SFE539: Liquid CO2 Extraction of Lithium-Ion Battery Electrolytes and LiPF6

Introduction

Lithium-ion batteries (LIBs) are used as energy storage systems for consumer and portable electronics and are a promising battery technology for electric or hybrid electric vehicles. Typically, LIBs are composed of a graphitic anode and a transition metal oxide or phosphate cathode with a polymeric or ceramic separator positioned between the anode and cathode. Charge transfer in the battery is conducted by lithium ions moving through a non-polar electrolyte solution. The electrolytes are composed of different linear carbonates, for example dimethyl carbonate (DMC) and ethyl methyl carbonate (EMC)) in a mixture with ethylene carbonate (EC), LiPF6 is generally used as a conducting salt.

LIBs lose capacity over time and have a limited useful life. Typically, the decomposition of electrolytes during battery cycling is accelerated by temperature effects and impurities in the cell. In addition, EU regulations require a minimum of 50% of the LIB cell to be recovered in recycling processes and the electrolyte represents a target component for the recycling of LIBs. The enormous growth rate of LIBs requires new environmentally friendly solvents such as supercritical CO2 to evaluate postmortem battery decomposition products and also optimize environmentally friendly recycling processes.

Materials

Liquid CO2 cylinder CO2 for SFE

Panasonic CGR18650CH Li-ion MH12210 (2.2 Ah, NMC/graphite) 18 650 cells

Anhydrous acetonitrile (ACN) (99.8%)

Propylene carbonate (PC) (99.9%)

Sample Preparation

The discharged cells (18 650) were frozen at -18 C for 10 hours. The cells were opened in a glove box (O2, H2O < 0.1 ppm) by slicing the two ends of the metal shell with an industrial cutter. The jelly roll as well as the stack, were removed of the shell, unwrapped and packed tightly into the extraction vessel.

Equipment

Applied Separations Supercritical Extraction Equipment including the Helix, SFE 2, SFE 4, or Basic model equipped with a co-solvent pump.

Supercritical Fluid Application Notes

Extraction Procedure

(Refer to references for detailed procedures)

All extraction experiments were done in a dry room (dew point: 65 C; H_2O < 5.4 ppm.

Liquid CO_2 Extraction with Co-Solvents

Extraction vessel: 50 ml or 100 ml
Sample: The jelly roll and stack
CO_2 Pressure: 60 bar
CO_2 Temperature: 25 C
Equilibration time: 30 min with CO_2 only
CO_2 Flow Rate: 15 L/min (measured as gas) for 2 minutes with 0.5 mls/min cosolvent (3:1, ACN: PC)
Static equilibration time : 5 minutes
Repeat the above static/ dynamic sequence as required for higher recoveries. (10 x)
Final dynamic extraction : CO_2 only for 20 minutes.
Collection: cryogenic trap filled with alumina at -78 C.

Analysis:

Ion chromatography

GC-MS

Results:

The electrolytes of a Panasonic 18650 cell were recovered at 89.1 wt% with liquid CO_2 and ACN:PC (3 : 1) as co- solvents. In addition, both ethylene carbonate EC and $LiPF_6$ were recovered.

Applied Separations

930 Hamilton Street
Allentown, PA 18101
610-770-0900
www.appliedseparations.com

Conclusion

CO2 as a solvent is useful for LIB cell extractions for postmortem and aging analyses. The quantitative extraction with subcritical/liquid and supercritical CO2 does not dilute the extract since CO2 evaporates upon collection at atmospheric pressure.

Electrolytes were recovered from a Panasonic 18 650 cell at 89.1 wt% using liquid CO2 and ACN–PC (3 : 1) as additional solvents.

The use of CO2 as an environmentally friendly solvent for the recycling of battery electrolytes and salts is a green solution to the problems associated with LIBS disposal.

References

Nowak S, Winter M. The role of sub-and supercritical CO2 as “processing solvent” for the recycling and sample preparation of lithium ion battery electrolytes. Molecules. 2017 Mar 6;22(3):403. https://pubmed.ncbi.nlm.nih.gov/28272327/

Liu Y, Mu D, Zheng R, Dai C. Supercritical CO 2 extraction of organic carbonate-based electrolytes of lithium-ion batteries. https://pubs.rsc.org/en/content/articlelanding/2014/ra/c4ra10530c

Grützke M, Mönnighoff X, Horsthemke F, Kraft V, Winter M, Nowak S. Extraction of lithium-ion battery electrolytes with liquid and supercritical carbon dioxide and additional solvents

Rsc Advances. 2015;5(54):43209-17.

Liu Y, Mu D, Dai Y, Ma Q, Zheng R, Dai C. Analysis on extraction behaviour of lithium-ion battery electrolyte solvents in supercritical CO2 by gas chromatography. Int. J. Electrochem. Sci. 2016 Sep 1;11(9):7594-604. http://www.electrochemsci.org/papers/vol11/110907594.pdf