**Supplementary Information**

**Green recovery of solid electrolytes from all-solid-state lithium-ion batteries by low-melting mixture solvents with tunable physical properties**

Yu Chen\*a, Xueqing Zhanga, Chenyang Wanga, Zhuojia Shia, Xihou Wanga, Jiayi Donga, Yanlong Wangb, Minghui Fengb

aDepartment of Chemistry and Material Science, Langfang Normal University, Langfang 065000, Hebei, China

bHebei Regional Geological Survey Institute, Langfang 065000, Hebei Province, P. R. China.

\* **Corresponding author: Yu Chen** − Department of Chemistry and Material Science, Langfang Normal University, Langfang 065000, Hebei Province, P. R. China. NO. 100 Aimin West Road, Langfang, Hebei Province, P.R. China. Phone: +86-316-2188211; Fax: +86-316-2112462. Email: yuchen@iccas.ac.cn

**Table S1.** **Effect of factors on the concentration and leaching efficiency of Li, Al, Zr and La from AlLLZO by LoMMSs**

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Factors | value | cLi / ppm | ηLi / % | cAl / ppm | ηAl / % | cZr / ppm | ηZr / % | cLa / ppm | ηLa / % |
| Molar ratio | 6:1 | 1098.8±32.8 | 92.5±1.9 | 13.1±1.6 | 7.6±0.8 | 27.1±1.5 | 0.6±0.02 | 322.6±5.7 | 2.9±0.05 |
| 10:1 | 829.0±5.5 | 69.9±0.5 | 10.4±2.5 | 6.0±1.5 | 18.9±0.7 | 0.4±0.02 | 218.1±6.8 | 2.0±0.06 |
| 14:1 | 844.8±46.3 | 73.1±3.9 | 12.8±1.8 | 7.4±1.0 | 22.0±4.7 | 0.5±0.10 | 240.4±31.5 | 2.2±0.28 |
| Time / h | 1 | 928.3±6.0 | 78.1±0.4 | 43.6±0.4 | 25.2±0.2 | 13.2±0.1 | 0.3±0.002 | 307.3±4.1 | 2.8±0.03 |
| 6 | 998.0±8.5 | 84.0±0.5 | 39.2±1.6 | 22.6±0.7 | 35.1±3.0 | 0.7±0.05 | 525.7±4.6 | 4.7±0.03 |
| 12 | 1071.3±5.3 | 90.2±0.3 | 15.2±4.1 | 8.8±2.0 | 18.9±1.1 | 0.4±0.02 | 288.1±8.4 | 2.6±0.06 |
| 24 | 1098.8±32.2 | 92.5±1.9 | 13.1±1.6 | 7.6±0.8 | 27.1±1.5 | 0.6±0.02 | 322.6±7.0 | 2.9±0.05 |
| 36 | 965.0±8.3 | 81.2±0.6 | 18.8±3.0 | 10.9±1.4 | 31.2±1.9 | 0.6±0.03 | 418.2±10.3 | 3.8±0.08 |
| 48 | 953.0±9.9 | 80.2±0.6 | 16.4±2.0 | 9.5±0.9 | 36.2±6.7 | 0.7±0.11 | 502.6±8.0 | 4.5±0.06 |
| LoMMSs mass  / g | 5 | 1098.8±32.2 | 92.5±1.9 | 13.1±1.6 | 7.6±0.8 | 27.1±1.5 | 0.6±0.02 | 322.6±7.0 | 2.9±0.05 |
| 10 | 401.7±13.1 | 67.6±1.8 | 5.5±0.6 | 6.3±0.6 | 19.7±0.5 | 0.8±0.02 | 195.3±5.2 | 3.5±0.08 |
| 15 | 262.5±12.2 | 66.3±2.5 | 2.9±0.9 | 5.1±1.3 | 14.7±0.5 | 0.9±0.03 | 115.5±3.7 | 3.1±0.08 |
| Temperature  / oC | 25 | 956.8±25.8 | 80.6±1.8 | 9.6±2.6 | 5.5±1.2 | 10.4±1.0 | 0.2±0.02 | 163.3±7.7 | 1.5±0.06 |
| 40 | 1005.3±8.3 | 84.6±0.6 | 11.1±1.8 | 6.4±6.4 | 14.0±1.2 | 0.3±0.02 | 222.1±11.5 | 2.0±0.08 |
| 60 | 1022.0±45.2 | 86.0±3.1 | 11.4±2.8 | 6.6±6.6 | 17.5±1.2 | 0.4±0.02 | 262.7±20.7 | 2.4±0.15 |
| 80 | 1098.8±32.2 | 92.5±1.9 | 13.1±1.6 | 7.6±0.8 | 27.1±1.5 | 0.6±0.02 | 322.6±7.0 | 2.9±0.05 |
| 100 | 670.7±27.5 | 56.5±1.9 | 8.1±2.0 | 4.6±1.0 | 61.2±2.7 | 1.3±0.04 | 583.8±30.5 | 5.2±0.22 |
| 120 | 627.0±17.3 | 52.8±1.2 | 4.9±1.4 | 2.8±0.6 | 19.1±1.5 | 0.4±0.03 | 223.1±7.0 | 2.0±0.07 |
| Scalability | ×1 | 1098.8±32.8 | 92.5±1.9 | 13.1±1.6 | 7.6±0.8 | 27.1±1.5 | 0.6±0.02 | 322.6±5.7 | 2.9±0.05 |
| ×100 | 1052.2±35.3 | 88.6±2.4 | 27.0±7.4 | 15.6±3.5 | 44.3±3.1 | 0.9±0.05 | 545.2±11.1 | 4.9±0.08 |

**Table S2. 55 kinds of anti-solvents for recovery of leachatea**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| NO. | Anti-solvents |  | NO. | Anti-solvents |  |
| 1 | 1,4-dioxane | Prec. | 29 | motor oil | No |
| 2 | 1,5-diazabicyclo[4.3.0]5-pelene | Prec. | 30 | toluene | No |
| 3 | 1,8-diazabicyclo[5.4.0]undec-7-ene | Prec. | 31 | methanol | No |
| 4 | 1-propanol | No | 32 | methyl tert-butyl ether | Prec. |
| 5 | collodion | No | 33 | polyethylene glycol 200 | No |
| 6 | 2-methyl-3-butyn-2-ol | No | 34 | levulinic acid | No |
| 7 | 5-norbornene-2-methanol | No | 35 | phytic acid | Prec. |
| 8 | N,N-dimethylformamide | No | 36 | benzene | No |
| 9 | N-methylpyrrolidone | No | 37 | lactic acid | No |
| 10 | N-methylacetamide | No | 38 | diisopropylamine | Prec. |
| 11 | ammonium hydroxide | Prec. | 39 | trichloromethane | No |
| 12 | phenol | No | 40 | triethylamine | Prec. |
| 13 | benzyl alcohol | No | 41 | triethanolamine | No |
| 14 | pyridine | Prec. | 42 | petroleum ether | No |
| 15 | aniline | Prec. | 43 | hydrazine hydrate | Prec. |
| 16 | glacial acetic acid | No | 44 | tetrabutylammonium hydroxide | No |
| 17 | malononitrile | Prec. | 45 | tetrahydrofuran | No |
| 18 | glycerol | No | 46 | propylene carbonate | No |
| 19 | acetone | Prec. | 47 | anhydrous formic acid | No |
| 20 | ultra-dry methylene chloride | No | 48 | anhydrous ethanol | No |
| 21 | dimethylsiloxane | No | 49 | anhydrous ethyl ether | No |
| 22 | ethyl acetate | No | 50 | 1,2-propanediol | Prec. |
| 23 | dimethyl sulfoxide | No | 51 | ethylene glycol dimethyl ether | No |
| 24 | acetylacetone | No | 52 | acetonitrile | Prec. |
| 25 | isopropyl alcohol | No | 53 | acetic anhydride | Prec. |
| 26 | orthopropionic acid | No | 54 | water | Prec. |
| 27 | cyclopentane | No | 55 | leachate | No |
| 28 | epichlorohydrin | Prec. |  |  |  |

a “Prec.” means precipitation and “No” means that there is no precipitation.

**Table S3. Physicochemical properties of PEG,** **LoMMSs PEG:BEA (6:1), leachate (5 g AlLLZO, 250 g LoMMSs PEG:BEA (6:1), 80 oC, 24 h)**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Physical properties | Sample | 1 | 2 | 3 | Mean | Standard deviation |
| Conductivity  / μS cm-1 | PEG | 1.167 | 1.164 | 1.166 | 1.1657 | 0.0015 |
| LoMMSs | 0.740 | 0.0739 | 0.739 | 0.7393 | 0.0006 |
| Leachate | 3.010 | 3.030 | 3.000 | 3.0133 | 0.0153 |
| Surface tension  / mN m-1 | PEG | 37.4 | 37.1 | 37.3 | 37.3 | 0.1 |
| LoMMSs | 39.4 | 39.2 | 39.5 | 39.4 | 0.1 |
| Leachate | 42.6 | 43.1 | 42.7 | 42.8 | 0.2 |
| Refractive index | PEG | 1.4601 | 1.4607 | 1.4610 | 1.4606 | 0.0005 |
| LoMMSs | 1.4674 | 1.4680 | 1.4678 | 1.4677 | 0.0003 |
| Leachate | 1.4678 | 1.4675 | 1.4679 | 1.4697 | 0.0002 |
| Optical rotation  / ° | PEG | 0.02 | 0.01 | 0.01 | 0.01 | 0.005 |
| LoMMSs | 1.55 | 1.55 | 1.60 | 1.57 | 0.02 |
| Leachate | 2.4 | 2.55 | 2.45 | 2.47 | 0.0 |
| Viscosity  / mPa s | PEG | 46.8 | 48.1 | 47.5 | 47.47 | 0.53 |
| LoMMSs | 116.2 | 114.6 | 119.4 | 116.73 | 2.00 |
| Leachate | 131.7 | 129.4 | 134.6 | 131.90 | 2.13 |
| Density  ρ / g cm-3 | PEG | 1.1128 | 1.1124 | 1.1125 | 1.1126 | 0.00021 |
| LoMMSs | 1.1262 | 1.1260 | 1.1258 | 1.1260 | 0.00020 |
| Leachate | 1.1329 | 1.1327 | 1.1327 | 1.1328 | 0.00012 |
| pH | PEG | 7.93 | 7.86 | 7.90 | 7.90 | 0.04 |
| LoMMSs | 5.05 | 5.06 | 5.07 | 5.06 | 0.01 |
| leachate | 5.82 | 5.80 | 5.80 | 5.81 | 0.01 |

**Table S4. Mass change of PEG, LoMMSs PEG:BEA (6:1) and leachate (5 g AlLLZO, 250 g LoMMSs PEG:BEA (6:1), 80 oC, 24 h)**

|  |  |  |  |
| --- | --- | --- | --- |
| t / h | mPEG / % | mLoMMSs / % | mleachate / % |
| 0 | 100.00 | 100.00 | 100.00 |
| 2 | 99.97 | 99.94 | 99.96 |
| 4 | 99.97 | 99.88 | 99.91 |
| 6 | 99.97 | 99.86 | 99.91 |
| 8 | 99.97 | 99.86 | 99.89 |
| 10 | 99.96 | 99.76 | 99.89 |
| 12 | 99.95 | 99.75 | 99.89 |

**Table S5. Cationic limit, anodic limit and electrochemical window of PEG, PEG:BEA (6:1) and leachate (5 g AlLLZO, 250 g LoMMSs PEG:BEA (6:1), 80 ℃, 24 h)**

|  |  |  |  |
| --- | --- | --- | --- |
| Sample | cationic limit / V | anodic limit / V | Electrochemical window / V |
| PEG | -3.299 | 3.501 | 6.800 |
| LoMMSs | -5.516 | 6.019 | 11.535 |
| Leachate | -0.589 | 0.522 | 1.111 |

**Table S6. Chemical shift of 1H and 13C NMR of PEG, PEG:BEA (6:1), leachate and PEG:BEA (6:1, 80 oC, 24 h)**

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Sample | PEG | BEA | LoMMSs | LoMMSs (80 oC 24 h) | Leachate | LoMMSs-PEG | LoMMSs-BEA | Leachate- LoMMSs | LoMMSs (80 oC 24 h)- LoMMSs |
| H1 / ppm | 4.9 |  | 4.4 | 5.2 | 3.6 | -0.5 |  | -0.8 | 0.8 |
| H2 / ppm | 6.3 |  | 5.7 | 6.5 | 4.8 | -0.6 |  | -0.9 | 0.8 |
| H3 / ppm |  | 9.3 | 8.8 | 9.6 | 7.9 |  | -0.5 | -0.9 | 0.8 |
| H4 / ppm |  | 8.7 | 8.3 | 9.0 | 7.4 |  | -0.4 | -0.9 | 0.7 |
| H5 / ppm |  | 6.2 | 5.7 | 6.5 | 4.8 |  | -0.5 | -0.9 | 0.8 |
| H6 / ppm |  | 4.5 | 4.4 | 5.1 | 3.5 |  | -0.1 | -0.9 | 0.7 |
| C1 / ppm | 60.8 |  | 60.8 | 60.8 | 60.8 | 0 |  | 0 | 0 |
| C2 / ppm | 70.2 |  | 70.2 | 70.2 | 70.2 | 0 |  | 0 | 0 |
| C3 / ppm | 72.3 |  | 72.3 | 72.3 | 72.3 | 0 |  | 0 | 0 |
| C4 / ppm |  | 168.5 | 168.4 | 168.4 | 169.3 |  | -0.1 | 0.9 | 0 |
| C5 / ppm |  | 132.7 | 132.7 | 132.7 | 132.3 |  | 0 | -0.4 | 0 |
| C6 / ppm |  | 130.5 | 130.6 | 130.6 | 131.7 |  | 0.1 | 1.1 | 0 |
| C7 / ppm |  | 129.4 | 129.4 | 129.4 | 129.3 |  | 0 | -0.1 | 0 |
| C8 / ppm |  | 128.1 | 128.1 | 128.1 | 128.0 |  | 0 | -0.1 | 0 |