Upcycling of Spent NCM Cathodes through Ionothermal Lithiation

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Ionic liquids (ILs) are a family of non-conventional molten salts that offer many advantages, such as negligible vapor pressures, negligible flammability, wide liquidus ranges, good thermal stability, and much synthesis flexibility. The unique solvation environment of these ILs provides new reaction or flux media for controlling formation of solid-state materials with a minimum perturbation of morphologies. A successful lithiation via ionothermal synthesis using cost-effective Li halide as Li source and recyclable ionic liquids (ILs) as solvents is first reported here for the upcycling of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM 111) cathodes. In addition, the ionic liquids can be readily recycled and reused after ionothermal lithiation. The lithiation of spent cathodes can realize the upcycling of spent cathode materials in lithium-ion batteries.

Lithium-ion batteries (LIBs) with high energy density make a significant contribution to solving energy storage issues but simultaneously cause serious environmental issues due to their hazardous materials, such as carcinogenic heavy metals and toxic electrolytes.[1] With the rapidly increasing use of LIBs in our highly electrified society, proper handling of end-of-life (EOL) LIBs has become an urgent and promising task, in which the regeneration of highly valuable cathode materials such as lithium metal oxides is the primary and motivated objective at present.[2-4] Current recycling technologies for cathode materials include pyrometallurgy based on a high-temperature smelting process,[3, 5-7] hydrometallurgy using aqueous chemistry,[8-12] and direct recycling or upcycling active materials retaining their original compound structure.[2, 13] Though pyrometallurgy and hydrometallurgy can return the valuable metals such as Li, Co, and Ni into the LIB production chain, the total destruction of cathode particles reduces the highly added value of the compound structure.[4, 14-19] In contrast, the key process of upcycling technology is to heal the compositional and structural defects of degraded Li-deficient cathode particles in EOL LIBs, which can retain the highly added value of cathode particles to the maximum extent.[20-23] As for the most popular cathode materials, NCM ($LiNi_xCo_yMn_zO_2$, $0 < x,y,z < 1$, $x + y + z = 1$), the irreversible structure change caused by Li loss is the main issue resulting in cathode capacity degradation.[24-27] The relithiation process can directly upcycle spent NCM particles to achieve pristine structure and stoichiometry but generally requires harsh experimental conditions such as high-temperature and/or high-pressure.[21, 28-30] Thus, it is still challenging but highly desirable to develop a scalable, cost-effective, and environment-friendly strategy for upcycling of spent NCM cathodes.

Targeting a mild experimental condition for upcycling of spent NCM, the ionothermal synthesis strategy stands out using ionic liquids (ILs) simultaneously as both the solvent and potential template or structure-directing agent in the formation of solids.[31-34] Our group have reported the first ionothermal synthesis of silica aerogel, in which ILs as the efficient solvents provided a long aging time for stable aerogel structures.[35] The ionicity of ILs supplies strong Coulombic interactions between the constituent ions and the intrinsic nonvolatility provides for the essentially null vapor pressure.[34, 36] Thus, compared to the classic solid-state sintering approach, the ionothermal synthesis strategy as an emerging flux method can achieve high-temperature phase products under lower temperature and ambient pressure.[31, 32, 37] The highly charged flux media offered by ILs provide efficient environments for transporting ionic reaction precursors.[38] The temperature range that IL fluxes can operate is from ambient temperature to as high as 300 ◦C, filling the low temperature gap of the traditional molten-salt flux method.[39] Herein, we apply the ionothermal strategy in the upcycling of spent NCM cathodes and report a successful relithiation of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM 111, **Scheme 1**), in which three different ILs 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)-imide ($[C_2mim][NTf_2]$), 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)-imide ($[C_4mim][NTf_2]$) and 1-ethanol-3-methylimidazolium bis(trifluoromethanesulfonyl)-imide ($[C_2OHmim][NTf_2]$) were chosen as flux solvent working at 150 °C under ambient pressure. Cost-effective lithium chloride (LiCl) and lithium bromide (LiBr) were chosen as a lithium source. The relithiated NCM 111 powder was separated from ILs by filtration and then washing with acetone, and ILs was recyclable for the next relithiation process. As relithiated NCM 111 (R-NCM) exhibited recovered structure and excellent electrochemical performance, which is almost the same as the pristine NCM (P-NCM) sample. The successful relithiation of delithiated NCM 111 (D-NCM) provides a novel method to achieve the upcycling of spent LIB cathodes.

The standard D-NCM with a chemical composition of $Li_{0.927}Ni_{0.337}Co_{0.331}Mn_{0.332}O_2$ was obtained by a chemical delithiation using the NO_2BF_4 oxidizer.[40] According to the XRD pattern (**Figure** 1a), D-NCM maintained the O3-type structure of pristine NCM (P-NCM), whose diffraction lines can be indexed based on the layered structure of α-$NaFeO_2$. The (108) and (110) diffraction lines of D-NCM shifted away from each other, the peak splitting between (108) and (110) of D-NCM was 1.05^o larger than that of P-NCM (0.76^o), and the integrated intensity ratio of I(003)/I(104) peaks became 2.18, also larger than that of P-NCM (1.76). Those changes in the XRD diagram suggested an expansion of the c parameter in D-NCM, due to the repulsive force generated from MO_6 slabs, which are positively charged in a delithiated state. Besides, the (110) diffraction line shifted to higher angles, indicating the contracted a-axis of D-NCM due to the smaller radius of transition metal ions at elevated valences. Thermogravimetric analysis (TGA) under the air atmosphere was used to evaluate the thermal stability of NCM materials (NCMs). D-NCM exhibited about 2.3% weight loss at 800 °C, much higher than P-NCM, which revealed a 0.2% weight loss at 800 °C. The major weight loss in D-NCM was originated from the oxygen evolution due to surface reconstruction begin with 175 °C. Thus, the XRD patterns, ICP results, and TGA curves can work together to investigate the crystal structure and chemical composition changes in NCMs during the delithiation/relithiation processes.

Targeting a succinct relithiation of D-NCM, impurities should be as little as possible along with the introduction of Li. Cost-effective LiBr was chosen as the prioritized lithium source because the oxidation product Br_2 could be easily removed from the reaction system by evaporation. Three ILs [C_2mim][NTf_2], [C_4mim][NTf_2] and [C_2OHmim][NTf_2] were synthesized and chosen as ionothermal solvents, because of their relatively low cost and excellent thermal stability under 300 °C (Figure S1).[41] For a typical relithiation process, D-NCM and LiBr were mixed in [C_2mim][NTf_2] and heated to 150 °C for 6 h. The relithiated powder was washed with acetone, ethanol, and acetone, and finally dried at 100 °C for 2 h and then calcined at 500 °C for 4 h (denoted as R-NCM-LiBr-C_2). As shown in Figure 1b, those XRD peak changes happened in D-NCM were successfully recovered in R-NCM-LiBr-C_2. The peak splitting between (108) and (110) of R-NCM-LiBr-C_2 was 0.75^o, almost the same as that of P-NCM (0.76^o), suggesting the successful restoration of the crystal structure. The Li molar ratio of R-NCM-LiBr-C_2 was calculated to be 1.070 based on ICP results, also the same as that of P-NCM (1.072), indicating the successful restoration of chemical composition. The TGA curve of R-NCM-LiBr-C_2 coincides with that of P-NCM, indicating excellent thermal stability of fully relithiated R-NCM-LiBr-C_2. As shown by SEM in Figure S2, no obvious morphological changes after relithiation demonstrate the ionothermal relithiation as a benign process to the particles.

The electrochemical performance of R-NCM-LiBr-C_2, D-NCM, and P-NCM were evaluated by both half-cell and full cell tests. The charge/discharge cycling performance was evaluated in a voltage range of 3–4.3 V at 1 C after four activation cycles at C/10 and their voltage profiles at different cycles are compared. As shown in **Figure 2**, the charge/discharge curves of R-NCM-LiBr-C_2 half cell almost coincided with that of P-NCM for the first 4 cycles at C/10. Especially for the first cycle, the charge capacity of R-NCM-LiBr-C_2 is 173.6 mAh/g, as large as that of P-NCM (175.3 mAh/g), much larger than that of D-NCM (145.9 mAh/g). The recovered charge capacity of R-NCM-LiBr-C_2 verified the full relithiation of D-NCM. The discharge capacities of P-NCM, D-NCM and R-NCM-LiBr-C_2 are almost the same, the recovered discharge capacity of D-NCM was originated from electrochemical relithiation, which always occurred for half-cell test due to excessive lithium in the lithium foil.[22] However, the electrochemical relithiation will not happen in the practical application, because no extra lithium can be used for electrochemical relithiation in a commercial full cell. Thus, the full cell test is the ultimate test to determine whether the relithiated cathode materials can work as well as new ones. To simulate the situation as practical as possible, we choose a high loading full cell test, in which the cathode active material density was as high as 10 mg/cm^2. The matched graphite anode was prepared according to the calculated capacity ratio (1.1:1) of the anode to cathode. The charge/discharge capacities of R-NCM-LiBr-C_2 were still as large as those of P-NCM, whereas D-NCM exhibited an attenuated capacity. The cycle stability of R-NCM-LiBr-C_2 was also consistent with P-NCM (Figure 2e). Thus, R-NCM-LiBr-C_2 has a fully recovered capacity when used as a LIB cathode. Similarly, R-NCM-LiBr-C_2OH using [C_2OHmim][NTf_2] as the solvent also exhibited a recovered XRD pattern and a fully recovered capacity (Figure S3 and S4). Thus, the ionothermal relithiation approach is indeed an effective way to direct regenerate NCM cathodes.

To shed light on the mechanism of chemical relithiation, we have investigated ionothermal relithiation under different reaction conditions, such as other ILs ([C_4mim][NTf_2]

and [C_2OHmim][NTf_2]), Li precursors (LiCl, $LiNTf_2$, LiOAc), and different temperatures. The products were named as R-NCM-(Li precursor)-(Cation in IL)-(Temperature). For example, R-NCM-LiCl-C_2OH-200 means the product synthesized by LiCl, [C_2OHmim][NTf_2] at 200 °C. R-NCM-LiCl-C_2OH-200 exhibited the highest Li molar ratio when using LiCl as Li source at 200 °C (**Figure 3**a, blue disks), suggesting the advantage of [C_2OHmim][NTf_2] as the solvent. The possible reason is that the hydrophilic hydroxide groups in C_2OHmim provide additional solubility for Li salts and interaction with D-NCM, beneficial to the relithiation reaction. The decrease of reaction temperature from 200 °C to 150 ^oC gave the product R-NCM-LiCl-C_2OH-150 a higher Li molar ratio (Figure 3a, red disk). Changing the Li precursor from LiCl to LiBr increased the Li molar ratio of products (Figure 3a, red disk to red square), suggesting a better relithiation performance of LiBr than that of LiCl. Further decrease in reaction temperature to 120 °C cannot achieve a better relithiation performance. The possible reason is the temperature 120 °C is too low to support enough reaction activity of LiBr. As shown in Figure 3b, the higher temperatures 225 °C and 250 °C cannot provide a full relithiation of D-NCM either. Thus, 150 ^oC is the optimal reaction temperature for the relithiation process. Other Li salts such as LiOAc and $LiNTf_2$ were also used as Li precursors but exhibited worse relithiation performance according to the TGA results (Figure 3b, hexagons and triangles). Because Br^- as the anion of LiBr is easier to be oxidized than other anions, and the oxidation products Br_2 can be removed by evaporation to promote the advance of lithiation reaction. Though the oxidation products of LiCl is Cl_2, which can automatically go out of the reaction system, the standard oxidation potential of Cl^- to Cl_2 is 1.358 V much higher than that of Br^- to Br_2 (1.065 v). Thus, LiBr is the optimal Li precursor for the relithiation process. When using LiBr as Li precursor at 150 °C, the products using all three ILs achieved a full relithiation whose Li molar ratios are almost the same as P-NCM (Figure 3a, red squares), suggesting the robust relithiation approach with ILs as solvents.

Recycle of ILs is an important step towards the economic recycling of NCM cathode. In this approach, as much as 98.7 % of ILs can be collected after the relithiation process (Table S1). Though the TGA results have shown the excellent thermal stability of ILs below 300 °C (Figure S1), FT-IR spectra were used here to further test the stability of the functional groups in ILs during the relithiation process. As shown in **Figure 4**, the FTIR spectra of [C_2OHmim][NTf_2] exhibits stretching vibrations of ν(alkyl C−H) between 2890 and 2968 cm^{-1} and broad absorption peaks of ν(O-H) at 3540 cm^{-1}, which are originated from the substituents on imidazole.[42] The broad absorption peak at 3160 cm^{-1} is corresponding to ν(C−H) at C4 and C5 sites, while the peak at 3120 cm^{-1} is corresponding to ν(C−H) at C2 on imidazolium ring (Figure 4).[42, 43] The absorption peak around 1569 cm^{-1} is due to the in-plane imidazolium ring deformation (Δring) and scissoring CH_2.[44] The principal absorption peaks at 1132 cm^{-1} and 1348 cm^{-1} were from NTf_2 anion, attributed to the symmetric SO_2 stretch [$v_s(SO_2)$] and asymmetric SO_2 stretches [$v_a(SO_2)$], respectively. The stretches of the CF_3 groups ($\nu(CF_3)$) exhibited a strong absorption peak at 1179 cm^{-1}. The absorption peak around 1054 cm^{-1} corresponds to NCH_3 twist in C_2OHmim and SNS asymmetric stretch (v_a(SNS)) in NTf_2.[45] After relithiation process at different temperatures (150, 200 or 250 °C), all the absorption peaks of recovered [C_2OHmim][NTf_2] are consistent well with those of fresh [C_2OHmim][NTf_2], suggesting the excellent stability of functional groups in ILs and the recyclability of ILs for the ionothermal relithiation process. The recyclable solvents and cost-effective Li sources are greatly conducive to the economic recycling of NCM cathode.

In conclusion, a novel ionothermal relithiation of delithiated NCM cathode was achieved by using ILs as the recyclable solvent and cost-effective lithium halide as Li precursor. The fully recovered NCM structure and chemical composition were verified by XRD, TGA and ICP characterization methods. The relithiated NCM exhibited excellent electrochemical performance as a pristine NCM in both half cell and full cell tests. The cycle stability of R-NCM was also demonstrated. Thus, this ionothermal relithiation synthesis provides a promising strategy for the upcycling of NCM cathodes.

Experimental Section

Materials: LiCl, LiBr, LiOAc, Li_2CO_3, $LiNTf_2$ and DMSO were purchased from Sigma-Aldrich without further purification. Standard delithiated NMC (D-NCM) of composition $Li_{0.9}(Ni_{0.33}Co_{0.33}Mn_{0.33})O_2$ were created and supplied by Drs. Pupek and Dahl at the MERF facility from the baseline NCM111 (P-NCM) provided by CAMP at Argonne National Laboratory. Imidazolium ionic liquids were synthesized according to previously published work.[41]

Relithiation Procedures: Stoichiometric amounts of D-NCM black powder (~2.5 mmol) and LiCl or other lithium precursor (~2.5 mmol) were mixed in ILs (~2.5 mL) in a 25 mL glass vial. After stirring for 10 minutes, the vial containing the mixtures was heated in a heating block up to 150 °C-250 °C within ~40 min and kept at this temperature for another 6 to 24 hours. After the mixture cooled down to room temperature, the black powder was separated from ILs by filtration. The recovered black powder was washed with acetone, ethanol twice, and finally with acetone. The black powder was dried in oven at ~100 °C for ~2 hours. For small scale experiments no calcination was used.

Chen et al. developed a ternary eutectic repair technology to relithiate spent NCM materials at 300 °C and annealed in oxygen with Li_2CO_3 at 850 °C, which is very promising.[28] In order for our ionothermal relithiation to be more economical, our process has been optimized. Since ionic liquid is one of the major contributions to the cost of ionothermal relithiation process, the strategies for cost reduction have been mainly focused on reducing the amount of ILs and reuse of ILs. Large scale (25 g) has been worked out by using about 50 mL of $[C_2mim][NTf_2]$, which is about only 20% IL amount used in the initial small scale experiments. The detailed procedure is as following, D-NCM black powder (25.3 g, ~0.263

mol), LiBr (3.40 g, ~0.0392 mol), and ILs (75.3 g, ~50 mL) were mixed well in a 150 mL Erlenmeyer flask capped with a rubber septum. The flask containing the mixtures was placed inside an oven, which then heated gradually up to 150 °C within ~30 min and kept at the temperature for another 6 hours. After the mixture cooled down to room temperature, the black powder was separated from IL by centrifugation and ~67.0 g of IL was recovered (~89.0%). The recovered black powder was washed with acetone, ethanol twice, and finally with acetone. The black powder was dried in oven at ~100 °C for ~1 hour and then calcined at 500 °C for 4 hours. 24.8 g of black powder was obtained (yield: 98.9%).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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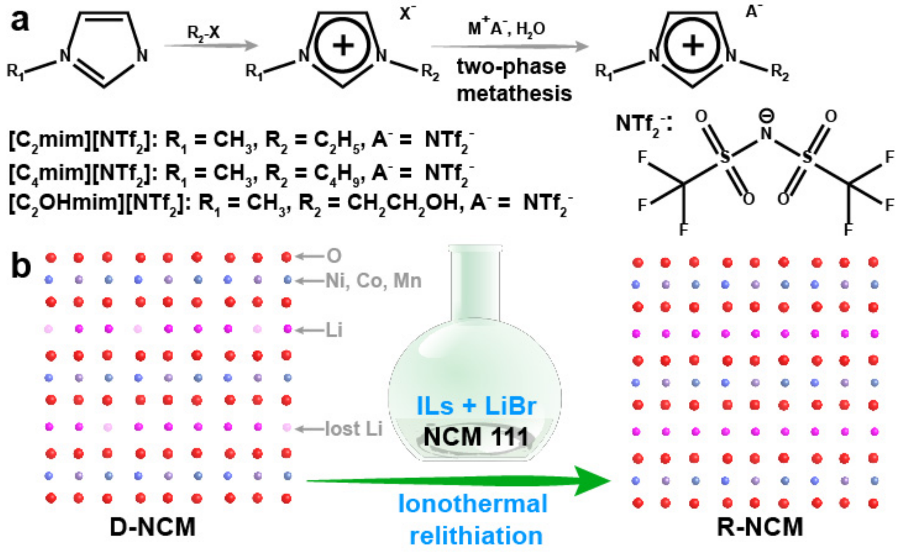

Scheme 1. a) Synthesis scheme of [C_2mim][NTf_2], [C_4mim][NTf_2] and [C_2OHmim][NTf_2]; b) Illustration of the relithiation process for Li composition recovery via ionothermal approach.

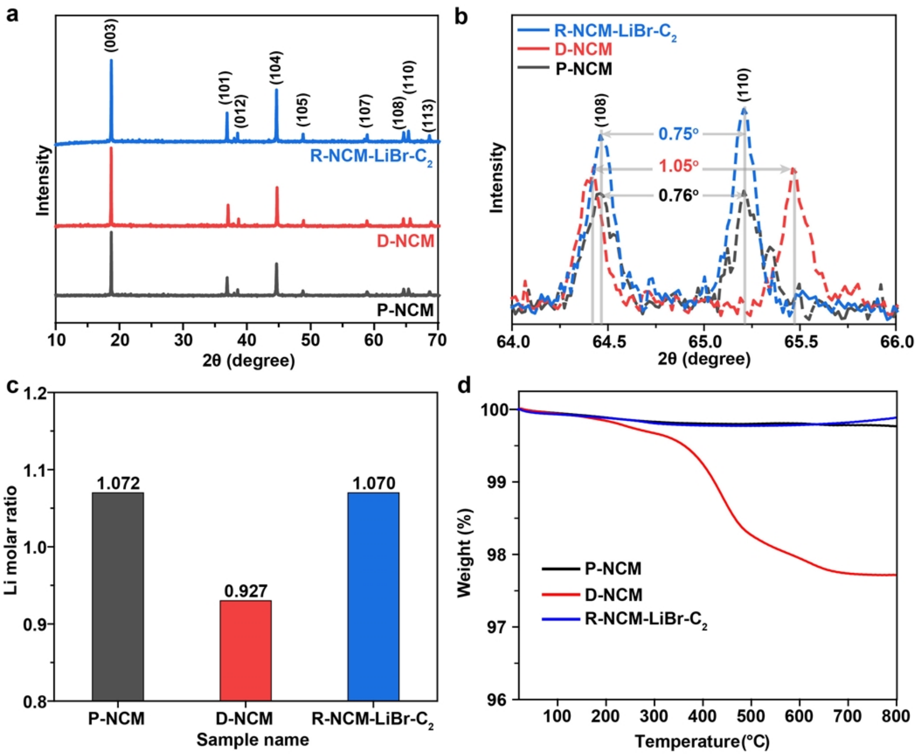

Figure 1. (a) and (b) XRD patterns for P-NCM, D-NCM, and R-NCM-LiBr-C_2; (c) Li molar ratio of P-NCM, D-NCM, and R-NCM-LiBr-C_2 based on ICP results; (d) TGA curves of P-NCM, D-NCM and R-NCM-LiBr-C_2.

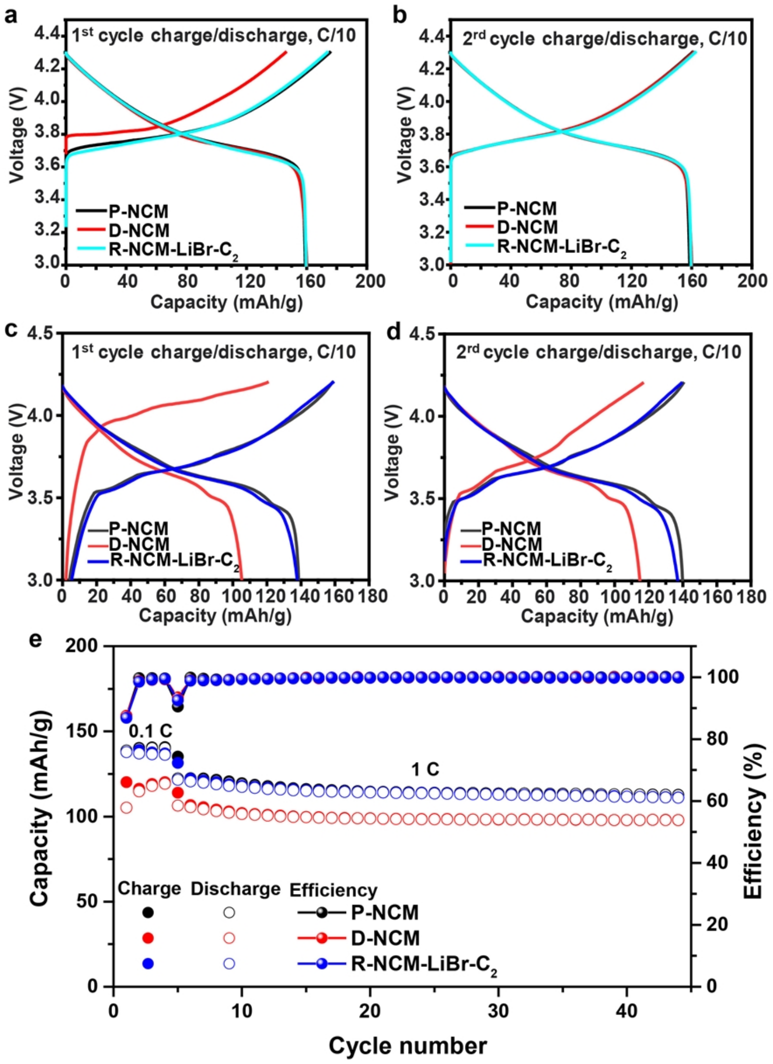

Figure 2. The first cycle (a) and second cycle (b) charge/discharge curves of P-NCM, D-NCM, and R-NCM-LiBr-C_2 for half-cell tests; The first cycle (c) and second cycle (d) charge/discharge curves of P-NCM, D-NCM, and R-NCM-LiBr-C_2 for full cell tests; e) Cycle performance of P-NCM, D-NCM, and R-NCM-LiBr-C_2 for full cell tests. The cathode active material density was as high as 10 mg/cm^2.

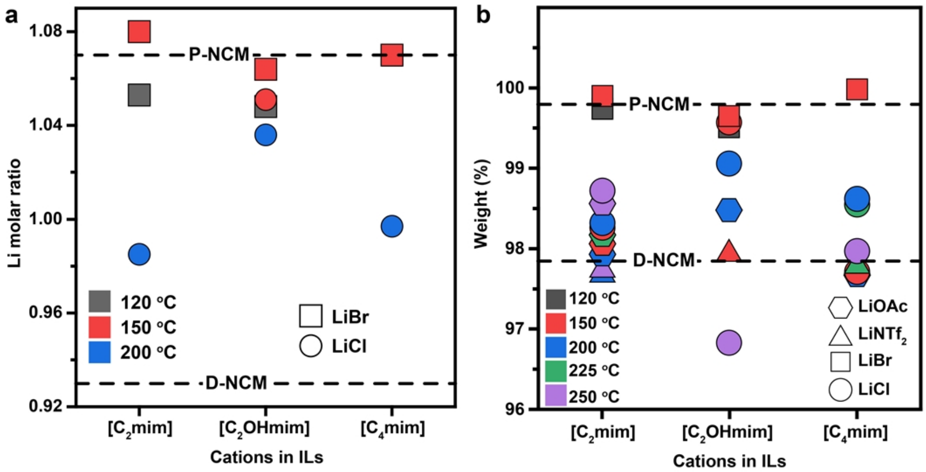

Figure 3. a) Li molar ratio of R-NCMs under different relithiation conditions calculated from ICP-OES results; b) Weight percentage (%) of R-NCMs under different relithiation conditions calculated from TGA results.

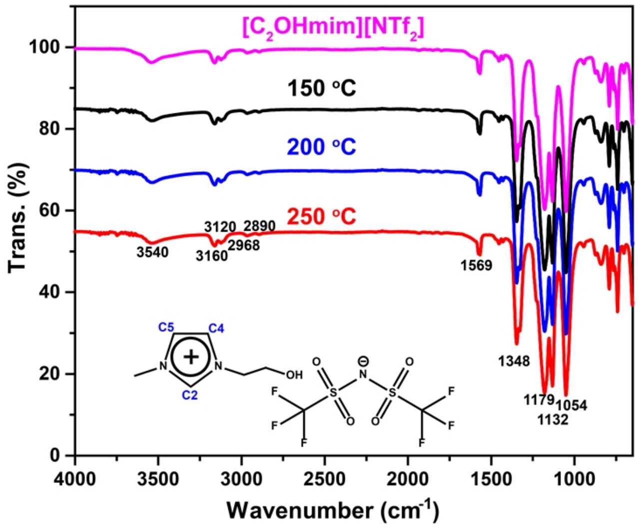

Figure 4. FTIR spectra for recycled [C$_2$OHmim][NTf$_2$] after relithiation processes at different temperatures.

A successful ionothermal relithiation using cost-effective Li halide as a Li source and recyclable ionic liquid as a solvent is first reported here for the upcycling of spent $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM) cathodes. The relithiated NCM exhibits excellent electrochemical performance as a pristine NCM in both half cell and full cell tests.

Keyword
ionic liquid, ionothermal synthesis, upcycling, batteries, structure-property relationships

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