 1:1, and the two GPEs comprising them.

This result confirms that by the immobilization of the high flash point electrolyte not only the leakage of the liquid electrolyte but also its evaporation could be reduced, which leads to an enhanced intrinsic safety. The EC:ADN-based GPE displayed a room temperature conductivity of 0.5 mS cm⁻¹ and a wide electrochemical stability window. The applicability of this new electrolyte system was proven in LFP / graphite and NCM / graphite full cells. Next to the thermal and electrochemical investigations the coordination of the lithium ions as well as the lithium ion mobility in the GPE were studied by means of NMR and Raman spectroscopy.

References

- [1] P. Isken, M. Winter, S. Passerini, A. Lex-Balducci J. Power Sources 225 (2013) 157.
- [2] P. Isken, C. Dippel, R. Schmitz, R.W. Schmitz, M. Kunze, S. Passerini, M. Winter, A. Lex-Balducci Electrochim. Acta 56 (2011) 7530.