

Novel electrolytes based on “Hindered glymes” - a strategy to prevent graphite exfoliation in Lithium secondary batteries

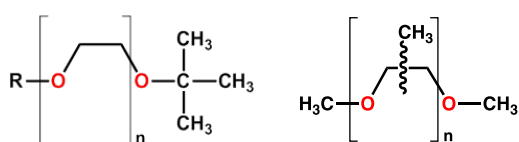
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Commercial lithium batteries use as electrolytes, mixtures of at least one cyclic carbonate, the most common of which is ethylene carbonate (EC) to which various proportions of propylene carbonate (PC) can be optionally added. Since such cyclic carbonates are either solid (EC) at room temperature, or highly viscous (PC), co-solvents or thinners are usually added, the most common of which are dimethyl carbonate (DMC), diethyl carbonate (DEC) and ethylmethylcarbonate (EMC). The solutes containing in the electrolyte compositions are usually selected from lithium salts with low lattice energy like LiBF_4 , LiCF_3SO_3 , $\text{Li}[\text{CF}_3\text{SO}_2)_2\text{N}]$, LiPF_6 . In practice, LiPF_6 is almost exclusively used because of its high conductivity and beside does not corrode aluminum, the current collector, at potentials up to 4.5 V vs $\text{Li}^+/\text{Li}^\circ$. The linear components (DMC, DEC, EMC) acting mainly as thinner of more viscous and high-melting EC, are however the least stable component and have low flash points that are serious handicaps for lifetime and safety. It thus makes it a critical requisite to reconsider the choice of the electrolyte, especially trying to get rid of the alkyl carbonate, fragile to reduction (RO^\cdot , RCO_2^\cdot) [1], and with low flash points (dimethyl carbonate, DMC, $\text{Fp} = 17^\circ\text{C}$). On the other hand, poly ethers are a good alternative, Moreover ethers [2, 3] are also easily biodegradable solvents that are very stable to reduction and anodically withstand up to 3.9 V but all formerly known representatives solvates Li^+ strongly enough to co-intercalate in the graphite negative electrode and exfoliate it. We have put forward a new electrolyte composition comprising a polyether to which a bulky *Tert*-butyl group is appended (“hindered glyme”), totally preventing co-intercalation while keeping good conductivity. This alkyl carbonate-free electrolyte shows remarkable cycle efficiency of the graphite electrode, not only at RT, but also at 50 and 70°C with lithium bis(fluorosulfonimide) salt. The two-ethylene bridge “hindered glyme”[4] has higher boiling point and a flash point of 80°C, a considerable advantage for safety.



Tert-G2: $n = 2$, $R = \text{Et}$

DP ($n = 2$)

Figure 1. Chemical structure of the glymes under study

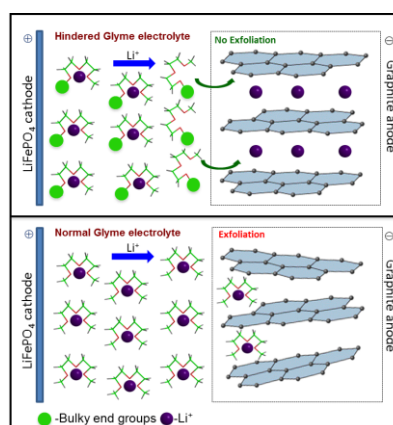


Figure 2. Concept of preventing solvent co-intercalation

1. D. Aurbach, B. Markovsky, I. Weissman, E. Levi, Y. Ein-Eli, *Electrochim. Acta* 45 (1999) 67-86.
2. D. Aurbach, E. Granot, *Electrochim. Acta* 42(1997) 697-718.
3. S. Tobishima, H. Morimoto, M. Aoki, Y. Saito, T. Inose, T. Fukumoto, T. Kuryu, *Electrochim. Acta* , 49 (2004) 979-978.
4. D. Shanmukaraj, S. Grugeon, S. Laruelle, M. Armand, *Chem Sus Chem*, 8(2015) 2691-269.