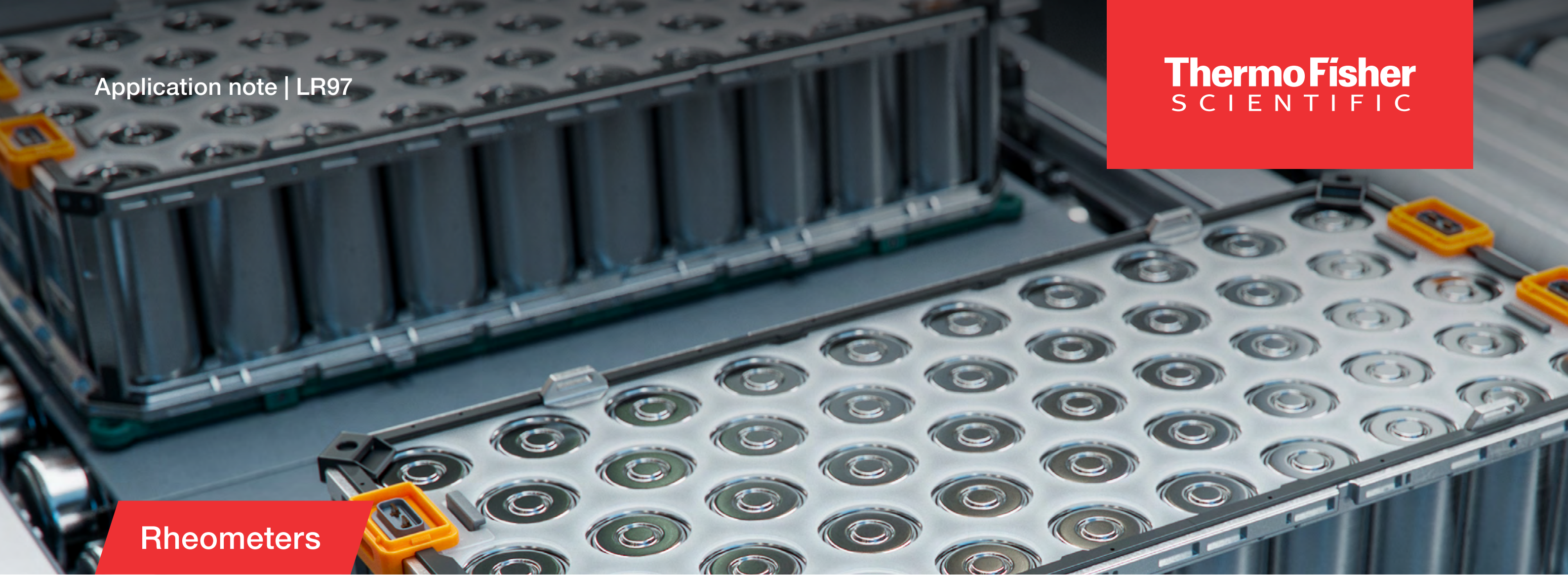
Application note | LR97



Rheometers

Improving the quality of dry lithium-ion cathode mixtures through torque rheometry

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Introduction

Lithium-ion battery production currently involves wet electrode processing, in which the solid electrode material is mixed with a liquid solvent to form a low-viscosity slurry that can be coated onto current collector foils via slot dies. Subsequently, the electrode coatings are dried in large ovens that occupy a large amount of space and consume an immense amount of energy. For the cathode, the toxic and expensive solvent NMP is conventionally used. NMP must be recycled, which leads to additional production expenses. To minimize such costs, efforts are being made to establish cost-effective and eco-friendly solvent-free cathode formulations. For these solvent-free mixtures, special binders are necessary to produce cathode mixtures that can be calendared into cathode sheets and laminated onto current collector foils. Polytetrafluoroethylene (PTFE), like POLYFLON® PTFE F-Series from Daikin (see Figure 1), has been proven suitable for dry processing of conventional lithium-ion batteries as well as solid-state batteries. PTFE, under certain processing conditions, can form fibrils interconnecting the cathode active material, as shown in the SEM image in Figure 2.

Figure 1: Daikin materials for test panel evaluation.

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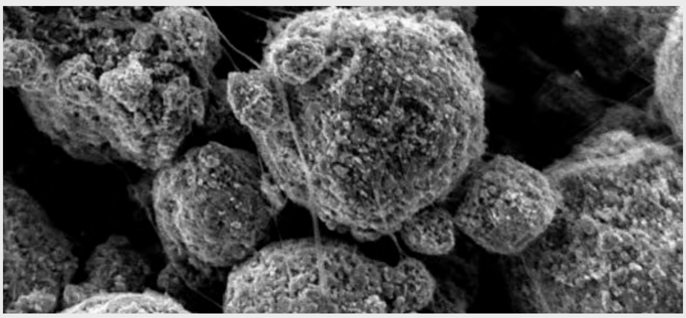
Figure 2: SEM image of PTFE fibrils interconnecting lithium iron phosphate cathode active material and schematic presentation of PTFE fibrillation and particle interconnection. Image courtesy of Daikin Chemical Europe GmbH.



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Mixing of such dry electrode formulations requires high shear forces that conventional planetary mixers, traditionally used for wet electrode slurry mixing, cannot provide. Corotating parallel twin-screw extruders can apply greater shear force, generally adjustable via the screw design, and as such they have become very attractive for continuous dry cathode mixing. For investigations of suitable cathode formulations and binder systems, a measuring mixer can be used to mix smaller amounts of samples batch-wise. Similar to a twin-screw extruder, measuring mixers with two co-rotating rotors can mix cathode material with PTFE to induce its fibrillation.

From the evolving dry cathode granulate (Figure 3A), cathode sheets (Figure 3B) can be formed and laminated onto the current collector foil (Figure 3C) using calendars.

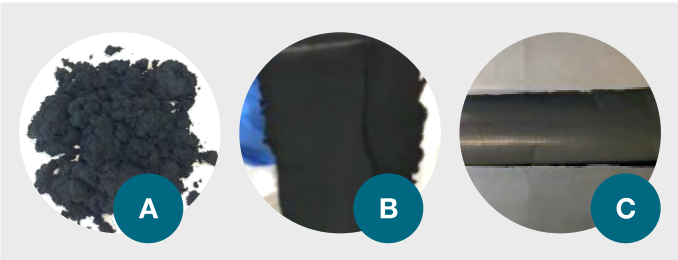


Figure 3: Cathode granulates (A) can be formed into cathode sheets (B) by calendaring and laminated onto current collector foil to form the electrode (C). Images courtesy of Daikin Chemical Europe GmbH.

Dry cathode mixing using HAAKE Rheomix OS Measuring Mixer

The Thermo Scientific™ HAAKE™ Rheomix 600 OS is a measuring mixer with two co-rotating rotors in a chamber with 70–100 ml working volume (depending on rotor type used). The Rheomix kneads and heats material batches while recording the material temperature and the torque applied to the rotors. The system and an inset picture of the open mixer chamber with two roller rotors after mixing a lithium iron phosphate cathode mixture are displayed in Figure 4.

Figure 4: HAAKE PolyLab OS Drive Unit connected to HAAKE Rheomix 600 Measuring Mixer.

The resulting functions of torque and temperature versus time, as displayed in Figure 5, correlate with the rheological changes within the material during mixing. For this reason, measuring mixers are also called torque rheometers. The torque curves are very specific to the material composition and demonstrate high reproducibility. The torque rise corresponds to an increase in material resistance against deformation. In the cathode mixtures tested in this study, the torque rises when PTFE is sheared, forming fibrils and interconnecting the cathode active material particles. These interconnections lead to inner friction, resulting in the simultaneous temperature increase, shown in Figure 5. The oscillation of the torque relates to material elasticity. After the fibrillation is complete and the maximum torque is reached, the PTFE fibrils stretch and orient into the direction of the shear. This diminishes the inner friction, and the torque and material temperature decrease until a steady state is reached.

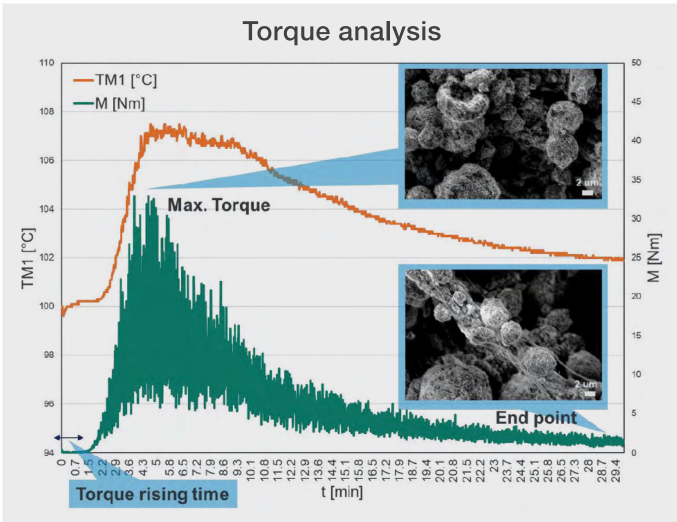
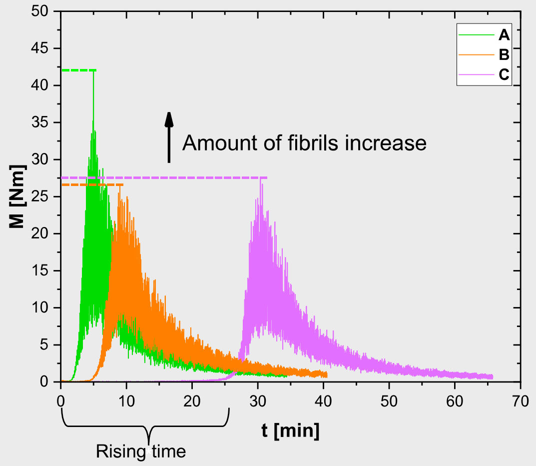


Figure 5: Torque and temperature of cathode mixture during mixing in a HAAKE PolyLab OS Rheomix 600 test mixer. Inserts show SEM images of the cathode mix with PTFE fibrils after 5 minutes and 30 minutes of mixing. Images courtesy of Daikin Chemical Europe GmbH.

Evaluation of PTFE grades using the measuring mixer

The lag time between the start of the measurement and the onset of the torque rise shows how much energy needs to be applied to initiate the PTFE fibrillation. The maximum torque is characteristic of the cohesion strength of the PTFE fibrils inside the material. Measurement of these properties allows for differentiation between cathode mixtures mixed with different PTFE grades. This is demonstrated in Figure 6, with three different PTFE grades labeled as A, B, and C.

The torque maxima and the rising times displayed in Figure 6 are summarized in Table 1. The cathode mixture with PTFE grade A could be identified as the one requiring the lowest energy input for PTFE fibrillation as well as the mixture exhibiting the highest cohesion.



PTFE grade		Max. torque [Nm]	Rising time [min]	Temperature [°C]
A	green line	42.9	1.8	100
B	orange line	26.7	5.2	100
C	magenta line	27.4	25.8	100

Table 1: Maximum torque and torque rising times of cathode mixtures mixed in HAAKE Rheomix 600 OS Measuring Mixer with three different PTFE grades; data read from torque curves in Figure 6.

Figure 6: Torque curves of cathode mixtures mixed with HAAKE Rheomix 600 OS using three different PTFE grades, labeled as A (green), B (orange), and C (magenta). Images courtesy of Daikin Chemical Europe GmbH.

The torque and temperature curves shown in Figure 7 evolve from mixer tests of cathode mixtures made with PTFE grade A, heated to 40, 60, 80, and 100 °C prior to mixing, respectively. The torque rising time decreases from 30 minutes at 40 °C preheating temperature to less than 5 minutes at 100 °C preheating temperature. Hence, heating the cathode premix before or during mixing can speed up the production time of PTFE-stabilized cathodes significantly. This is easily realized in a continuous twin-screw extrusion process.

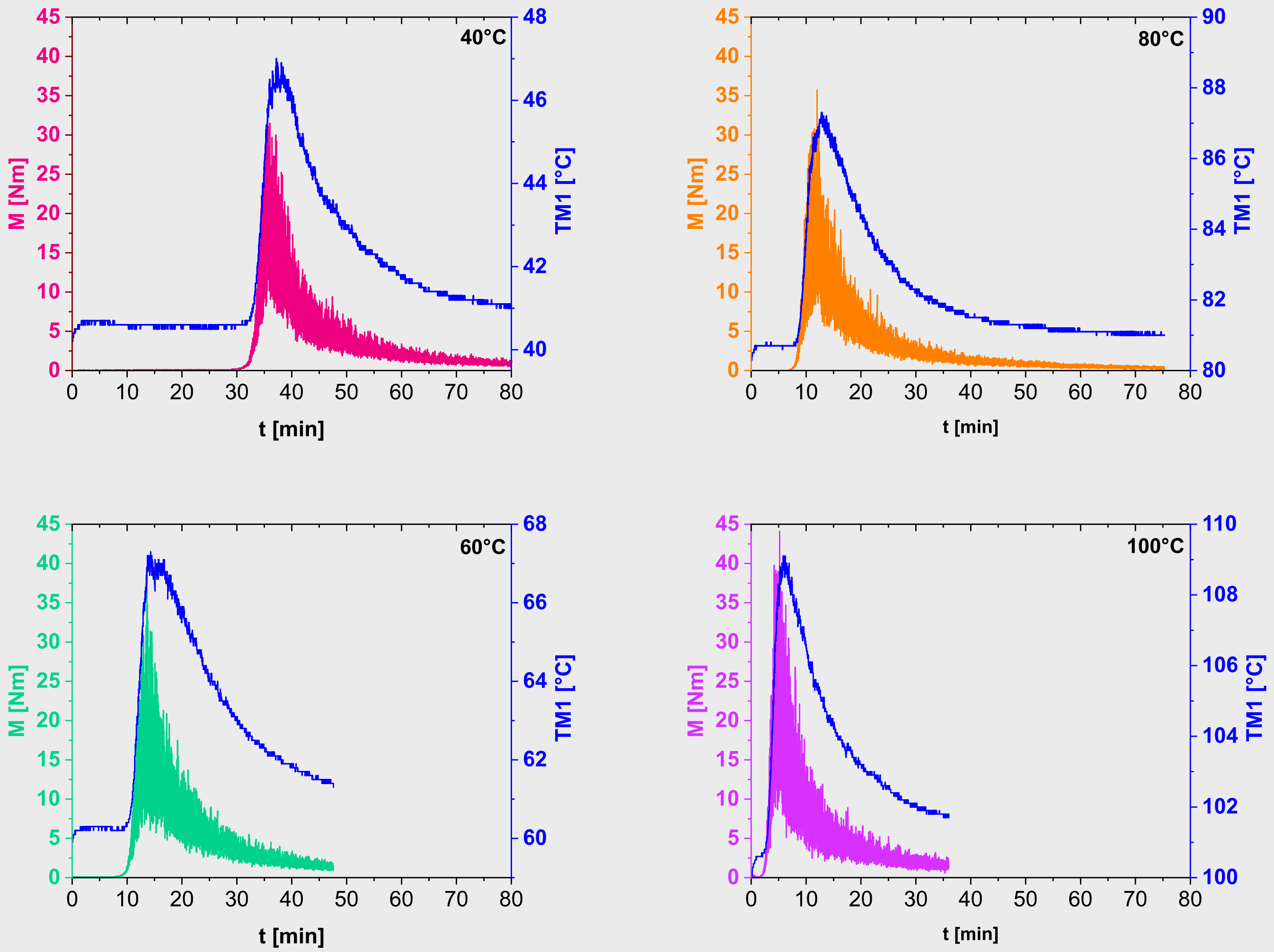


Figure 7: Torque and material temperature of cathode mixtures during mixing in PolyLab OS Rheomix 600 with preheating of the material to 40 °C (upper left), 60 °C (lower left), 80 °C (upper right), and 100 °C (lower right). Images courtesy of Daikin Chemical Europe GmbH.

Conclusion

Dry cathode processing decreases energy consumption and increases cost-effectiveness of lithium-ion battery production, and can be effectuated using PTFE binder systems. PTFE forms fibrils when sheared with cathode active material during mixing. The PTFE grade and appropriate processing parameters need to be identified on a small scale. Thermo Fisher Scientific provides lab-scale measuring mixers and twin-screw extruders for dry cathode development; these instruments can fit into compact spaces and require small sample quantities. Suitable PTFE grades for dry cathode mixing could be identified with a HAAKE Rheomix 600 Measuring Mixer. Furthermore, it was shown that increasing the processing temperature shortens the mixing time.

Further information

The presented data result from the ProLiT project (project grant number: 03XP0413G) funded by the Federal Ministry of Education and Research (BMBF), and research studies from Daikin Chemical Europe GmbH. All SEM measurements were performed by the Analytical Department of the Daikin Chemical Europe Innovation Center by T. Brändel. Daikin provides various PTFE grades for dry processing, so please contact Daikin to determine which PTFE grades best suit your specific needs. For more information, please visit **daikinchem.de**

We invite you to contact us to discuss how we can support you with twin-screw compounding and rheology at **thermofisher.com/contactusMC**.