Electronic Supplementary Information

Title

Removal of phosphorus and fluorine from wastewater containing PF_6^- via accelerated decomposition by Al^{3+} and chemical precipitation for hydrometallurgical recycling of lithium-ion batteries

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Table S-1 Concentrations of F^- measured by fluoride-ion selective electrode in the sample solutions dissolving $Al_2(SO_4)_3$ and NaF mixed with TISAB 1 or 2 solution.

Prepared F^- conc. (ppm)	Prepared Al^{3+} conc. (mM)	Measured F^- conc. with TISAB 1 (ppm)	Measured F^- conc. with TISAB 2 (ppm)
□10	10	0.0687	9.91
	100	0.0155	8.70
100	10	0.578	96.8
	100	0.0722	77.3
200	10	1.46	192
	100	0.139	142

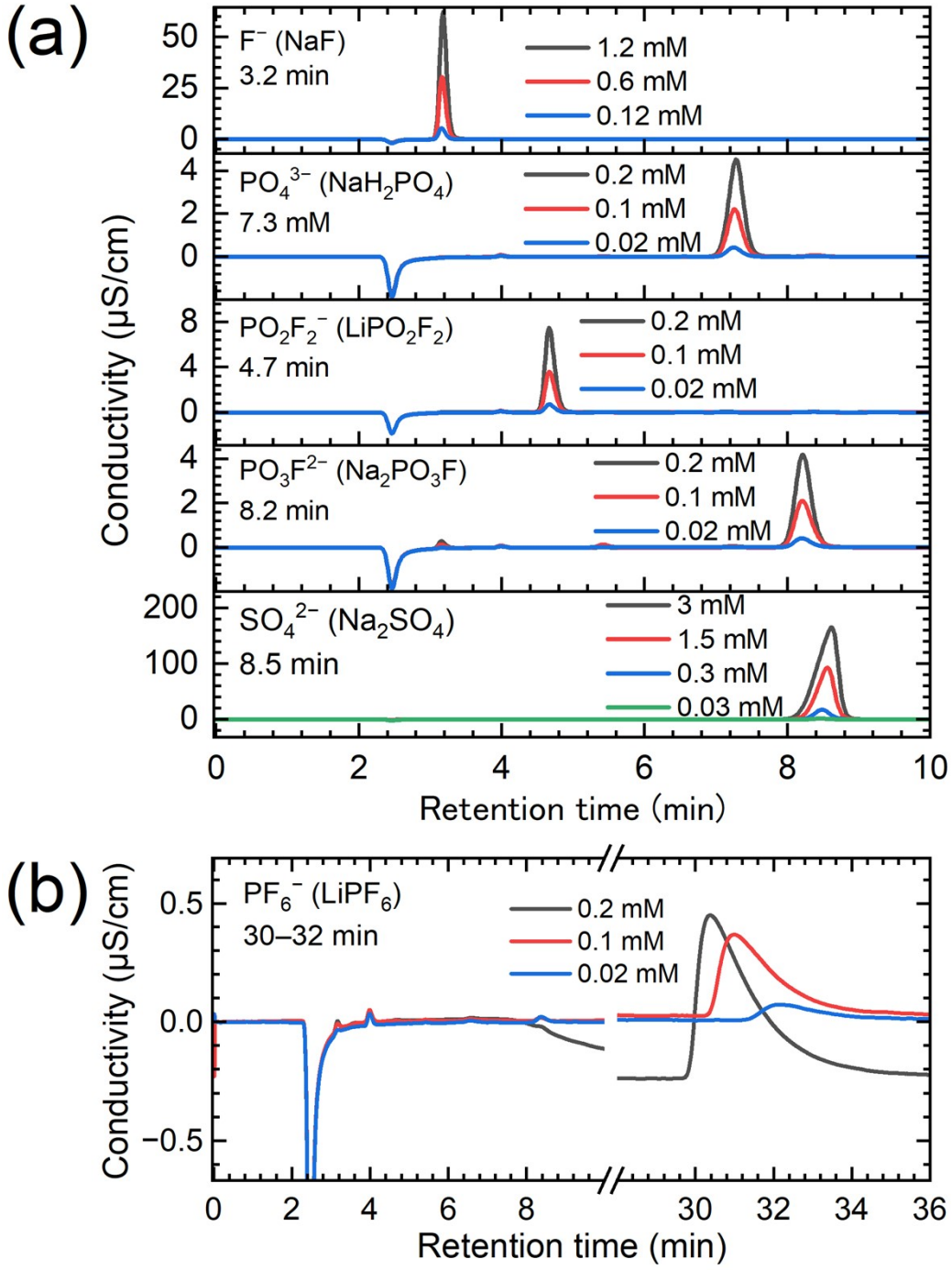

Fig. S-1 Ion chromatograms of standard solutions of (a) NaF, NaH_2PO_4, $LiPO_2F_2$, Na_2PO_3F, Na_2SO_4, and (b) $LiPF_6$.

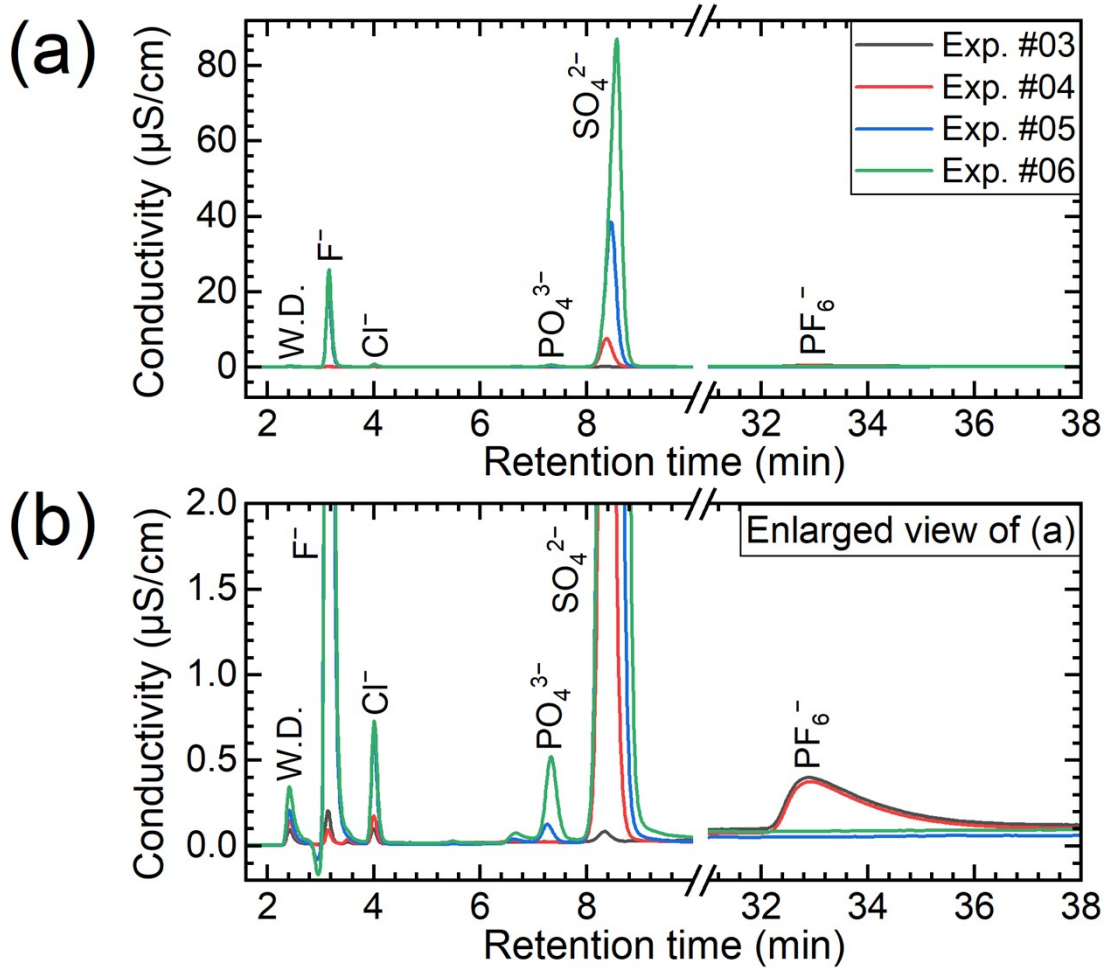

Fig. S-2 (a) Ion chromatograms of the supernatant of sample solutions after keeping 10 mM $LiPF_6$ + 108 mM $Ca(OH)_2$ + 0–200 Al-mM $Al_2(SO_4)_3$ solutions at 90 °C for 24 h according to procedure B and (b) enlarged view of (a). The sample solutions were diluted one hundredfold with the eluent and 20 µL of diluted solution were injected. The prepared concentration of $Al_2(SO_4)_3$ was 0 Al-mM in Exp. #03, 50 Al-mM in Exp. #04, 100 Al-mM in Exp. #05, and 150 Al-mM in Exp. #06. (W.D. = Water Dip)

Input data for running PHREEQC at the condition A shown in Table 2.

```
---------------------------------------------------------------------------------------------------------------------
PHASES
        Ettringite
                Ca6Al2(OH)12(SO4)3:26H2O = 6 Ca+2 + 2 Al(OH)4- + 3 SO4-2 + 4 OH- + 26 H2O
                        log_k -44.9
SOLUTION 1
        pH      4 charge
        units mmol/L
        Al      50
        S       75
        P       5
        F       30
        Li      5
EQUILIBRIUM_PHASES 1
        Ettringite              0.0 0.0
        Gypsum                  0.0 0.0
        Hydroxylapatite         0.0 0.0
        Fluorite                0.0 0.0
        Gibbsite                0.0 0.0
        Portlandite 0.0 0.0
USER_GRAPH
        -headings Ca(OH)2 pH Ettringite Gypsum Hydroxylapatite Fluorite Gibbsite    Portlandite
        -axis_titles Ca(OH)2 pH precipitate
        -start
                10 graph_x RXN
                20 graph_y -la("H+")
                30 graph_sy EQUI("ettringite") EQUI("Gypsum") EQUI("Hydroxylapatite")
EQUI("Fluorite") EQUI("Gibbsite") EQUI("Portlandite")
        -end
REACTION 1
        Ca(OH)2 1
                0.25 moles par 500 steps
END
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```

Input data for running PHREEQC at the condition B for Al/Ca < 2/3 shown in Table 2.

```
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PHASES
        Ettringite
                Ca6Al2(OH)12(SO4)3:26H2O = 6 Ca+2 + 2 Al(OH)4- + 3 SO4-2 + 4 OH- + 26 H2O
                log_k       -44.9
SOLUTION_MASTER_SPECIES
# PF6- is defined as X-
        X       X-      0.0     145     145
SOLUTION_SPECIES
        X- = X-
                log_k       0.0
SOLUTION 2
        pH      12 charge
        units mmol/L
        Ca      108
        Li      10
        X       10
EQUILIBRIUM_PHASES 1
        Ettringite          0.0 0.0
        Gypsum              0.0 0.0
        Hydroxylapatite     0.0 0.0
        Fluorite            0.0 0.0
        Gibbsite            0.0 0.0
        Portlandite 0.0 0.0
USER_GRAPH
        -headings Al2(SO4)3 pH Ettringite Gypsum Hydroxylapatite Fluorite Gibbsite    Portlandite
        -axis_titles Al2(SO4)3 pH precipitate
        -start
                10 graph_x RXN
                20 graph_y -la("H+")
                30 graph_sy EQUI("ettringite") EQUI("Gypsum") EQUI("Hydroxylapatite")
EQUI("Fluorite") EQUI("Gibbsite") EQUI("Portlandite")
        -end
REACTION 1
        Al2(SO4)3 1
                0.1 moles par 500 steps
END
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```

Input data for running PHREEQC at the condition B for Al/Ca > 2/3 shown in Table 2.

```
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PHASES
        Ettringite
                Ca6Al2(OH)12(SO4)3:26H2O = 6 Ca+2 + 2 Al(OH)4- + 3 SO4-2 + 4 OH- + 26 H2O
                log_k       -44.9
SOLUTION 3
        pH          12 charge
        units mmol/L
        Ca          108
        Li          10
        P           10
        F           60
EQUILIBRIUM_PHASES 1
        Ettringite              0.0 0.0
        Gypsum                  0.0 0.0
        Hydroxylapatite         0.0 0.0
        Fluorite                0.0 0.0
        Gibbsite                0.0 0.0
        Portlandite 0.0 0.0
USER_GRAPH
        -headings Al2(SO4)3 pH Ettringite Gypsum Hydroxylapatite Fluorite Gibbsite    Portlandite
        -axis_titles Al2(SO4)3 pH precipitate
        -start
                10 graph_x RXN
                20 graph_y -la("H+")
                30 graph_sy EQUI("ettringite") EQUI("Gypsum") EQUI("Hydroxylapatite")
EQUI("Fluorite") EQUI("Gibbsite") EQUI("Portlandite")
        -end
REACTION 1
        Al2(SO4)3 1
                0.1 moles par 500 steps
END
------------------------------------------------------------------------------------------------------------------------
```