Polarisability-dependent separation of lithium iron phosphate (LFP) and graphite in dielectrophoretic filtration

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Abbreviations: LIB, Lithium-ion batteries**; DEP,** dielectrophoresis**; LFP,** lithium iron phosphate

Abstract

Lithium-ion batteries (LIB) are integrated in a wide range of electronic devices that are an integral part of our modern world. Growing number of LIBs that reach their end of life demands development of effective recycling strategies to recover rare and/or expensive battery materials. Dielectrophoresis (DEP) is an electrokinetic particle manipulation technique that allows for selective particle separation based on properties, such as material, size, and shape. Here, we demonstrate separation of lithium iron phosphate (LFP) and graphite using dielectrophoretic filtration. Graphite and LFP are two common LIB anode and cathode materials. We demonstrate both: non-selective separation using pure suspensions of both graphite and uncoated LFP and an isolation of graphite from a mixture of uncoated LFP and graphite. We confirmed that LFP shows negative DEP while graphite shows positive DEP. We determined the conductivity at which material-selective polarisability-based separation becomes possible, thus, proofing the concept of sorting of non-carbon coated lithium iron phosphate ($LiFePO_4$) and graphite. These results reinforce one possibility of using DEP filtration as a potential method for direct physical recycling of battery material waste.

1. Introduction

Lithium-ion batteries (LIBs) are used in many electronic devices that surround our everyday life. The constantly growing number of LIBs that reach their end of life demands development of an appropriate recycling procedure. Cathode active materials are usually lithium metal oxides while the anode active material is graphite. Demand of graphite in the context of LIB production is 10-20 times higher than that of lithium [1]. To reduce dependence on natural or synthetic virgin graphite, proper recycling methods for this material are essential [1]. The most common methods for LIB recycling are pyrometallurgy, hydrometallurgy, and direct physical [2]. Pyrometallurgy does not require any pre-treatment but suffers from large energy

needs and can cause environmental pollution with toxic gases that are produced during the process. Additionally, for a full recovery, pyrometallurgy must always be followed by a hydrometallurgical step to treat the alloy [3]. Hydrometallurgy involves huge consumption of chemical reagents [2]. Both hydrometallurgy and pyrometallurgy focus only on the recovery of the main cathode components, graphite is lost in both processes. Direct physical recycling processes focus on using particle technology to directly separate and recover the cathode and anode active material, however, universally applicable methods to achieve this task are lacking.

Here, we research dielectrophoresis (DEP) as a method to separate cathode and anode material. DEP allows for a particle separation based on polarisability. Our group developed several approaches to treat particle systems at high throughput using DEP [4–6]. Here, we are expanding the scope of dielectrophoretic filtration towards polarisability-dependent separation of LIB materials of different conductivities. Dielectrophoretic filtration [5,7-11] is a macroscopic high-throughput DEP method based on applying an electric field across a porous dielectric material (filter). This filter disturbs the electric field, creating local field extrema which can be used to selectively trap particles by dielectrophoresis. The dielectrophoretic force is proportional to the electric field strength and linearly dependent on the Clausius-Mossotti (CM) factor [12]. The CM factor is influenced by the complex permittivities of the particle and the medium in which the particle is submerged. At low frequencies, the CM factor depends only on the medium and particle conductivities. Therefore, DEP can be used for material-selective separation by controlling and tuning the conductivity of the suspension medium. When medium conductivity becomes significantly higher than the conductivity of the target particles, the particles are getting pushed away from electric field maxima, they are said to experience negative dielectrophoresis (nDEP).

When the medium conductivity is lower than the particle conductivity, then the particles are attracted towards the local field maxima, they are said to experience positive DEP (pDEP). Particles that experience pDEP will become immobilized in local field maxima in the filter and we can use DEP filtration to selectively trap target particles. It is possible to recover the trapped particles by switching off the electric field. In another work from our group, graphite particles were isolated from significantly smaller carbon black-coated LFP particles (i.e., conductive particles) through pDEP using electrode-based dielectrophoresis [6]. While both particles showed pDEP, separation was possible because the DEP force is volume dependent. Here, we show that graphite particles can be isolated from uncoated, i.e., non-conductive, LFP particles of comparable size using dielectrophoretic filtration. Thus, we show polarisability-dependent sorting of particles. We show that we can separate graphite powder from a mixture of graphite and uncoated lithium-iron phosphate powder in aqueous suspension. While this study aims to expand the scope of DEP filtration, we also pave the towards solving an important problem in the recycling of LIB, i.e., the selective recovery of graphite from LIB waste.

2. Material and Methods

The main components of our setup are the particle suspension, filter cell and analysis module (Fig. 1).

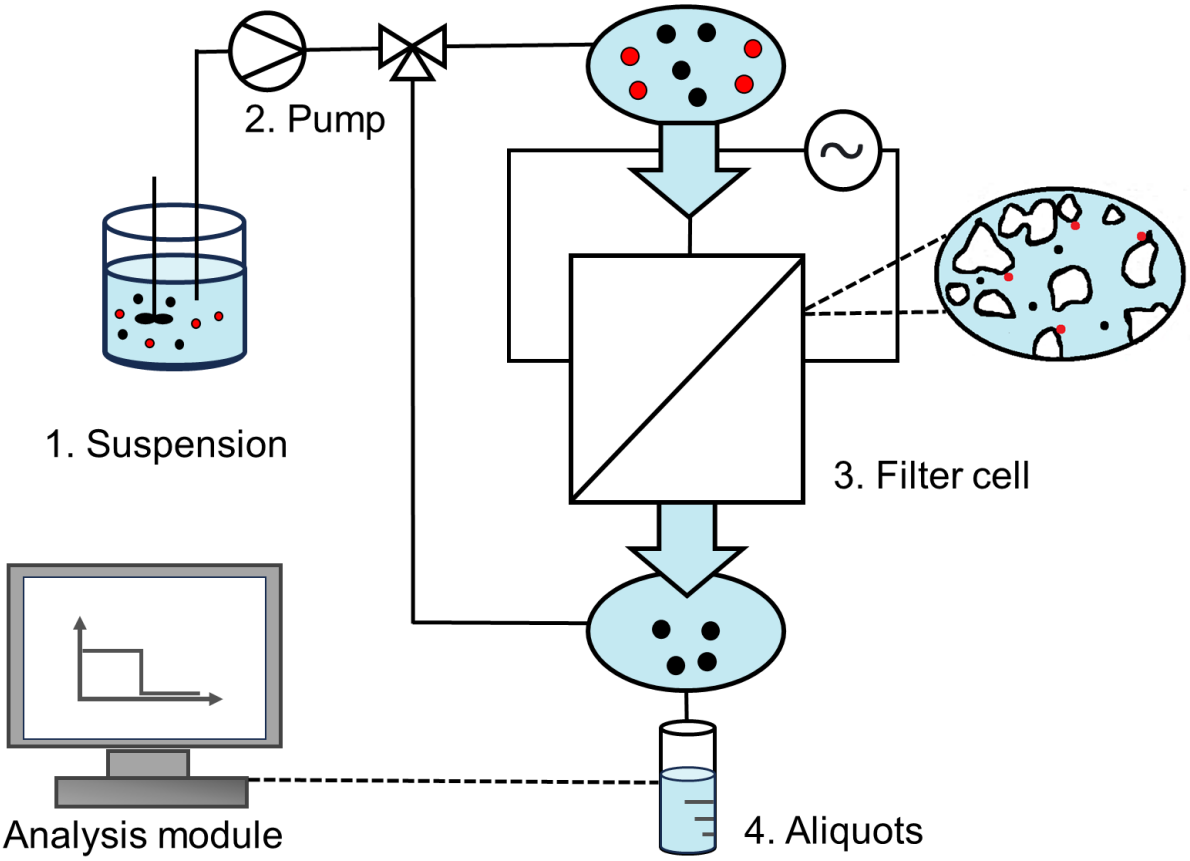

Figure 1. DEP filtration, a schematic setup of the filtration experiment.

The core of the setup, the DEP filter unit, is identical to the one used in Ref. [7, 9]. The filter cell has dimensions of 8×29×18 mm^3 and is made of polytetrafluoroethylene. Here, we are using a packed bed filter of grained silica material (sand) as filter matrix. The matrix is characterized in detail in Ref. [7]. The pores of the filter are ≥ 20 times larger than the size of the investigated particles. Two macroscopic electrodes, made of the stainless steel, are mounted inside the filter cell region at a distance of 8 mm. An ac electric field was applied across these electrodes. The signal was generated by a function generator (HM8131, Hameg Instruments GmbH, Germany) and amplified by a voltage amplifier (PZD700A, TREK Inc., USA). The resulted voltage on the setup was measured using the power analyser LMG670 (ZES ZIMMER ElectronicSystems GmbH, Germany). The suspension was delivered to the filter cell with a peristaltic pump (REGLO Analog,Ismatec, Switzerland).

During all the experiments, the flow rate was constant and kept at 360 mL/h. The connecting tubes are accompanied with a three-way valve, allowing for the suspension to go either via the filter cell to the analysis module, or via the bypass to the analysis module.

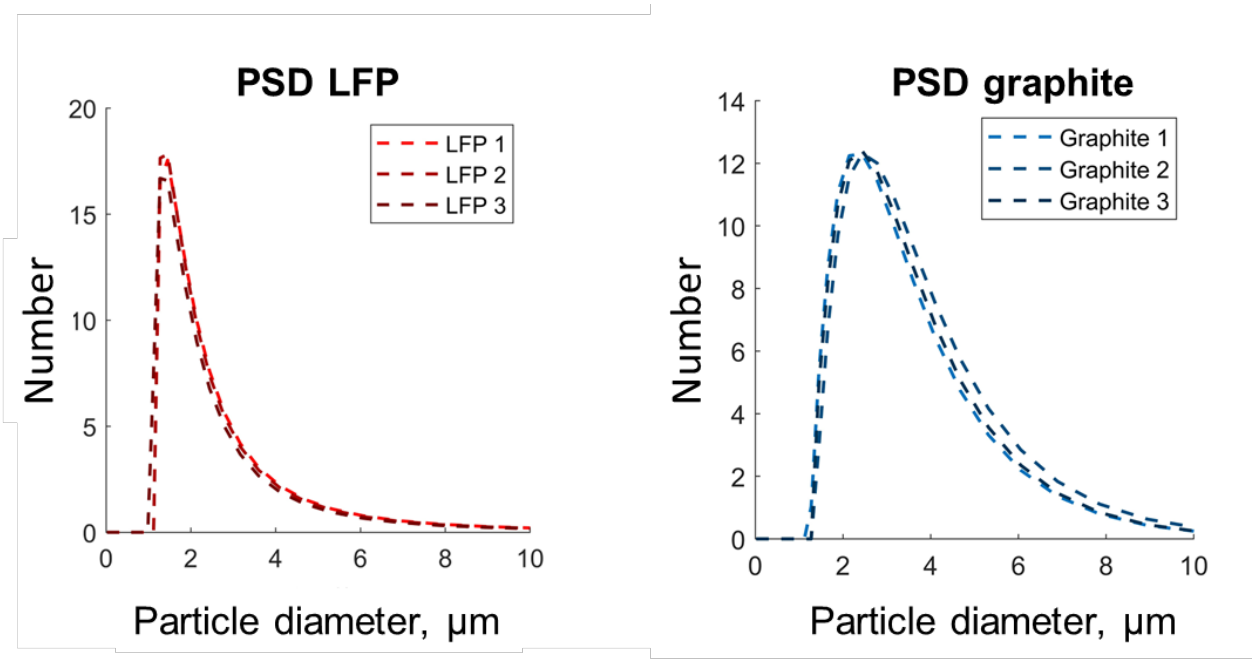

Figure 2. Particle size distribution (PSD), number-based and additionally normalized distribution of two particle systems (LFP and graphite), measured three times each with laser diffraction.

Particle suspensions were uncoated lithium iron phosphate (LFP) and graphite. Virgin material was purchased commercially in the form of the fine powders with particle size less than 5 µm (company information) from Sigma-Aldrich. Graphite (TIMCAL KS-6) was purchased as powder with mean particle size ≤3.4 µm (company information) from MSE Supplies. Before experimentation, we additionally measured the particle size distributions using laser diffraction (LD, Mastersizer 2000, Malvern Panalytical GmbH, United Kingdom), see Fig. 2 (more details are in supplementary materials), and found that the results fall close into the size range given by the companies. Pure particle suspensions were prepared by suspending particle in pure deionized water (Omniatap 6 UV/UF, Starkpure GmbH, Germany) to a concentration 4 mg/L (graphite) and 8 mg/L (LFP). We further added Tween

20 solution (Sigma-Aldrich, Germany) to a final concentration of 0.004% vol. The conductivity of the final suspension was tuned by adding 0.1 M KCl to a final value of 1–15 μS/cm. Through the experimental stage, the suspension was always disturbed with a stirring magnet. For the preparation of the mixture suspension, graphite and LFP were mixed into one beaker in the same concentrations as they were in separate suspensions before.

The trapping efficiency of the separate mixtures was qualitatively measured using a spectrometer (HORIBA, FluorMAX-4) on-line reflection measurement combined with MATLAB processing [7, 13]. The suspension was flowing through a quartz cuvette (176.762-QS, Hellma). A qualitative estimate of (non-selective) separation efficiency is given by on-line measuring the reflection of the particles at the outlet of the setup. The particles are not ideal spheres (supplier information) so that we can only qualitatively measure their concentration like this. The processing of the signal was done similar to our previous work, by the use of the MATLAB script from the previous study, which calculates the trapping efficiency by subtracting from 100 % a ratio of the signal from the particles going freely to the filter, to the signal of the particles, recorded while the electric field was on [7, 13].

To address quantitatively the separation efficiency of LFP in a mixture with graphite, we used atomic absorption spectroscopy (AAS). For AAS, we collected a defined volume of around 20 mL of the suspension into 50 mL volumetric flasks during the different stages of the experiment. The LFP was dissolved by adding 3 mL 65 % nitic acid (VWR International, Belgium) and 3 mL 30 % hydrogen peroxide (Sigma-Aldrich, Germany). After the volumetric flasks were topped up with pure deionized water, the lithium content inside the prepared mixture was determine with AAS using a Solaar 989 QZ AA Spectrometer (Unicam, England) with a GF90+ furnace and an FS90+ autosampler.

3. Results and Discussion

The graphite particles have a significantly higher bulk conductivity value than the aqueous suspension and we expect them to show pDEP behaviour. The uncoated LFP particles, however, have a low conductivity value of around 10^{-7}–10^{-8} S/cm, which is lower than that of the medium and they should therefore demonstrate nDEP behaviour [14, 15].

We have firstly investigated if LFP indeed shows negative DEP in a simple setup. A 50 µL drop of the LFP suspension at 30 µS/cm conductivity was placed on top of an interdigitated electrode array and we directly observed particle movement using a microscope. For this, a voltage of 20 V_{RMS} at 15 kHz was applied with a signal generator (Rigol DG4062, Rigol Technologies EU GmbH, Puchheim, Germany). The particle movement was recorded using an inverted microscope (ECLIPSE Ts2R-FL, Nikon Instruments Europe BV, Amsterdam, Netherlands) and a CMOS camera (Grasshopper GS3-U3-51S5C-C, FLIR Systems Inc., Wilsonville, OR, USA). The interdigitated electrodes have an arm width and gap width of 100 µm and were fabricated using standard cleanroom techniques. Upon application of the voltage, LFP particles indeed accumulated in the space between the electrodes, which is typical behaviour for particles that show nDEP (see Fig. 3 and the video in the supplement).

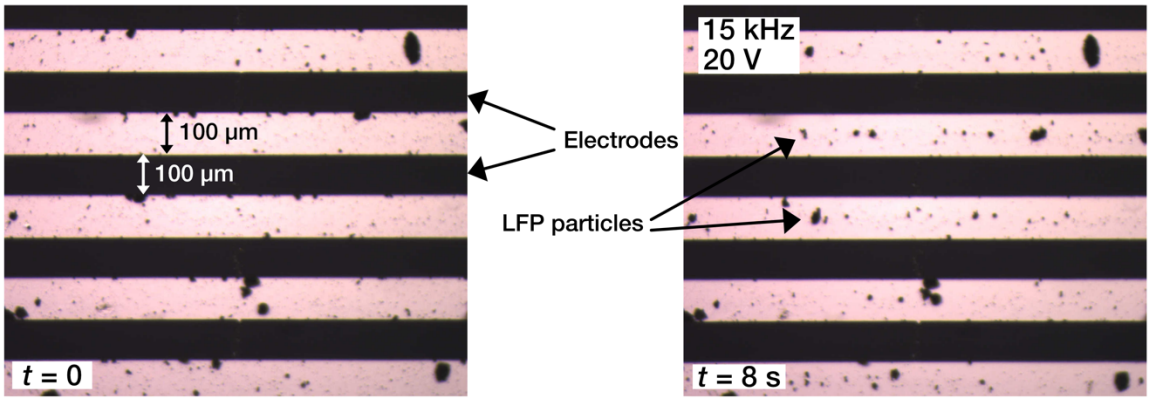

Figure 3. Behaviour of LFP (black particles) in an array of interdigitated electrodes at 20 V and 15 kHz and at a conductivity of 30 µS/cm. Upon application of an electric field, the

randomly distributed LFP particles (left) are predominantly repelled to the space between the electrodes (right). This is typical behaviour for particles that experience nDEP. Electrode distance is 100 µm.

We then performed LFP and graphite separation experiments with our filter cell setup. In individual (non-selective) experiments, at 5 $\mu S/cm$, the trapping of both graphite increases with voltage, as expected from the DEP theory for pDEP particles (Fig. 4, left). The trapping of LFP also increases with voltage, which might be due to to nDEP retention, as we have previously observed [9].

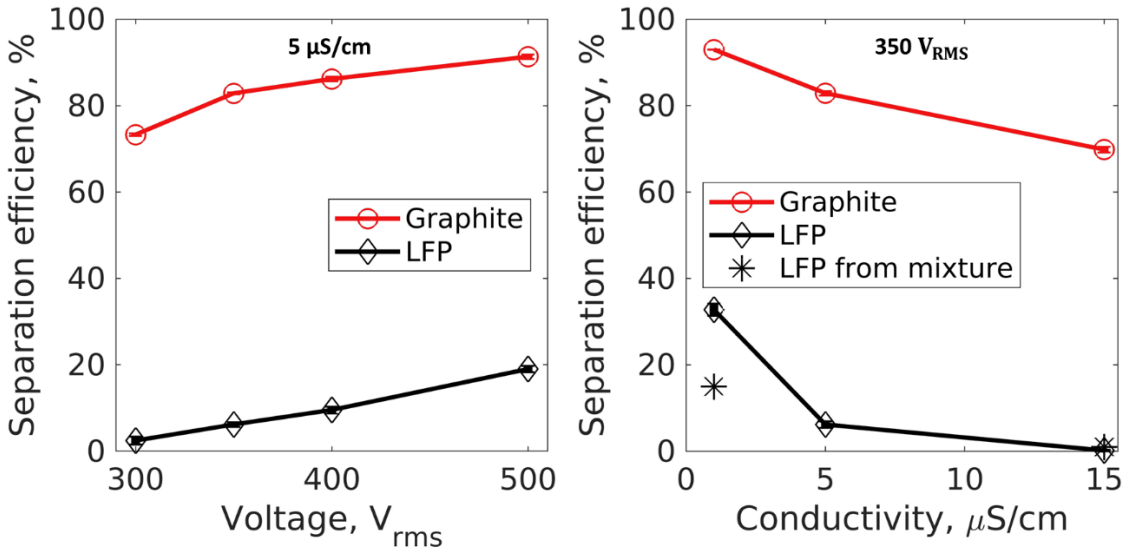

Figure 4. DEP trapping efficiency of two separate powders, analysed with the reflection measurement and an additional result of trapping of only LFP from the mixture (*) at 15 kHz, 360 mL/h flow rate. Left: Dependence on the voltage (at 5 $\mu S/cm$ conductivity); right: dependence on the conductivity (at 350 V_{RMS} voltage) with their respective standard deviations from three repetitions.

While at 300 V_{rms}, LFP shows almost no trapping, it does show appreciable separation of almost 20 % at 500 V_{rms}. Further, we observed that LFP trapping decreases with increasing

175 solution conductivity (Fig. 4, right). While at 1 µS/cm and 350 V_{rms}, LFP shows trapping above
176 30 %, it drops to 1% at 15 µS/cm. Graphite trapping efficiency also drops slightly with
177 increasing conductivity, from 90% at 1 µS/cm to 70% at 15 µS/cm. Thus, at 15 µS/cm, LFP
178 trapping is negligible while graphite trapping is high. The mechanism why LFP shows higher
179 trapping at lower conductivities is unclear. Its bulk conductivity value should be well below 1
180 µS/cm and from microscopy experiments, we know that LFP shows nDEP at 30 µS/cm. We
181 could not perform microscopy experiments at lower conductivities, as the required particle
182 load was too high to achieve lower conductivities. The small decline of the trapping efficiency
183 for graphite is believed to be associated with thermal effects at the higher conductivities of
184 aqueous suspension. Such an explanation was given for a similar observation with
185 polystyrene particles, assuming that an increase in conductivity raises temperature due to
186 more energy dissipation and this in turn increases a natural convection of the fluid creating
187 more “undirected” fluid motion [9].
188 To separate graphite from a mixture of graphite and LFP of similar size, both particles were
189 added in one suspension. The trapping efficiency of LFP was evaluated at 15 kHz, 350 V_{rms}
190 using the AAS protocol at two solution conductivities, 1 and 15 µS/cm, respectively. The
191 trapping efficiency of LFP in these experiments is plotted as stars in Fig. 4. Similar to the
192 pure particle experiments, LFP showed a trapping efficiency of roughly 1 % at 15 µS/cm and
193 of 15 % at 1 µS/cm. The difference between trapping efficiency in pure particle and mixture
194 experiments (i.e., black dots vs. black stars in the right Fig. 4) is probably because two
195 different measurement techniques were used. As mentioned, reflection measurement can
196 only give a qualitative estimate of separation, while AAS actually measures lithium content
197 and gives more precise results, as also observed before [6]. We did not measure the graphite

concentration in mixture experiments and thus assume that graphite shows a separation efficiency similar to pure particle experiments.

4. Conclusions

Our research indicates the potential of dielectrophoretic filtration as an additional purification step for recycling of battery materials. Our findings demonstrate that by manipulation of the conductivity of the liquid medium, we can selectively separate graphite from a mixture of graphite and uncoated LFP using DEP filtration. This is based on differences in the polarisability of both particles. Additional research is required to further estimate the technique in use. Especially, it is essential to evaluate the proper recovery rate of the target particles and to tune the filter matrix geometrical parameters to avoid unwanted nDEP trapping of non-target particles. It's important to note that while we successfully separated commercially available particles, the application to real black mass with graphite-coated LFP poses additional challenges.

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Author contributions

Mariia Kepper: conceptualization, project administration, methodology, investigation, validation, visualization, formal analysis, writing – original draft, review & editing**. Alica**

Rother: investigation (AAS), data curation, formal analysis (AAS). **Jorg Thöming**: methodology, resources, review & editing. **Georg Pesch**: conceptualization, project administration, methodology, validation, supervision, writing - review & editing.

Data Availability

An online repository (referred as supplementary materials in this text) is accompanying this article and contains of details on the evaluation of DEP data, additional details on the measurement of the particle-size distribution data of the LFP and graphite, notes on AAS analysis and a video demonstrating nDEP of LFP [13]. Additional information is available from the corresponding author upon a reasonable request.

Conflict of interest

The authors declare no competing interests.

5. References

[1] Natarajan S, Aravindan V. An Urgent Call to Spent LIB Recycling: Whys and Wherefores for Graphite Recovery. Adv Energy Mater 2020; 10: 2002238.

[2] Al-Shammari H, Farhad S. Chapter 13 - Separating battery nano/microelectrode active materials with the physical method. In: Farhad S, Gupta RK, Yasin G, Nguyen Remanufacturing, and Reusing TABT-NT for BR (eds). Micro and Nano Technologies. Elsevier, 2022, pp 263–286.

[3] Windisch-Kern S, Gerold E, Nigl T, Jandric A, Altendorfer M, Rutrecht B et al. Recycling chains for lithium-ion batteries: A critical examination of current

challenges, opportunities and process dependencies. Waste Manag 2022; 138: 125–139.

[4] Giesler J, Weirauch L, Thöming J, Baune M, Pesch GR. Separating microparticles by material and size using dielectrophoretic chromatography with frequency modulation. Sci Rep 2021; 11: 16861.

[5] Weirauch L, Giesler J, Baune M, Pesch GR, Thöming J. Shape-selective remobilization of microparticles in a mesh-based DEP filter at high throughput. Sep Purif Technol 2022; 300: 121792.

[6] Giesler J, Weirauch L, Rother A, Thöming J, Pesch GR, Baune M. Sorting Lithium-Ion Battery Electrode Materials Using Dielectrophoresis. ACS Omega 2023; 8: 26635–26643.

[7] Kepper M, Karim MN, Baune M, Thöming J, Pesch GR. Influence of the filter grain morphology on separation efficiency in dielectrophoretic filtration. Electrophoresis. 2023; 1–10.

[8] Pesch GR, Lorenz M, Sachdev S, Salameh S, Du F, Baune M et al. Bridging the scales in high-throughput dielectrophoretic (bio-)particle separation in porous media. Sci Rep 2018; 8: 10480.

[9] Lorenz M, Malangré D, Du F, Baune M, Thöming J, Pesch GR. High-throughput dielectrophoretic filtration of sub-micron and micro particles in macroscopic porous materials. Anal Bioanal Chem 2020; 412: 3903–3914.

[10] Weirauch L, Lorenz M, Hill N, Lapizco-Encinas BH, Baune M, Pesch GR et al. Material-selective separation of mixed microparticles via insulator-based dielectrophoresis. Biomicrofluidics. 2019; 13:64112.

[11] Zhou G, Imamura M, Suehiro J, Hara M. A dielectrophoretic filter for separation and

263 collection of fine particles suspended in liquid. In: Conference record of the 2002
264 IEEE industry applications conference. 37th IAS annual meeting (Cat.
265 No.02CH37344). Vol. 2. Pittsburgh, PA, USA: IEEE; 2002. pp. 1404–11.
266 [12] Pohl HA. The Motion and Precipitation of Suspensoids in Divergent Electric Fields. J
267 Appl Phys 1951; 22: 869–871.
268 [13] Kepper M, Rother A. Online repository for "Polarisability-dependent separation of
269 lithium iron phosphate (LFP) and graphite in dielectrophoretic filtration". Zenodo.2023,
270 https://doi.org/10.5281/zenodo.10120331.
271 [14] Yang M-R, Ke W, Wu S. Improving electrochemical properties of lithium iron
272 phosphate by addition of vanadium. J Power Sources 2007; 165: 646–650.
273 [15] Wang GX, Bewlay SL, Konstantinov K, Liu HK, Dou SX, Ahn J-H. Physical and
274 electrochemical properties of doped lithium iron phosphate electrodes. Electrochim
275 Acta 2004; 50: 443–447.