

Energimyndighetens titel på projektet – svenska Icke-brandfarliga elektrolyter för säkrare litium-jon-batterier	
Energimyndighetens titel på projektet – engelska Non-flammable electrolytes for safer lithium-ion batteries	
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Förord

The Swedish Energy Agency has financed the project.

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Sammanfattning

Detta projekt har handlat om den brandfarliga vätskekomponenten som finns i litiumjonbatterier och dess ersättning med icke brandfarliga alternativ. Den första delen av projektet undersökte flera lovande elektrolyter som redan rapporterats i litteraturen och testade dem under identiska förhållanden. Därefter valdes särskilt lovande elektrolyter ut för vidare studier och nya formuleringar föreslogs och testades. Flera tekniker användes inklusive elektrokemisk batteritestning, ytanalys med röntgenfotoelektron-spektroskopi, såväl som andra inklusive gasanalys, elektrodresistansmätningar och kärnmagnetisk resonansspektroskopi. Projektet resulterade i en högkvalitativ analys av många elektrolytssystem och djupgående karakterisering av ett antal intressanta batterisystem. Hittills har en vetenskaplig artikel publicerats och ytterligare tre är under förberedelse. Resultaten har även

presenterats vid internationella konferenser. Det förväntas att resultaten kommer att vara viktiga för den framtida utvecklingen av säkrare och mer hållbara litiumjonbatterier.

Summary

This project has dealt with the flammable liquid component contained within lithium-ion batteries and its replacement with non-flammable alternatives. The first part of the project investigated several promising electrolytes reported already in the literature, testing them under identical conditions. Thereafter, particularly promising electrolytes were selected for further study, and novel formulations proposed and tested. Several techniques were employed including electrochemical battery testing, surface analysis by X-ray photoelectron spectroscopy, as well as others including gas analysis, electrode resistance measurements, and nuclear magnetic resonance spectroscopy. The project resulted in a high quality analysis of many electrolyte systems and in-depth characterisation of a number of interesting battery systems. So far one scientific article has been published and three more are under preparation. The results have also been presented at international conferences. It is expected that the results will be important for the future development of safer and more sustainable lithium-ion batteries.

Inledning/Bakgrund

One of the main challenges in the introduction of rechargeable battery technologies in society is to continuously improve their safety attributes, creating more sustainable devices. Lithium-ion batteries (LIBs) use a liquid electrolyte comprising highly flammable organic carbonate solvents (e.g. ethylene carbonate, diethyl carbonate) and a lithium salt (e.g. lithium hexafluorophosphate). Electrolytes with high ionic conductivities allow for fast diffusion of Li ions between anode and cathode. A short-circuit, mechanical abuse or overcharging can initiate a ‘thermal runaway’, which is likely to cause combustion of the electrolyte. Such occurrences, as presented in mainstream media, pose serious safety implications to consumers. Many efforts are being made to reduce or eliminate the liquid electrolyte, for instance through the introduction of solid-state electrolytes. While these can offer comparable bulk ionic conductivities and high mechanical strength, they suffer from low Li ion diffusion across grain boundaries, poor wetting of electrodes, and difficulties with mass production. It is expected that liquid electrolytes will remain for many years, while the use of flame-retarding solvents or additives is seen as the most cost-effective method to improve safety (rather than ionic liquids or high salt-solvent ratios).

There are three particularly interesting groups of flame-retarding compounds previously reported for non-flammable electrolytes: carbonates, ethers, and phosphates, for which there are several examples of each to be shown flame-retarding properties. Many studies had presented limited battery testing data, each using different cell chemistries and testing parameters. In addition, many use half-cell configurations with lithium metal as the counter electrode, which may not

reflect the true performance of a full cell system. The lack of a clear picture demonstrated the need for systematic studies on a wide array of non-flammable electrolyte chemistries to benchmark performance against the state-of-the-art.

Poor performance, usually characterised by rapid capacity fading, can be the result of several factors but is often associated with degradation of electrode-electrolyte interfaces. Extensive build-up of the solid electrolyte interphase (SEI) through decomposition of the electrolyte or structural transformation of the active material particle surfaces can lead to inhibited Li-ion diffusion. State-of-the-art graphite anodes combined with carbonate electrolytes, however, form highly stable interfaces. This is relatively well-documented, compared with other anode materials or electrolytes, through advanced characterisation of the SEI composition, thickness, and impedance. Performing such detailed studies of battery interfaces allows for an in-depth understanding of and correlation with their performance, and can be applied to the design of novel non-flammable electrolytes.

The purpose of this project was to further the knowledge and understanding of potential non-flammable liquid electrolytes for the latest generation of lithium-ion batteries. With liquid electrolytes expected to remain the predominant electrolyte for the ever-growing lithium-ion battery market over the next decade, there is considerable incentive to improving their safety.

The project leader was Andrew Naylor at Uppsala University, and the project ran from 2021-08-01 to 2024-03-31, financed by the Swedish Energy Agency.

Genomförande

Part 1 of the project involved evaluating and benchmarking a selection of electrolytes from the current literature against a state-of-the-art flammable liquid electrolyte (e.g. 1 M LiPF₆ in EC:EMC 3:7) for a chosen cell chemistry (e.g. NMC811 – Si-graphite). This was performed by selecting a wide range of chemistries that had been shown as promising for non-flammable electrolytes, and testing all under the same conditions by various electrochemical methods including battery cycling.

Part 2 of the project involved assessing the interfacial properties at the electrodes for a variety of different non-flammable electrolyte chemistries. This was primarily performed by X-ray photoelectron spectroscopy (XPS), both in-house and at synchrotron facilities.

Part 3 of the project involved development of novel non-flammable electrolyte formulations. This was performed by using the knowledge from parts 1 and 2 to identify formulations that are expected to display interesting performance. Battery testing and further interfacial characterisation was performed.

Resultat

In relation to Part 1, eight non-flammable solvent systems were examined in this study. Table 1 summarizes their compositions and flammability characteristics.

Table 1: Descriptions of the non-flammable solvent systems studied in this work. Abbreviations: ARC = accelerated rate calorimetry, DSC = differential scanning calorimetry, SET = self-extinguishing time, FP = flash point. Pass/fail refers to a visual inspection of the burning behavior after being exposed to a flame source. All ratios of liquid mixtures are vol/vol; solid additives refer to mass/mass relative to the total amount of LiPF₆ in the electrolyte.

Non-flammable solvent	Co-solvent	Additives	Characterization of flammability
2,2,2-trifluoroethyl methyl carbonate (FEMC)	10 vol% fluoroethylene carbonate (FEC) ^{21,22}	None	Pass/fail ²³ , ARC ^{22,24}
1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropylether (TTE)	60 vol% FEC ²²	None	ARC ²²
Methyl difluoroacetate (MFA)	None ^{25–29}	2 vol% vinylene carbonate (VC) ^{28,29}	DSC ^{25,26,28–30}
Bis(2,2,2-trifluoroethyl) carbonate (TFEC)	30 vol% propylene carbonate (PC) ^{31–33}	1 vol% FEC ³³	SET ³³ , FP ³³
Tris(2,2,2-trifluoroethyl) phosphate (TFEP)	70 vol% EC:DEC (1:1) ³⁴	None	SET ^{34,35} , DSC ^{36,37}
	70 vol% GBL (γ -butyrolactone) ³⁸	3 wt% lithium difluoro(oxalato) borate (LiODFB) ³⁸	SET ³⁸
Trimethyl phosphate (TMP)	80 vol% GBL ³⁹	2 vol% VC + 5 vol% vinyl ethylene carbonate (VEC) ³⁹	Pass/fail ⁴⁰ , SET ^{20,41–43}
Dimethyl methylphosphonate (DMMP)	90 vol% EC:DEC (1:1) ⁴⁴	5 wt% lithium bis(oxalato)borate (LiBOB) ⁴⁴	SET ^{44,45}

References from the table are found in the original article:

F. Gebert, M. Longhini, F. Conti, A. J. Naylor, An electrochemical evaluation of state-of-the-art non-flammable liquid electrolytes for high-voltage lithium-ion batteries, *Journal of Power Sources*, **2023**, 556, 232412.

DOI: [10.1016/j.jpowsour.2022.232412](https://doi.org/10.1016/j.jpowsour.2022.232412)

Figure 1 shows the linear sweep voltammetry (LSV) and dQ/dV plots for the eight electrolytes as well as the benchmark LP57. The oxidation current is observed to be particularly large for the MFA electrolyte, as well as three out of four of the phosphate/phosphonate electrolytes. This suggests that the hydrofluorocarbon-based electrolytes tend to exhibit a better oxidation stability. This is also observed in dQ/dV plots where the phosphate/phosphonate electrolytes show many more reactions at lower cell voltages, indicating their poorer stability.

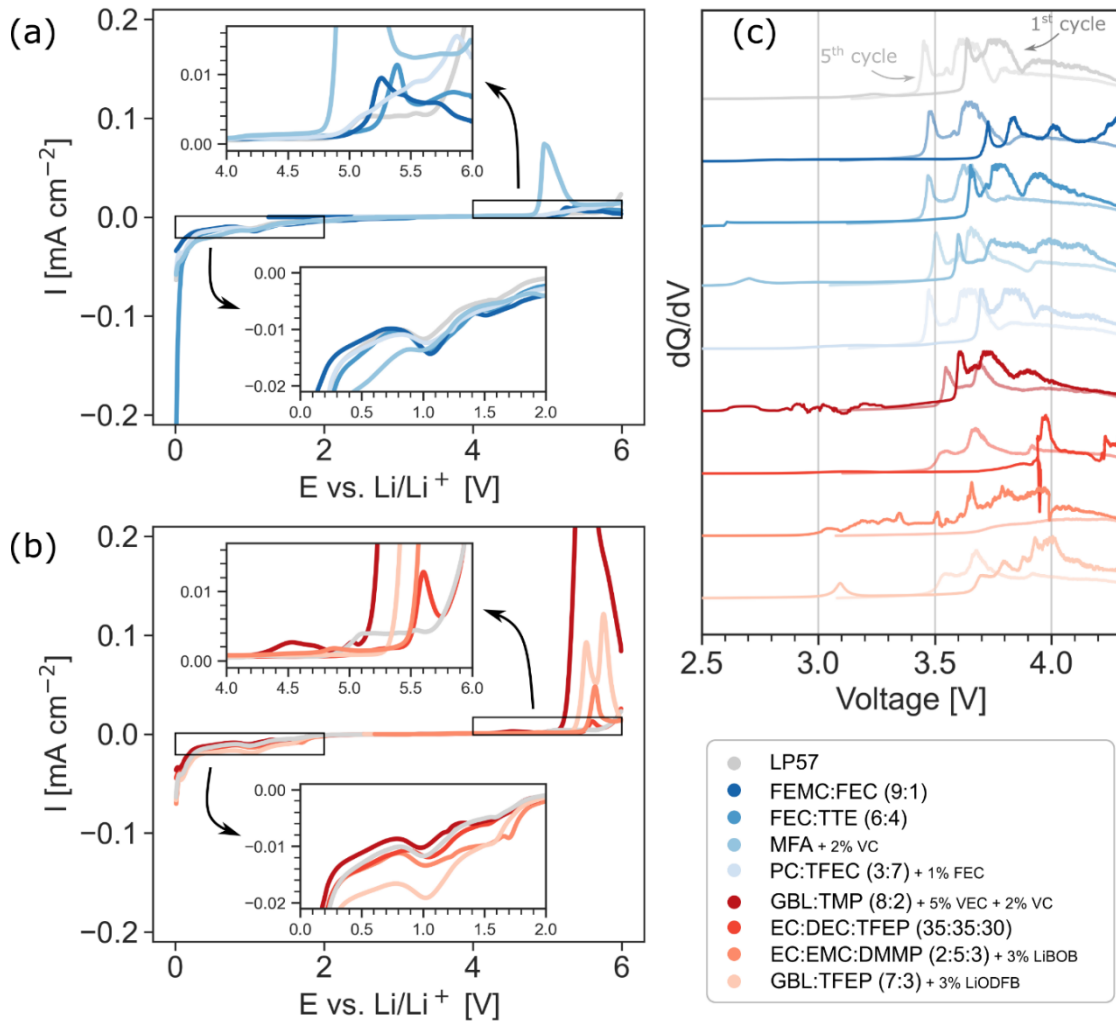


Figure 1: linear sweep voltammetry (LSV) of the (a) hydrofluorocarbon-based and (b) phosphate/phosphonate-based non-flammable electrolytes studied in this work. Anodic and cathodic sweeps were done using carbon-coated copper and carbon-coated aluminum working electrodes, respectively. (c) dQ/dV plots of the 1st and 5th cycles (at C/10) of NMC622|graphite containing each electrolyte.

Figure 2 shows the galvanostatic cycling performance of the eight electrolytes against the benchmark. It is clear that for the NMC622-graphite system studied, the hydrofluorocarbon-based electrolytes give greater long-term performance over 500 cycles than the phosphate/phosphonate electrolytes.

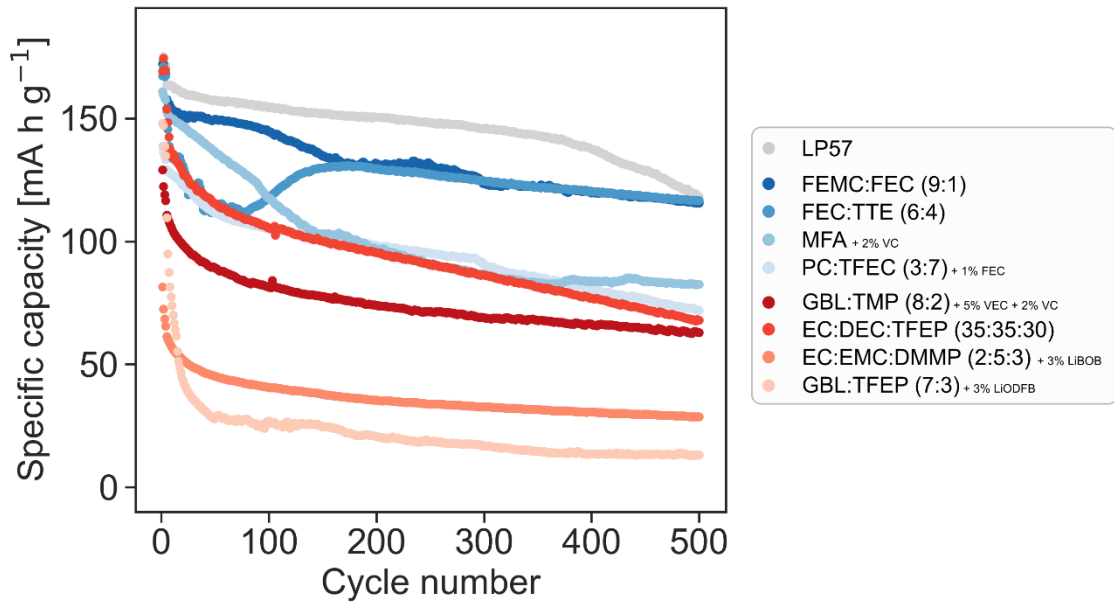


Figure 2: Galvanostatic cycling performance of the non-flammable electrolytes studied in this work, grouped into phosphate/phosphonate-based and fluorinated carbonate/ester/ether-based, with LP57 shown as a benchmark.

Figure 3 shows a similar trend where most of the hydrofluorocarbon-based electrolytes enable better rate capability than the phosphate/phosphonate electrolytes. However, the benchmark LP57 still demonstrates the best rate capability of all the electrolytes tested.

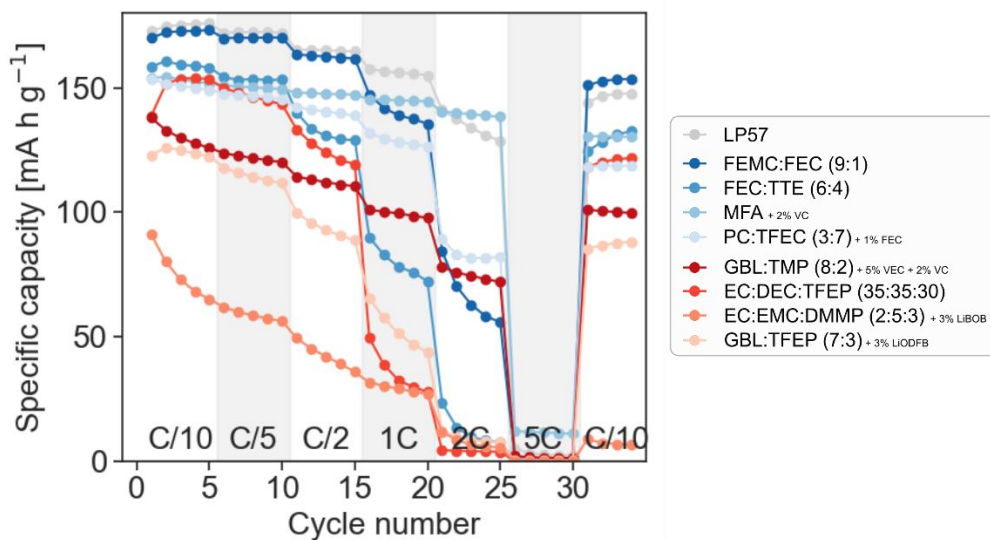


Figure 3: Rate capability of the electrolytes based on organophosphorus compounds (red traces) and fluorinated carbonates, esters and ethers (blue traces).

Figure 4 presents the internal resistance of each cell during battery cycling: the cells containing phosphates or phosphonates develop a higher resistance over time than those with hydrofluorocarbons. Even within each group, the resistance values are largely consistent with the rate capabilities. It is likely that SEI growth accounts for most of the increase in resistance, since all systems are identical except for the electrolyte, and probably explains at least in part the phosphate/phosphonate group's significantly poorer cycling stability.

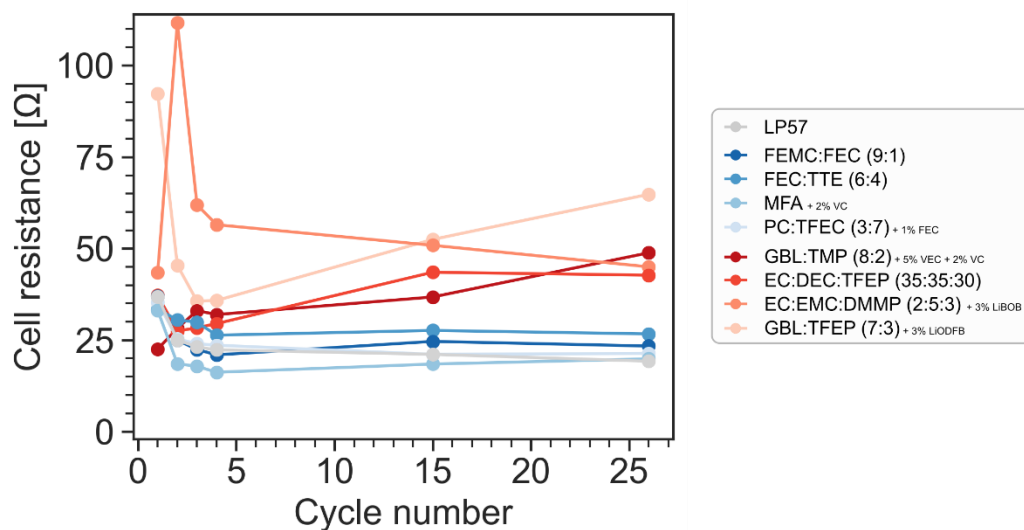


Figure 4: Internal resistance of NMC622|graphite cells containing various non-flammable electrolytes during cycling, as obtained by intermittent current interruption. Resistance values represent means during charge steps. Cycles 1–2, 15 and 26 (containing ICI steps) were carried out at a C-rate of C/10, while cycles 3–4 were carried out at C/5. Cycles 5–14 and 16–25 (without ICI) were carried out at a C-rate of C/2.

From this study, it was determined that the phosphorus-free electrolytes generally performed better than the phosphorus-containing ones. This was observed also in rate testing, cell resistance measurements, and indicated also in LSV and dQ/dV measurements. This is thought to be most likely due to the interface layer formation, including the SEI on the anode side, where the hydrofluorocarbon electrolytes are more likely to be able to form compounds such as semicarbonates that can enable effective lithium ion conductivity.

In relation to parts 2 and 3 of the project, three promising electrolytes have been further studied in-depth in this project: FEMC + FEC, TFEC, and LiBOB + TEP. However, the results are not yet published so are not included in this report.

Diskussion

The results presented here demonstrate an advancement in the understanding of non-flammable liquid electrolytes for lithium-ion batteries. The knowledge gained through understanding the role of various non-flammable solvents, co-solvents and additives will be valuable in the further development of lithium-ion batteries that are more safe and sustainable. Once all the results are published in scientific journals, industrial producers of lithium-ion batteries will be able to benefit from the knowledge generated from this project. A large amount of knowledge has been acquired at the University which will be used in further projects and education settings.

Publikationslista

1. F. Gebert, M. Longhini, F. Conti, A. J. Naylor, An electrochemical evaluation of state-of-the-art non-flammable liquid electrolytes for high-voltage lithium-ion batteries, *Journal of Power Sources*, **2023**, 556, 232412.
DOI: [10.1016/j.jpowsour.2022.232412](https://doi.org/10.1016/j.jpowsour.2022.232412)
2. F. Gebert, A. J. Naylor, A study of the SEI formed by 1,1,1-trifluoroethyl methyl carbonate with and without fluoroethylene carbonate additive in lithium-ion batteries, *In preparation*.
3. M. B. Shemirani, F. Gebert, A. J. Naylor, Bis(2,2,2-trifluoroethyl) carbonate-based flame-retarding electrolytes for lithium-ion batteries, *In preparation*.
4. F. Gebert, R. Lundström, W. van Ekeren, A. J. Naylor, Unravelling the challenges of using triethyl phosphate-based electrolytes in lithium-ion batteries, *Submitted*.

Referenser, källor

[Klicka här och skriv]

Bilagor

- Administrativ bilaga 'Project P2021-90019 slutrapport-admin-bilaga-ke.pdf'
- Vetenskapliga artiklar:
 - F. Gebert, M. Longhini, F. Conti, A. J. Naylor, An electrochemical evaluation of state-of-the-art non-flammable liquid electrolytes for high-voltage lithium-ion batteries, *Journal of Power Sources*, **2023**, 556, 232412.
'Gebert et al - An electrochemical evaluation JPS 2023.pdf'

- Känslig information som ej ska publiceras i Energimyndighetens projektdatabas: further results from the project 'KÄNSLIG INFORMATION Attachment to final report for project P2021-90019.pdf'