

## LITHIUM-ION BATTERIES

### Interphase identity crisis

Interphases that form on the anode surface of lithium-ion batteries are critical for performance and lifetime, but are poorly understood. Now, a decade-old misconception regarding a main component of the interphase has been revealed, which could potentially lead to improved devices.

Stefan A. Freunberger

Few would doubt the profound impact that Li-ion batteries have had on society since they were commercialized 30 years ago, with further developments expected to revolutionise electrified transport. Surprisingly to the outsider, however, one of the most important components of Li-ion batteries is not understood at a level that could serve to improve it in an informed way. This component is the solid–electrolyte interphase, which forms during the first few cycles of battery operation when the negative electrode (anode) reaches highly reducing potentials and the organic electrolyte is decomposed<sup>1,2</sup>. The purpose of the interphase is to act as a Li<sup>+</sup>-conducting, electronically insulating film, which prevents further electrolyte decomposition during subsequent cycles. While the prominent role of the interphase is clear for the performance and lifetime of the cell, neither its composition nor formation or ion transport mechanism are fully understood.

Now writing in *Nature Chemistry*, Wang, Xu, Eichhorn, and colleagues<sup>3</sup> show that the main component is not the previously assumed lithium ethylene dicarbonate (LEDC) but the analogous monocarbonate (Fig. 1a). This finding has profound implications on interphase formation and ion-transport mechanism, stability, and, most importantly, points to ways by which potentially better artificial interphases could be engineered.

Much of the energy advantage that Li-ion batteries have over other batteries is because of the much larger potential difference between cathode and anode. The anode, for example, is made of graphite, which stores  $\text{Li}^+$  ions at only a few 100 mV above the Li-metal-plating potential, the lowest amongst the metals. Despite the large stability window of the organic carbonate electrolytes used, the electrodes still operate outside the stability range of the electrolyte. Electrodes therefore need to get covered by passivation layers that are some 10s of nms thick that are made from electrolyte decomposition products and that prevent further decomposition. Ethylene carbonate is recognized as an indispensable electrolyte component for a stable interphase, which implies that its decomposition (reduction) products are instrumental in forming an interphase. Li alkyl carbonates ( $\text{R-OCO}_2\text{Li}$ ) were previously identified as the main reduction products of organic carbonate solvents and hence the ethylene-carbonate-derived LEDC was thought to be the all-important interphase component. This was supported — in several groups independently — by a range of spectroscopic methods applied to native interphases and comparisons to chemically synthesized LEDC<sup>1,4</sup>.

Wang, Xu, Eichhorn, and colleagues have now revealed that the previously synthesized compound was in fact not LEDC as thought, but the related lithium ethylene monocarbonate (LEMC), Fig. 1a. They show that previous synthesis did not successfully form the required dilithium alkoxide intermediate ( $\text{LiO-CH}_2\text{-CH}_2\text{-OLi}$ ), but only the monolithiated  $\text{HO-CH}_2\text{-CH}_2\text{-OLi}$ , which then gave LEMC in contact with  $\text{CO}_2$ . To clear all doubts, they synthesized LEDC through a new route and thoroughly characterized both compounds using a suite of techniques. The difference between LEDC and LEMC may seem subtle, but is decisive for cell performance. While LEDC is practically insulating as previously suggested theoretically<sup>5</sup>, LEMC shows high  $\text{Li}^+$  conductivity similar to ceramic solid-state  $\text{Li}^+$  conductors<sup>6</sup>. The researchers identified the reason for the good  $\text{Li}^+$  conductivity through single-crystal-structure determination. While the  $\text{Li}^+$  in pure alkyl carbonates is

coordinated by carbonate oxygen only and hence strongly bound, partial coordination by OH groups — which may also rotate — makes the  $\text{Li}^+$  more mobile in LEMC.

The lithium alkyl carbonates are largely insoluble in the parent alkyl-carbonate solvents. To study their reactions, the researchers used dimethylsulfoxide as solvent, where the compounds are sparingly soluble. This enabled the complex equilibria and interconversions occurring at the interphase to be revealed — as illustrated in Fig. 1a. Particularly relevant is the very facile hydrolysis of LEDC to LEMC. This may point to a possible formation pathway to LEDC via reduction of the ethylene carbonate in the electrolyte<sup>2</sup>, which, however, cannot persist in the battery environment because of unavoidable traces of protons. Other pathways to LEMC are nucleophilic additions of hydroxide ( $\text{OH}^-$ ) or methoxide ( $\text{CH}_3\text{O}^-$ ) to ethylene carbonate<sup>7</sup>.

Wang, Xu, Eichhorn, and colleagues also showed that all of these compounds, except for LEDC, also prevail in native interphases collected from batteries. Being the major functional compound and a much better  $\text{Li}^+$  conductor than most other compounds in the interphase, LEMC's properties largely determine  $\text{Li}^+$  conduction through the interphase. Its chemical stability also largely determines interphase stability towards protons or electrolyte components. Important in this context is that LEMC in contact with dimethylcarbonate from the electrolyte gets covered by a very thin layer of insulating lithium methyl carbonate (LMC), creating a 'LMC-capped LEMC organic layer' as a major interphase feature (Fig. 1b). The OH group of LEMC at the very interface to graphite could potentially get reduced to the OLi analogue, which is likely an even better  $\text{Li}^+$  conductor than LEMC.

The team lead by Wang, Xu, and Eichhorn, contributed a great deal of new mechanistic insights into interphase formation, conversion and the critical importance of LEMC. They have added a critical piece of information to the already complex knowledge of interphase reactions<sup>1,2,7</sup>. Nevertheless, the pathway towards LEMC, via LEDC or nucleophilic attack of ethylene carbonate,

could not unequivocally be clarified and it is also not clear how far the Li<sup>+</sup> coordination environment of pure LEMC is preserved in the complex mixture of a real interphase.

Looking forward, understanding that LEMC is the main interphase component opens pathways to engineer potentially better artificial interphases. One direction could be to make use of OH groups to facilitate Li<sup>+</sup> motion as they appear surprisingly stable at these reducing potentials. Another possibility the researchers mention is to process chemically synthesized LEMC into a thin-film solid electrolyte to produce solid-state batteries. With a conductivity beyond 10<sup>-6</sup> S·cm<sup>-1</sup> it rivals widely used ceramic electrolytes<sup>6</sup> and could present a low-cost, easily processable alternative. Whether these strategies will lead to batteries with improved performance remains to be seen, but the studies of Wang, Xu, Eichhorn and colleagues certainly add important insight into the underlying chemistry occurring at the important Li-ion battery interphase.

*Stefan A. Freunberger\**

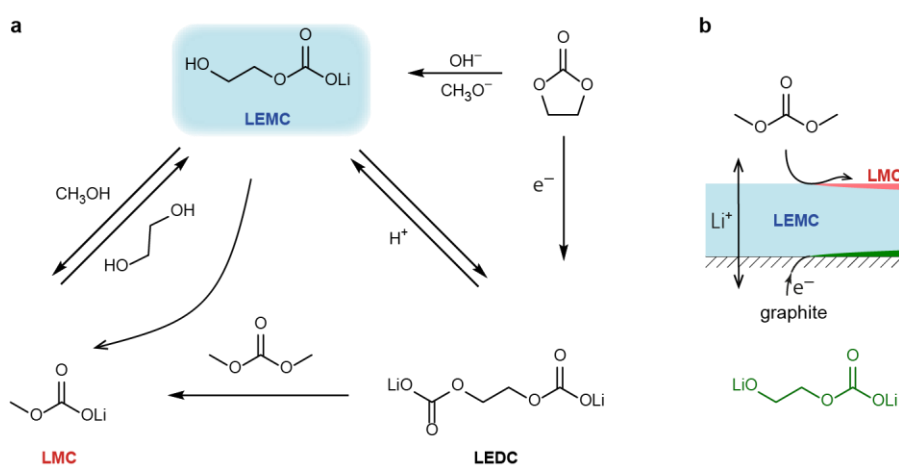
*Graz University of Technology, Stremayrgasse 9, 8010 Graz, Austria*

*e-mail: [freunberger@tugraz.at](mailto:freunberger@tugraz.at)*

#### References:

- 1 Xu, K. *Chem. Rev.* **114**, 11503–11618 (2014).
- 2 Aurbach, D., Markovsky, B., Shechter, A., Ein-Eli, Y. & Cohen, H. *J. Electrochem. Soc.* **143**, 3809-3820 (1996).
- 3 Wang, L. *et al. Nat. Chem.* (2019).
- 4 Gireaud, L., Grugeon, S., Laruelle, S., Pilard, S. & Tarascon, J.-M. *J. Electrochem. Soc.* **152**, A850-A857 (2005).
- 5 Borodin, O., Smith, G. D. & Fan, P. *J. Phys. Chem. B* **110**, 22773-22779 (2006).

- 6 Janek, J. & Zeier, W. G. *Nat. Energy* **1**, 16141 (2016).
- 7 Gachot, G. *et al. J. Power Sources* **178**, 409-421 (2008).



**Fig. 1 | Lithium ethylene monocarbonate in the solid–electrolyte interphase. a,** Interconversion equilibria of ethylene-carbonate- and dimethyl-carbonate-derived interphase components as revealed in dimethylsulfoxide solutions. Analogous reactions may occur when in contact with liquid alkyl carbonate electrolytes, albeit slower due to low solubility. **b,** The likely occurrence of lithium ethylene monocarbonate (LEMC) in a real SEI as ‘lithium methyl carbonate (LMC) capped LEMC organic layer’, which may be reduced to the lithium alkoxide analogue at the highly reducing graphite surface. Note that other interphase components like  $\text{Li}_2\text{CO}_3$ , polymers, or salt degradation products are omitted in this simplified picture. Panel **a** adapted from ref.<sup>3</sup>, NPG.