

## Supplementary Information

### Capric acid-driven three-phase antisolvent precipitation strategy for recycling metal and lixiviant from leachate of spent sodium-ion batteries cathode

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**Table S1. Price of synthetic LoMMSs and antisolvent in cyclic experiments**

| No. | chemical reagents             | Purity (%)                | CAS        | Price a /\$ per 100 g (or 100 ml) <sup>a</sup> |
|-----|-------------------------------|---------------------------|------------|------------------------------------------------|
| 1   | polyethylene glycol 200 (PEG) | AR                        | 25322-68-3 | 1.53                                           |
| 2   | phytic acid (PHA)             | 70 wt in H <sub>2</sub> O | 83-86-3    | 8.23                                           |
| 3   | acetamide (ACE)               | 99.0                      | 60-35-5    | 3.49                                           |
| 4   | urea (UR)                     | 99.0                      | 57-13-6    | 42.69                                          |
| 5   | benzoic acid (BA)             | 99.5                      | 65-85-0    | 1.48                                           |
| 6   | citric acid (CIA)             | 99.0                      | 77-92-9    | 1.42                                           |
| 7   | capric acid (CA)              | 99.0                      | 334-48-5   | 0.95                                           |

**Table S2. Summary of chemical names, abbreviations, purity, suppliers, and the precipitation efficiency by antisolvents.**

| Entry | Antisolvents or other chemicals                 | Abbre.                        | Purity                     | Suppliers                 | Prec. <sup>a</sup> | $\eta_{Na}/\%$ | $\eta_{V}/\%$ |
|-------|-------------------------------------------------|-------------------------------|----------------------------|---------------------------|--------------------|----------------|---------------|
| 1     | 1,4-dioxane                                     | DX                            | 99.0%                      | Rhnwa                     | ×                  |                |               |
| 2     | 1,5-diazabicyclo[4.3.0]non-5-ene                | DBN                           | 98%                        | Innochem                  | ×                  |                |               |
| 3     | 1,8-diazabicyclo[5.4.0]undec-7-ene              | DBU                           | 99.0%                      | McLean                    | ×                  |                |               |
| 4     | n-propanol                                      | PrOH                          | 99.0%                      | Aladdin                   | √(2)               | 47.6±0.7       | 42.4±0.2      |
| 5     | collodion                                       | COL                           | ≥5.0%                      | Tianjin Damao             | ×                  |                |               |
| 6     | 2-methylbut-3-yn-2-ol                           | MBY                           | 98%                        | Innochem                  | ×                  |                |               |
| 7     | 5-norbornene-2-methanol                         | NBM                           | 98.0%                      | Ark Pharm                 | ×                  |                |               |
| 8     | 5-norbornene-2-carboxylic acid                  | NBCA                          | 99.0%                      | Aladdin                   | ×                  |                |               |
| 9     | N,N-dimethylformamide                           | DMF                           | ≥99.5%                     | Tianjin Bohua             | √(2)               | 79.3±0.6       | 99.5±0.3      |
| 10    | N-methylpyrrolidone                             | NMP                           | ≥99.0%                     | Aladdin                   | √(2)               | 50.2±0.5       | 48.0±0.6      |
| 11    | N-methylacetamide                               | NMA                           | >99.0%                     | Tokyo Chemical Industry   | √(2)               | 51.4±0.4       | 47.7±0.3      |
| 12    | ammonium hydroxide                              | NH <sub>4</sub> OH            | 25~28% in H <sub>2</sub> O | Aladdin                   | √(2)               | 94.4±0.1       | 98.6±0.1      |
| 13    | aniline                                         | PhNH <sub>2</sub>             | ≥99.5%                     | Tianjin Guangfu           | ×                  |                |               |
| 14    | phenol                                          | PhOH                          | ≥99.0%                     | Chemical Reagent          | ×                  |                |               |
| 15    | benzyl alcohol                                  | BnOH                          | 99.0%                      | Innochem                  | √(2)               | 53.8±1.1       | 48.3±0.1      |
| 16    | pyridine                                        | PY                            | >99.0%                     | Shanghai Chemical         | ×                  |                |               |
| 17    | acetic acid                                     | ACA                           | ≥99.5%                     | Tianjin Bohua             | √(2)               | 55.8±1.2       | 66.4±0.5      |
| 18    | nitric acid                                     | HNO <sub>3</sub>              | 65~68% in H <sub>2</sub> O | Tianjin Damao             | √(2)               | 39.0±1.3       | 31.3±0.2      |
| 19    | edible oil                                      | EO                            | NA                         | SuperMarket               | ×                  |                |               |
| 20    | glycerol                                        | GLY                           | ≥98.0%                     | Sinopharm                 | ×                  |                |               |
| 21    | propanone                                       | PP                            | >99.6%                     | Tianjin Jindong Tianzheng | √(2)               | 38.6±0.4       | 28.2±0.3      |
| 22    | dichloromethane                                 | DCM                           | 99.9%                      | Innochem                  | ×                  |                |               |
| 23    | silicone oil                                    | SOI                           | NA                         | Innochem                  | ×                  |                |               |
| 24    | ethyl acetate                                   | EAC                           | 99.0%                      | Aladdin                   | ×                  |                |               |
| 25    | dimethyl sulfoxide                              | DMSO                          | AR                         | Tianjin Chemical Reagent  | √(2)               | 53.1±0.9       | 46.9±0.3      |
| 26    | levulinic acid                                  | LEA                           | 98.0%                      | Innochem                  | ×                  |                |               |
| 27    | isopropanol                                     | IPA                           | 99.5%                      | Aladdin                   | √(2)               | 49.1±0.4       | 42.0±0.2      |
| 28    | 1-butyl-3-methylimidazolium hexafluorophosphate | BMIMPF <sub>6</sub>           | 97.0%                      | McLean                    | ×                  |                |               |
| 29    | propanoic acid                                  | PA                            | 99.0%                      | Tianjin Guangfu           | ×                  |                |               |
| 30    | tetrabutyl titanate                             | TBT                           | ≥98.0%                     | Tianjin Bohua             | ×                  |                |               |
| 31    | cyclopentane                                    | cPen                          | 96.0%                      | Aladdin                   | ×                  |                |               |
| 32    | epichlorohydrin                                 | ECH                           | 99.0%                      | Tianjin No.6 Chemical     | ×                  |                |               |
| 33    | engine oil                                      | ENO                           | NA                         | Mobil                     | ×                  |                |               |
| 34    | toluene                                         | PhMe                          | ≥99.5%                     | Tianjin Chemical Reagent  | ×                  |                |               |
| 35    | methyl alcohol                                  | MeOH                          | ≥99.9%                     | Tianjin Bohua             | √(2)               | 57.7±0.9       | 52.2±0.3      |
| 36    | methyl tert-butyl ether                         | MTBE                          | >99.0%                     | Aladdin                   | ×                  |                |               |
| 37    | polyethylene glycol 200                         | PEG                           | NA                         | Innochem                  | ×                  |                |               |
| 38    | polyethylene glycol 600                         | PEG600                        | NA                         | Tianjin Tianli            | ×                  |                |               |
| 39    | phytic acid                                     | PHA                           | 70% in H <sub>2</sub> O    | Aladdin                   | ×                  |                |               |
| 40    | benzene                                         | PhH                           | ≥99.5%                     | Tianjin Chemical Reagent  | √(3)               | 73.4±1.6       | 91.9±0.9      |
| 41    | lactic acid                                     | LA                            | 85~90% in H <sub>2</sub> O | Innochem                  | ×                  |                |               |
| 42    | diisopropylamine                                | DIPA                          | ≥99.0%                     | Innochem                  | ×                  |                |               |
| 43    | trichloromethane                                | TCM                           | ≥99.0%                     | Tianjin Jindong Tianzheng | ×                  |                |               |
| 44    | triethylamine                                   | TEA                           | 99.0%                      | Aladdin                   | ×                  |                |               |
| 45    | triethanolamine                                 | TEOA                          | ≥ 85.0%                    | Tianjin Dongli Tianda     | ×                  |                |               |
| 46    | naphtha                                         | NA                            | 99%                        | Tianjin Chemical Reagent  | ×                  |                |               |
| 47    | hydrazine hydrate                               | HH                            | 80.0% in H <sub>2</sub> O  | Tianjin Dingshengxin      | ×                  |                |               |
| 48    | tetrabutylammonium hydroxide                    | TBAH                          | 25% in H <sub>2</sub> O    | Aladdin                   | √(2)               | 54.7±1.2       | 44.6±0.6      |
| 49    | hydrobromic acid                                | HBr                           | 40% in H <sub>2</sub> O    | Aladdin                   | √(2)               | 76.4±0.3       | 94.6±0.0      |
| 50    | cyclohexane                                     | cHex                          | 99.5%                      | Tianjin Chemical Reagent  | ×                  |                |               |
| 51    | tetrahydrofuran                                 | THF                           | 99.0%                      | Tianjin Bohua             | √(2)               | 18.7±2.8       | 6.3±0.5       |
| 52    | propylene carbonate                             | PCA                           | >98.0%                     | Aladdin                   | √(2)               | 48.2±2.0       | 40.5±0.2      |
| 53    | tetrabutylammonium hydroxide                    | TBAH                          | 40% in MeOH                | Innochem                  | √(2)               | 66.6±0.4       | 90.2±0.0      |
| 54    | formic acid                                     | FA                            | 98.0%                      | Aladdin                   | √(2)               | 55.2±0.3       | 60.7±0.2      |
| 55    | ethanol                                         | EtOH                          | 99.9%                      | Innochem                  | √(2)               | 49.3±1.1       | 43.0±0.2      |
| 56    | diethyl ether                                   | DE                            | ≥99.0%                     | Tianjin Jindong Tianzheng | ×                  |                |               |
| 57    | ethylene glycol                                 | EG                            | 99.0%                      | Aladdin                   | √(2)               | 56.4±0.1       | 49.5±0.2      |
| 58    | ethylene glycol diethyl ether                   | EGDE                          | > 99.0%                    | Beijing Chemical Reagent  | √(2)               | 16.7±1.3       | 0.5±0.7       |
| 59    | acetonitrile                                    | MeCN                          | > 99.0%                    | Tianjin Bohua             | √(2)               | 55.5±1.2       | 49.5±0.5      |
| 60    | ethyl vinyl ether                               | EVE                           | > 98.0%                    | Adamas                    | ×                  |                |               |
| 61    | n-butyl acetate                                 | BuOAc                         | > 99.0%                    | Tianjin Second Chemical   | ×                  |                |               |
| 62    | acetic anhydride                                | AA                            | ≥98.5%                     | Tianjin Chemical Reagent  | ×                  |                |               |
| 63    | hydrogen peroxide                               | H <sub>2</sub> O <sub>2</sub> | 30.0% in H <sub>2</sub> O  | Tianjin Chemical Reagent  | √(2)               | 57.4±1.3       | 51.7±0.3      |
| 64    | acetylacetone                                   | AAC                           | 99.0%                      | Aladdin                   | ×                  |                |               |
| 65    | 1-octyl-3-methylimidazolium hexafluorophosphate | OMIMPF <sub>6</sub>           | 95.0%                      | McLean                    | ×                  |                |               |
| 66    | 1-butyl-3-methylimidazolium tetrafluoroborate   | BMIMBF <sub>4</sub>           | 99%                        | Innochem                  | ×                  |                |               |
| 67    | polyethylene glycol 300                         | PEG300                        | NA                         | Innochem                  | ×                  |                |               |
| 68    | capric acid                                     | CA                            | 99.0%                      | Innochem                  | √(3)               | 86.8±3.1       | 50.5±0.6      |
| 69    | n-pentane                                       | PEN                           | 97.0%                      | Aladdin                   | ×                  |                |               |
| 70    | water                                           | H <sub>2</sub> O              | distilled water            | Self-made                 | √(2)               | 63.5±0.6       | 51.8±0.5      |
| 71    | benzoic acid                                    | BA                            | 99.5%                      | Innochem                  |                    |                |               |
| 72    | acetamide                                       | AC                            | 99.0%                      | Aladdin                   |                    |                |               |
| 73    | citric acid                                     | CIA                           | 99.0%                      | Innochem                  |                    |                |               |
| 74    | urea                                            | UR                            | 99.0%                      | Aladdin                   |                    |                |               |

<sup>a</sup> Entries 1-70 are classified as antisolvents, while other entries are not. The symbol √ denotes precipitation, while × indicates no precipitation observed. The numbers 2 and 3 in parentheses indicate two phases and three phases, respectively..

**Table S3. Concentration of Na and V before and after adding antisolvents**

| Lixiviant        | Concentration Before  |                      | Antisolvents                  | Concentration After Antisolvent |                      | Efficiency After          |                    |
|------------------|-----------------------|----------------------|-------------------------------|---------------------------------|----------------------|---------------------------|--------------------|
|                  | Precipitation         |                      |                               | Precipitation                   |                      | Antisolvent Precipitation |                    |
|                  | C <sub>Na</sub> / ppm | C <sub>V</sub> / ppm |                               | C <sub>Na</sub> / ppm           | C <sub>V</sub> / ppm | η <sub>Na</sub> / %       | η <sub>V</sub> / % |
| PEG:PHA<br>(6:1) | 3712.2±52.3           | 4584.8±114.6         | NH <sub>4</sub> OH            | 211.5±5.8                       | 63.8±3.5             | 94.4±0.1                  | 98.6±0.1           |
|                  |                       |                      | CA                            | 499±116.6                       | 2268.5±24.9          | 86.8±3.1                  | 50.5±0.6           |
|                  |                       |                      | DCM                           | 785.7±22.5                      | 23.1±11.8            | 79.3±0.6                  | 99.5±0.3           |
|                  |                       |                      | HBr                           | 895.7±10.3                      | 246.7±1.4            | 76.4±0.3                  | 94.6±0             |
|                  |                       |                      | PhH                           | 1008.8±63.3                     | 369.7±43.3           | 73.4±1.6                  | 91.9±0.9           |
|                  |                       |                      | TBAH                          | 1264.5±14.9                     | 447.9±1.5            | 66.6±0.4                  | 90.2±0             |
|                  |                       |                      | H <sub>2</sub> O              | 1383.7±22.5                     | 1921.8±22.3          | 63.5±0.6                  | 58.1±0.5           |
|                  |                       |                      | MeOH                          | 1602±34.4                       | 2189.5±11            | 57.7±0.9                  | 52.2±0.3           |
|                  |                       |                      | H <sub>2</sub> O <sub>2</sub> | 1614.7±48.2                     | 2214.8±10            | 57.4±1.3                  | 51.7±0.3           |
|                  |                       |                      | EG                            | 1651±5.1                        | 2317.5±8             | 56.4±0.1                  | 49.5±0.2           |
|                  |                       |                      | ACA                           | 1672.5±42.5                     | 1540.5±20.8          | 55.8±1.2                  | 66.4±0.5           |
|                  |                       |                      | MeCN                          | 1684±44.7                       | 2316±25.8            | 55.5±1.2                  | 49.5±0.5           |
|                  |                       |                      | FA                            | 1698.7±11.8                     | 1800.7±10.1          | 55.2±0.3                  | 60.7±0.2           |
|                  |                       |                      | TBAH                          | 1716±42.4                       | 2539±25.1            | 54.7±1.2                  | 44.6±0.6           |
|                  |                       |                      | BnOH                          | 1749±38.8                       | 2369±4.3             | 53.8±1.1                  | 48.3±0.1           |
|                  |                       |                      | DMSO                          | 1775.5±35.2                     | 2434±13.3            | 53.1±0.9                  | 46.9±0.3           |
|                  |                       |                      | NMA                           | 1841±10.9                       | 2398.8±12.1          | 51.4±0.4                  | 47.7±0.3           |
|                  |                       |                      | NMP                           | 1886.3±14.9                     | 2384±30.6            | 50.2±0.5                  | 48±0.6             |
|                  |                       |                      | EtOH                          | 1922±38.1                       | 2613.2±5.3           | 49.3±1.1                  | 43±0.2             |
|                  |                       |                      | IPA                           | 1927.5±12.7                     | 2660.5±6.4           | 49.1±0.4                  | 42±0.2             |
|                  |                       |                      | PCA                           | 1963±78                         | 2729.5±6.7           | 48.2±2                    | 40.5±0.2           |
|                  |                       |                      | PrOH                          | 1983.7±24.3                     | 2642.3±11.3          | 47.6±0.7                  | 42.4±0.2           |
|                  |                       |                      | HNO <sub>3</sub>              | 2311.8±50.9                     | 3151±12.8            | 39±1.3                    | 31.3±0.2           |
|                  |                       |                      | PP                            | 2326.7±17.7                     | 3291.7±11.1          | 38.6±0.4                  | 28.2±0.3           |
|                  |                       |                      | THF                           | 3080.3±102.6                    | 4295±15.5            | 18.7±2.8                  | 6.3±0.5            |
|                  |                       |                      | EGDE                          | 3154.7±43.3                     | 4563.8±33.6          | 16.7±1.3                  | 0.5±0.7            |

**Table S4. Leaching efficiency of Na and V by CTAP strategy.**

|               | $\eta_{\text{Na}} / \%$ | $\eta_{\text{V}} / \%$ |
|---------------|-------------------------|------------------------|
| leachate-1    | 96.4±1.5                | 80.6±2.1               |
| leachate-2    | 67.8±4.5                | 73.7±1.9               |
| leachate-3    | 47.1±2.9                | 59.5±2.0               |
| leachate-4    | 33.2±0.9                | 38.4±2.1               |
| leachate-5    | 15.6±2.1                | 23.8±4.1               |
| antisolvent-1 | 86.8±3.1                | 50.5±0.6               |
| antisolvent-2 | 54.1±5.3                | 39.9±3.8               |
| antisolvent-3 | 32.2±1.7                | 30±2.5                 |
| antisolvent-4 | 17.4±1.8                | 6.3±0.9                |
| antisolvent-5 | 8.2±4.5                 | 2.7±1.3                |

**Table S5. Physical property of PEG, PHA, LoMMSs and leachate (80 °C, 24 h, 0.1 g NVP, 5 g PEG:PHA (6:1)).**

| Physical property                       | Sample        | 1st    | 2nd    | 3rd    | Mean   | Standard deviation |
|-----------------------------------------|---------------|--------|--------|--------|--------|--------------------|
| Viscosity<br>/ mPa s                    | PEG           | 42.1   | 40.6   | 43.2   | 42.0   | 1.1                |
|                                         | PHA           | 924.0  | 913.0  | 917.0  | 918.0  | 4.5                |
|                                         | PEG:PHA (6:1) | 442.0  | 450.0  | 449.0  | 447.0  | 3.6                |
|                                         | Leachate      | 479.0  | 480.0  | 475.5  | 478.2  | 1.9                |
| pH                                      | PEG           | 5.94   | 7.73   | 7.69   | 7.12   | 0.84               |
|                                         | PHA           | 2.70   | 2.90   | 2.90   | 2.80   | 0.10               |
|                                         | PEG:PHA (6:1) | 0.08   | 0.04   | 0.05   | 0.06   | 0.02               |
|                                         | Leachate      | 0.22   | 0.18   | 0.20   | 0.20   | 0.02               |
| Density<br>/ g cm <sup>-3</sup>         | PEG           | 1.1219 | 1.1218 | 1.1216 | 1.1218 | 0.0001             |
|                                         | PHA           | 1.2934 | 1.2937 | 1.2935 | 1.2935 | 0.0001             |
|                                         | PEG:PHA (6:1) | 1.2680 | 1.2677 | 1.2677 | 1.2678 | 0.0001             |
|                                         | Leachate      | 1.2843 | 1.2849 | 1.2848 | 1.2847 | 0.0003             |
| Surface tension<br>/ mN m <sup>-1</sup> | PEG           | 45.7   | 45.8   | 46.5   | 46.0   | 0.4                |
|                                         | PHA           | 64.5   | 62.1   | 63.7   | 63.4   | 1.0                |
|                                         | PEG:PHA (6:1) | 33.8   | 33.4   | 32.8   | 33.3   | 0.4                |
|                                         | Leachate      | 36.1   | 36.3   | 36.7   | 36.4   | 0.2                |