Supporting Information

Improving the cyclability performance of lithium-ion batteries by Introducing Lithium Difluorophosphate ($LiPO_2F_2$) Additive

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1. The cyclic voltammogram of graphite/Li and $LiCoO_2$/Li cells

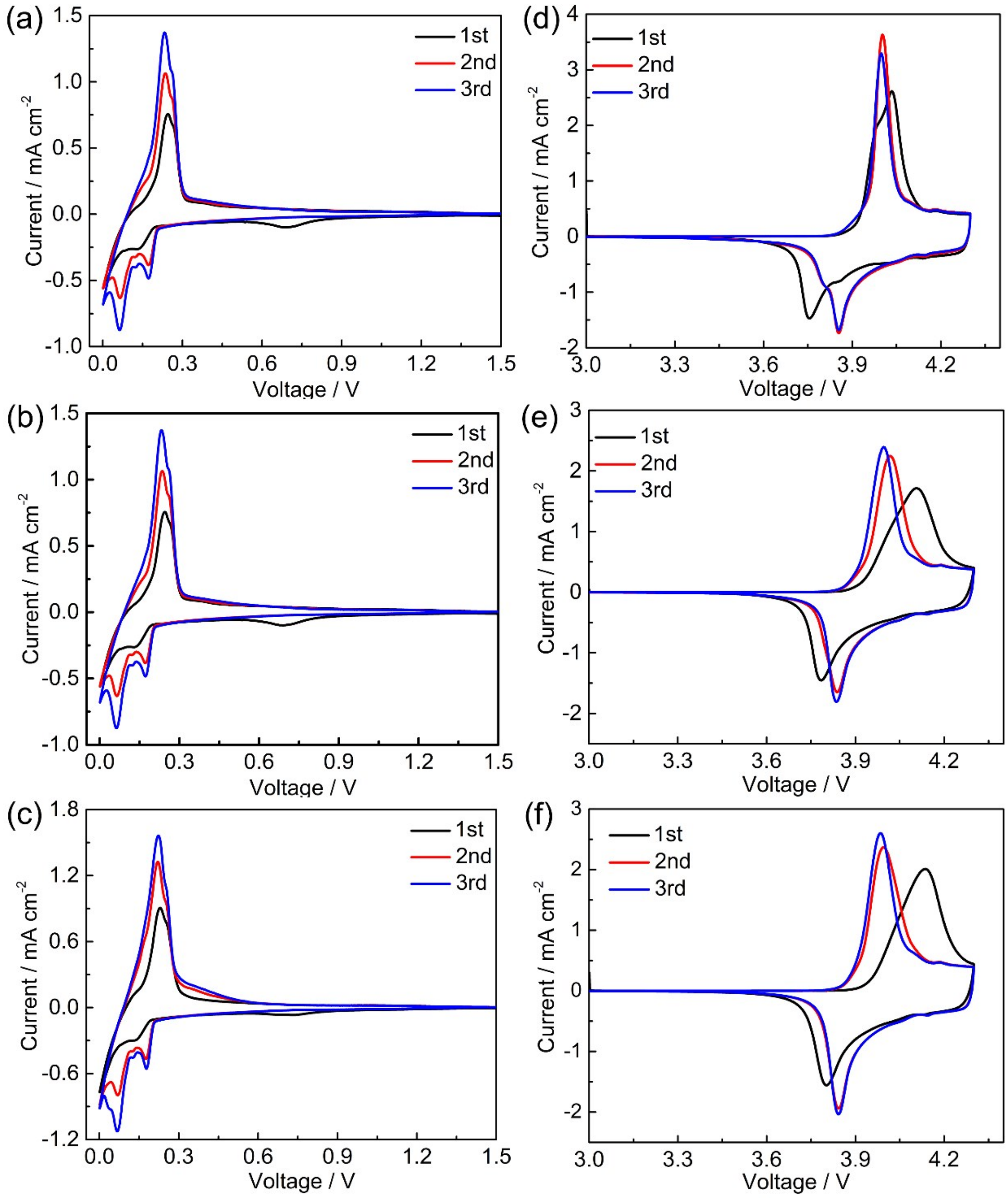

Fig. S1. Cyclic voltammogram of the graphite/Li cells with electrolytes A0 (a); A1 (b); A2 (c). The scan rate is 0.1mV/ s^{-1}. Cyclic voltammogram of the $LiCoO_2$/Li cells with electrolytesA0 (d); A1 (e); A2 (f). The scan rate is 0.1 mV s^{-1}.

2. Capacity retention of $LiPO_2F_2$ and other additives in different batteries

Table S1 capacity retention of $LiPO_2F_2$ and other additives in different batteries

electrolyte	additive	capacity retention (Li/graphite)	capacity retention (Li/$LiCoO_2$)	capacity retention (graphite/$LiCoO_2$)
		50th	100th	70th
1M $LiFP_6$/[EC+DMC(3/7)]	1.6wt% $LiPO_2F_2$	99.53%	98.8%	98.5%
1 M $LiClO_4$/PC	3wt% VC	96%	-	-
	3wt% FEC	94.5%	-	-
	3wt% ES	0	-	-
1 M $LiPF_6$ / [EC+DMC+EMC(1/1/1)]	3wt% TPSA	-	85%	-
1 M $LiPF_6$/(EC+EMC)	0.5wt% LiBOB	-	-	97.1%
	2wt% LiBOB	-	-	96.6%
	1wt% LiBOB + 0.5wt% VEC	-	-	96.8%
	1wt% LiBOB + 2wt% VC	-	-	97.74%
	2wt% VC	-	-	97.3%

3. The impedance spectroscopic analysis

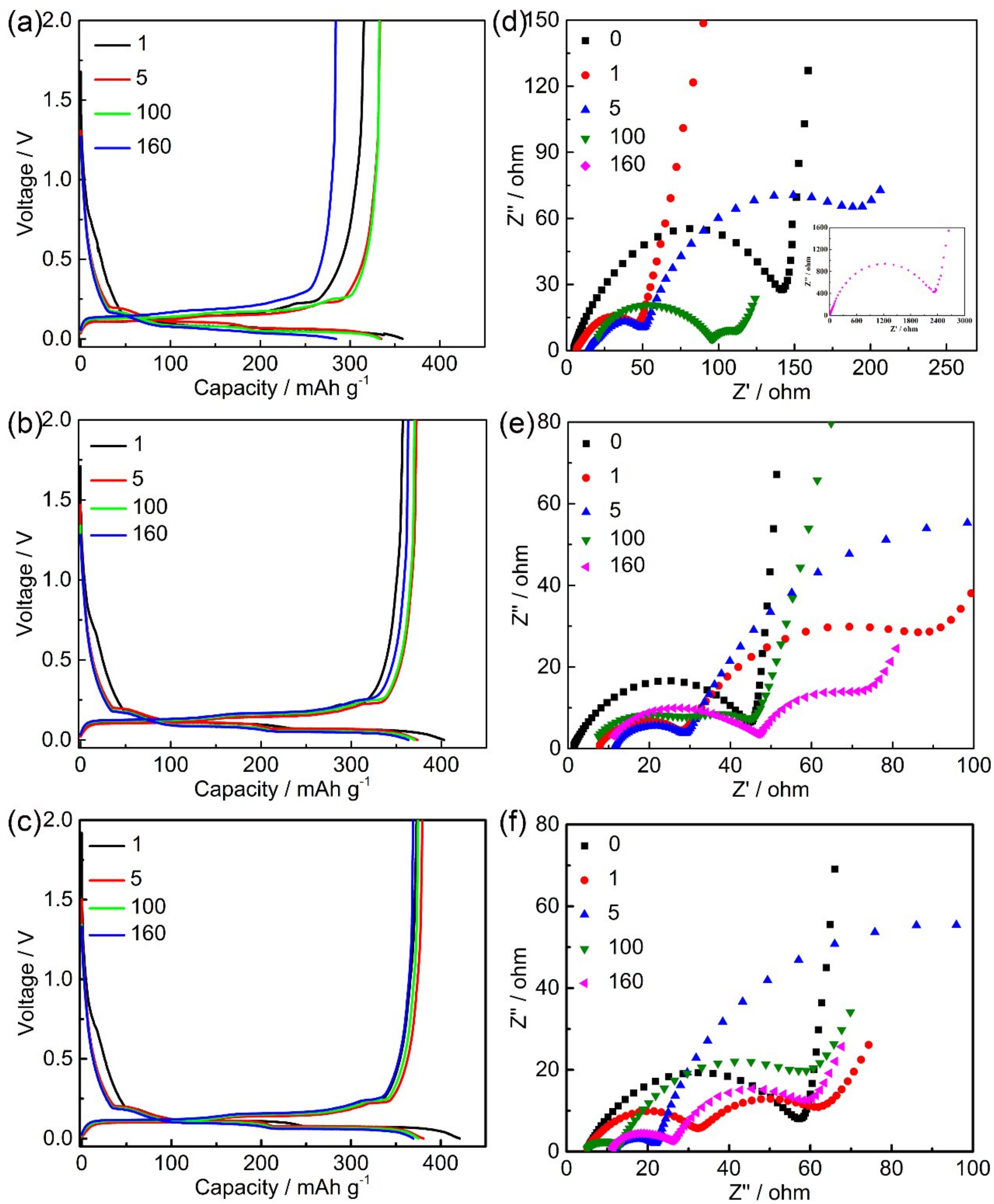

Fig. S2. Selected discharge-charge curves of graphite/Li cells with electrolytes A0 (a); A1 (b); A2 **(c)** at the cycles of 1st, 5th, 100th and160th at 0.2 C in the potential range of 0-2V at 25 °C.

EIS spectra of the graphite/Li cells with electrolytes A0 (d); A1 (e); A2 (f) after storage for 24 h, 1st, 5th, 100th and 160th cycles at 0.2 C in the potential range of 0-2V at 25 °C.

We list R_{ct} values of graphite/Li and $LiCoO_2$/Li half-cells in the table S2 and S3

Table S2. R_{ct} values of graphite/Li cells with A0, A1, and A2 after different cycles

Cycle Number	R_{ct} of A0 (Ω cm^2)	R_{ct} of A1 (Ω cm^2)	R_{ct} of A2 (Ω cm^2)
0	11	5	6
1	42	19	21
5	27	13	11.9
100	60	15	12.4
160	1700	17	15.8

Table S3. R_{ct} values of $LiCoO_2$/Li cells with A0, A1, and A2 after different cycles

Cycle Number	R_{ct} of A0 (Ω cm^2)	R_{ct} of A1 (Ω cm^2)	R_{ct} of A2 (Ω cm^2)
0	140	47	58
1	80	64	50
5	120	70	56
100	150	55	50
160	2200	60	48

4. The morphology and distribution of elements on the graphite electrode

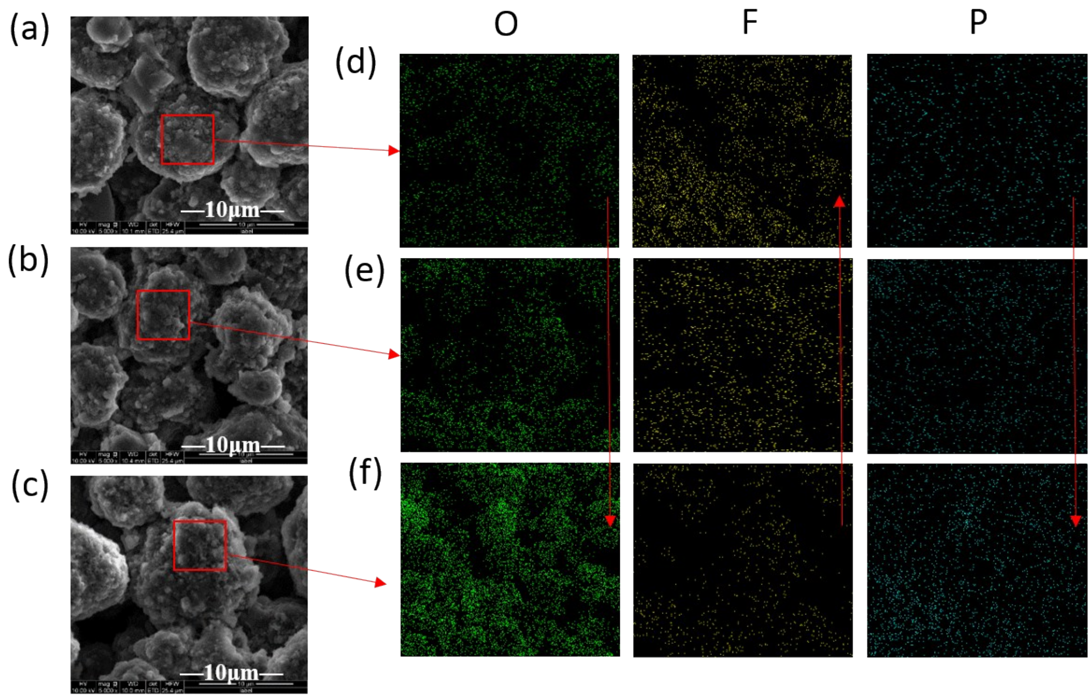

Fig. S3. The morphology and distribution of elements on graphite electrode surface by SEM and EDX after 160 cycles. The cell with electrolytes A0 (a); A1 (b); A2 (c). EDX mapping of the red region and the elements of the oxygen, fluorine, and phosphor. The cell with electrolytes A0 (d); A1 (e); A2 (f).

5. XPS spectra of the $LiCoO_2$ electrodes

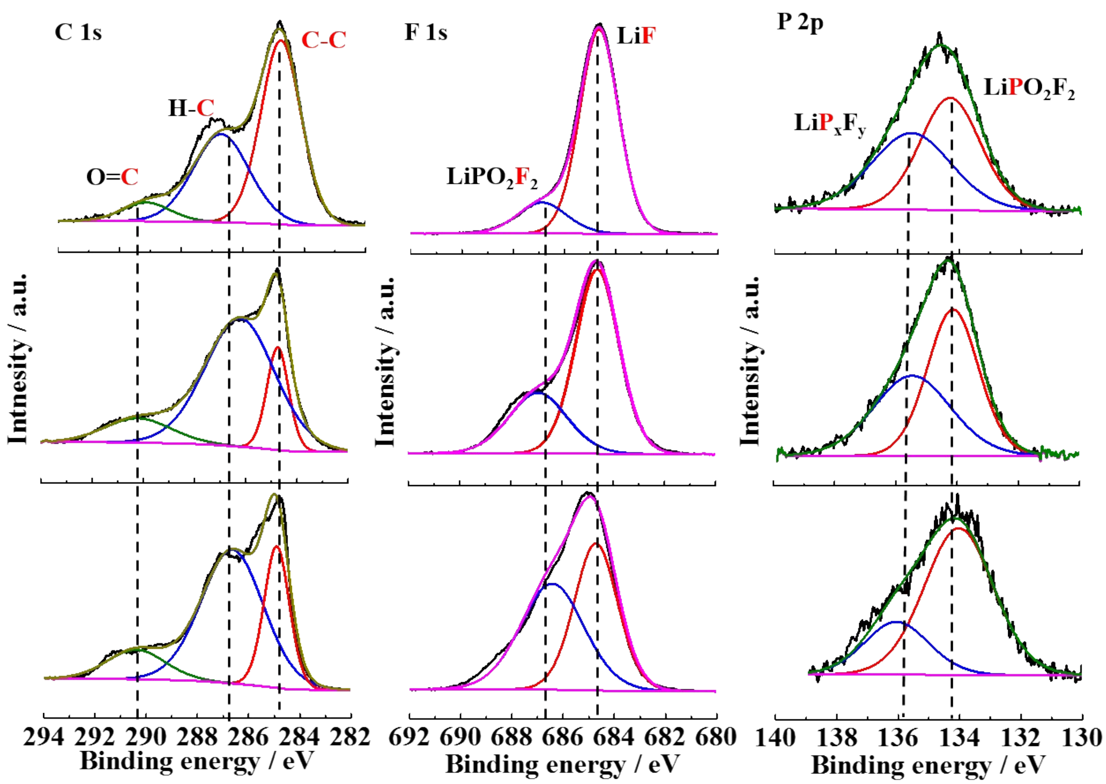

Fig. S4. C 1s, F 1s and P 2p XPS spectra of the $LCoO_2$ electrodes from the (top row) the cell with the electrolyte A0, the cell with the electrolyte A1, and the (bottom row) cell with the electrolyte A2 after 160 cycles at 25°C.

In the C 1 s spectra, the peak located at 284.8 eV is assigned to C-C. The peak at 286.7 eV is attributed to C-O bond, and the peak at 289.9 eV is classified to OCO_2 group. These groups can be attributed to $ROCO_2Li$, ROLi and Li_2CO_3 species, which result from the decomposition of the electrolyte on the electrode surface.[1] In the F 1 s spectra and P 2p spectra[2]. We get the same spectra with the results of the graphite surface.

1. M. Xu, L. Hao, Y. Liu, W. Li, L. Xing and B. Li, *J. Phys. Chem. C*, 2011, 115, 6085-6094.
2. M. Q. Xu, Y. L. Liu, B. Li, W. S. Li, X. P. Li and S. J. Hu, *Electrochem. Commun.*, 2012, 18, 123-126.