Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting Information

Electrochemical lithium recovery with lithium iron phosphate: What causes performance degradation and how can we improve the stability?

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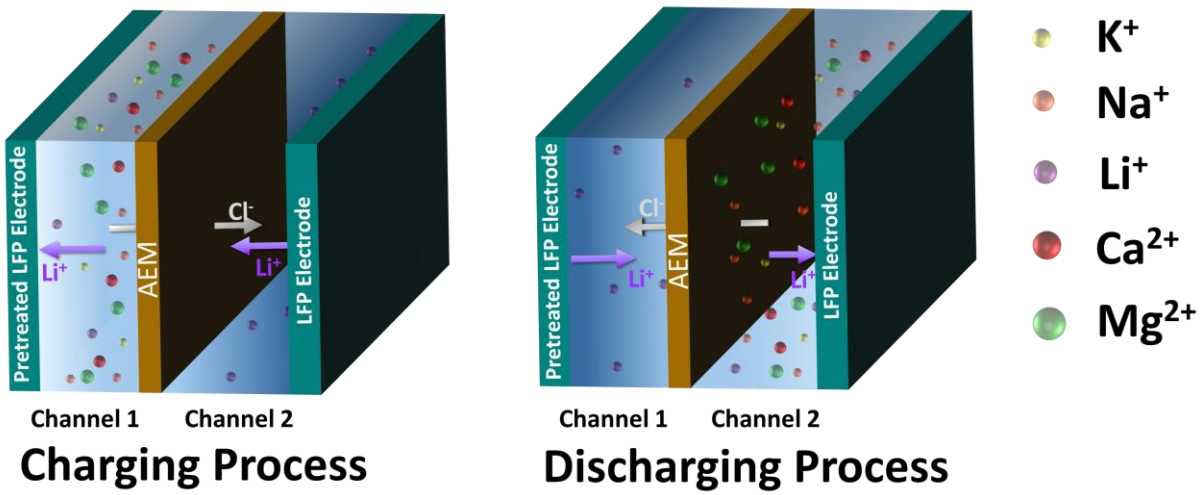

Figure S1. Schematic diagram of the principle of symmetric $LiFePO_4$ electrode during the charging and discharging process

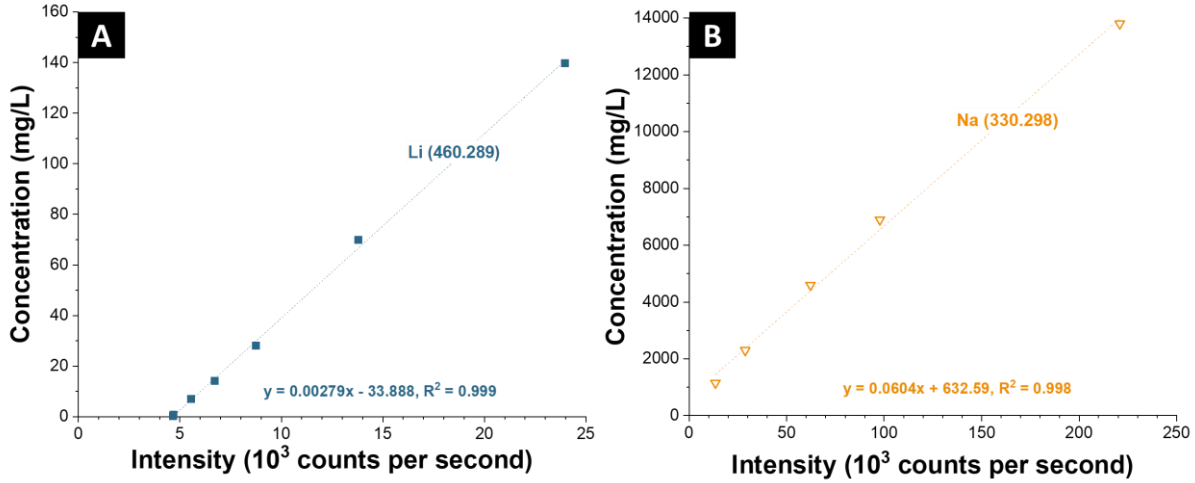

Figure S2. Calibration curves (i.e., the relation of ion concentration and characteristic peak intensity) of lithium (A) and sodium (B).

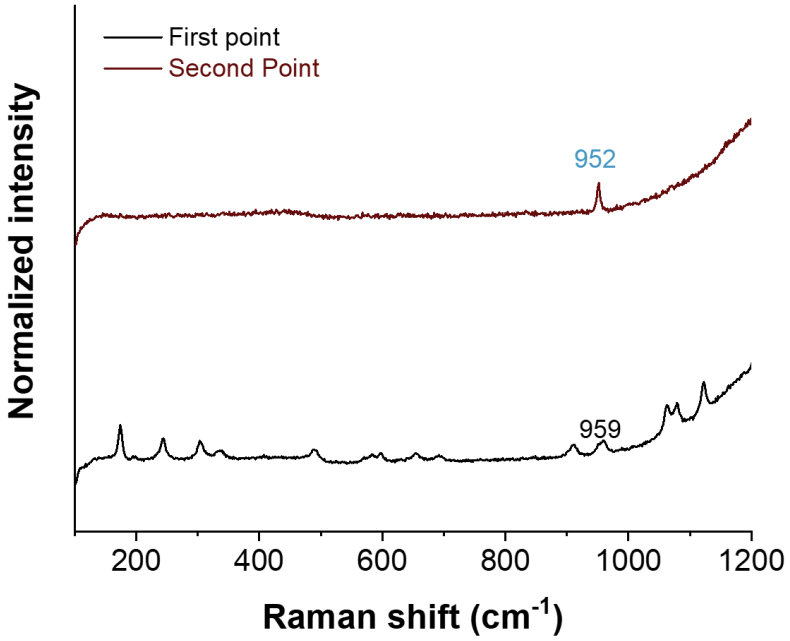

Figure S3. Raman spectra of delithiated $LiFePO_4$ recorded at different point on the sample.

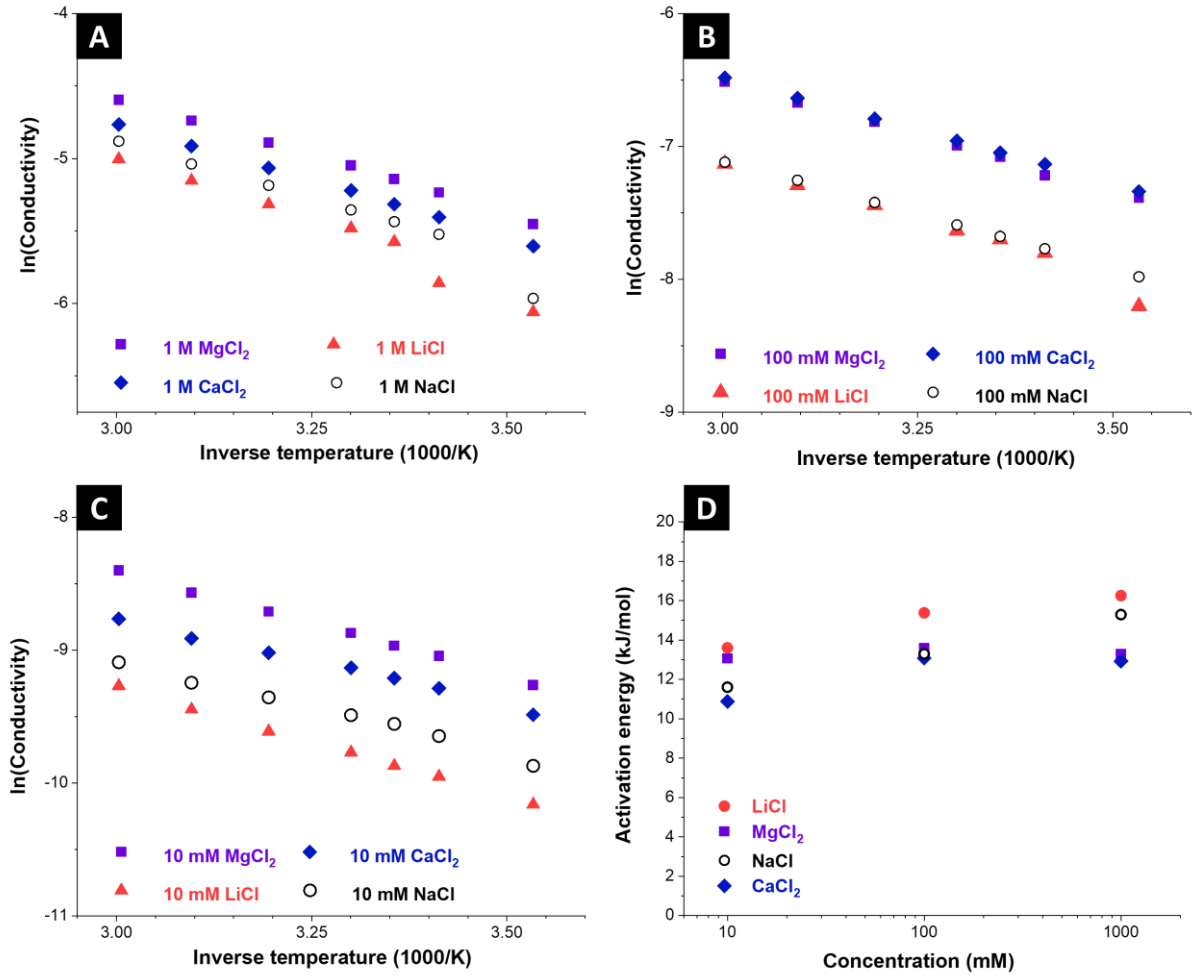

Figure S4. Plot of the electrolyte conductivity as a function of the reciprocal of the temperature (T^{-1}) in 1 mM (A), 100 mM (B), and 10 mM (C) LiCl, NaCl, $MgCl_2$ and $CaCl_2$ electrolyte and the activation energy of Na^+, Li^+, Mg^{2+}, and Ca^{2+} at various concentration (D).

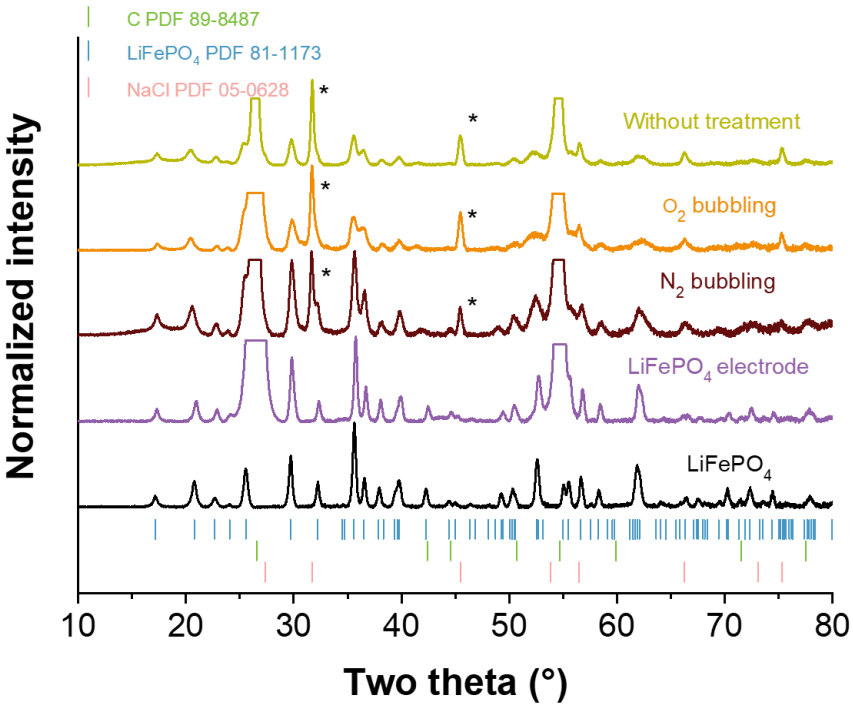

Figure S5. The post-mortem X-ray diffractograms of $LiFePO_4$ after 100 cycles in 5 mM LiCl + 50 mM NaCl with N_2-flushing, O_2-flushing, and without pre-treatment. The diffraction pattern were normalized to the reflections not associated with the graphite foil.

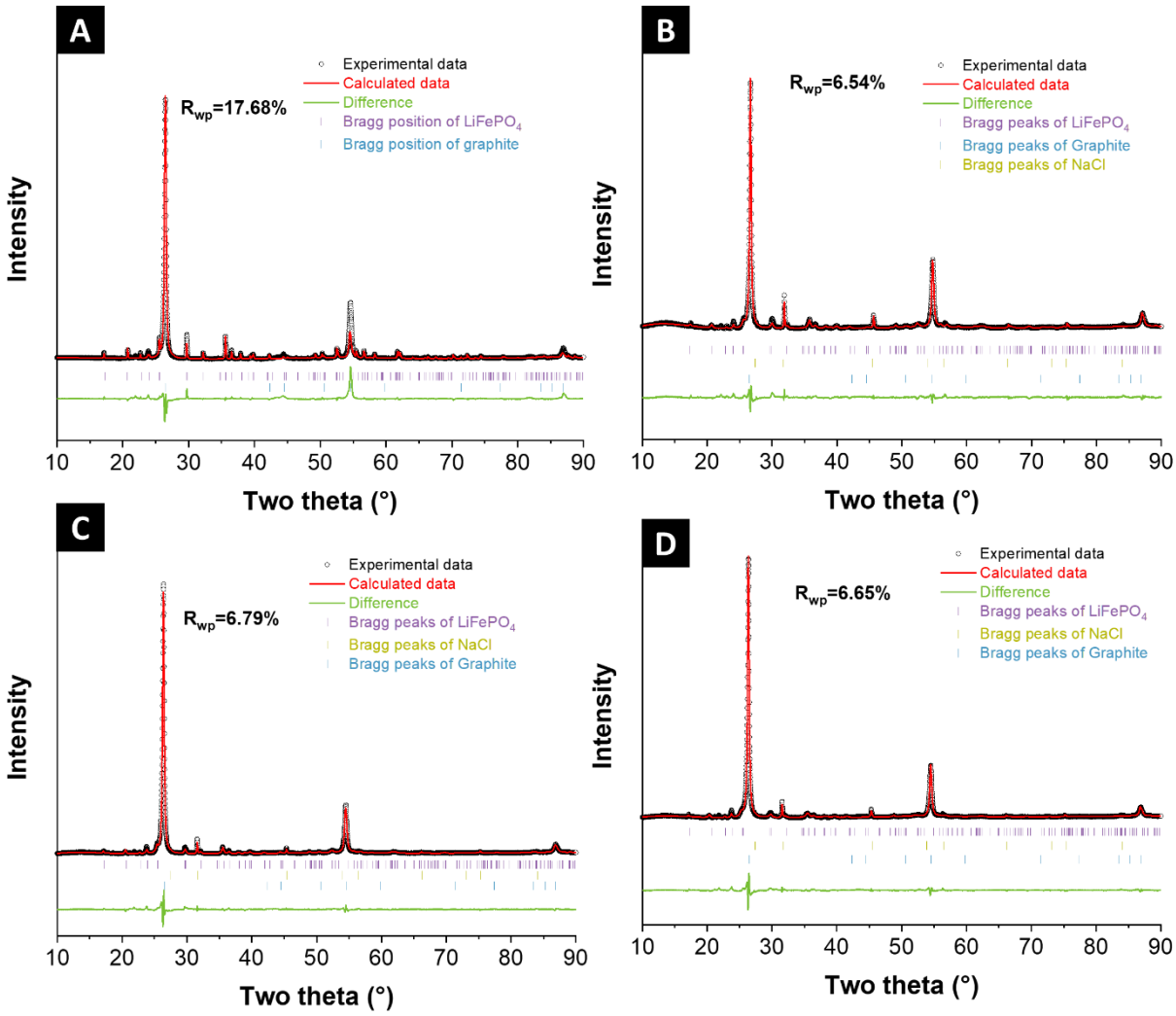

Figure S6. The X-ray Rietveld refinement fitting of initial $LiFePO_4$ electrode (A) and $LiFePO_4$ electrode after 100 cycles in 5 mM LiCl + 50 mM NaCl with without pre-treatment (B), N_2-flushing (C), and O_2-flushing (D).

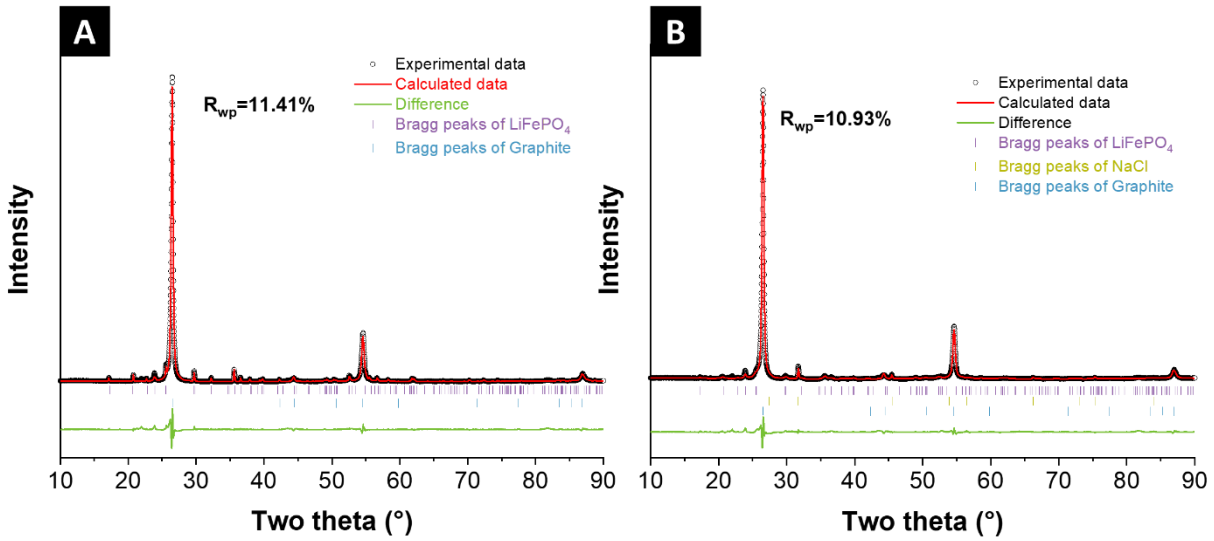

Figure S7. X-ray Rietveld refinement fitting of the initial $LiFePO_4$/C electrode (A), and the $LiFePO_4$/C electrode after 100 cycles in aqueous 5 mM LiCl + 50 mM NaCl.

Table S1: The concentration of dissolved oxygen after O_2-flushing and N_2-flushing.

Condition	Concentration of O_2 (ppm)
Initial	8.8
O_2 bubbling for 24 h	12.5
N_2 bubbling for 24 h	4.0

Table S2: Results of the elemental analysis (CHNS).

Sample	Carbon content (mass%)
$LiFePO_4$	2.4±0.6
$LiFePO_4$/C	4.4±0.7

Table S3: The formal potential of $LiFePO_4$ in LiCl, NaCl, $MgCl_2$ and $CaCl_2$ with the concentration of 1 M, 100 mM, and 10 mM.

Electrolyte	Average potential E_f (V vs. Ag/AgCl)
1 M LiCl	0.18
1 M NaCl	0.08
1 M $MgCl_2$	0.1
1 M $CaCl_2$	0.07
100 mM LiCl	0.12
100 mM NaCl	0.09
100 mM $MgCl_2$	0.10
100 mM $CaCl_2$	0.03
10 mM LiCl	0.09
10 mM NaCl	0.07
10 mM $MgCl_2$	0.08
10 mM $CaCl_2$	0.06