

Supplementary Information

Exploiting Cationic Vacancies for Increased Energy Densities in Dual-Ion Batteries

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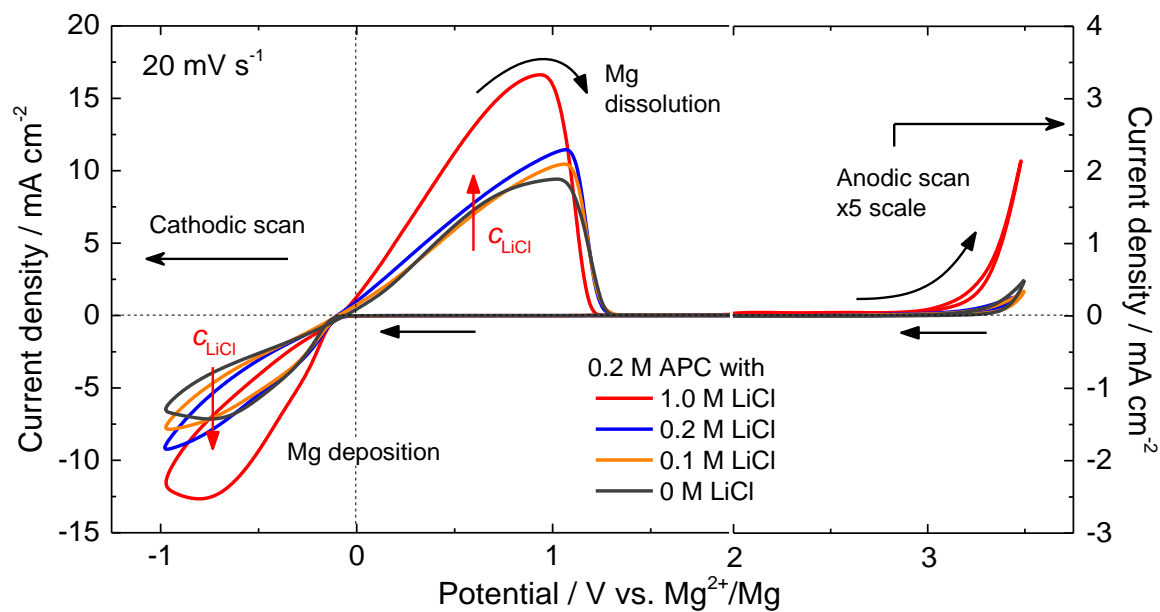


Figure S1 (a) Cyclic voltammograms for a Pt foil working electrode (1.27 cm²) in APC with various LiCl concentrations (scan rate: 20 mV s⁻¹).

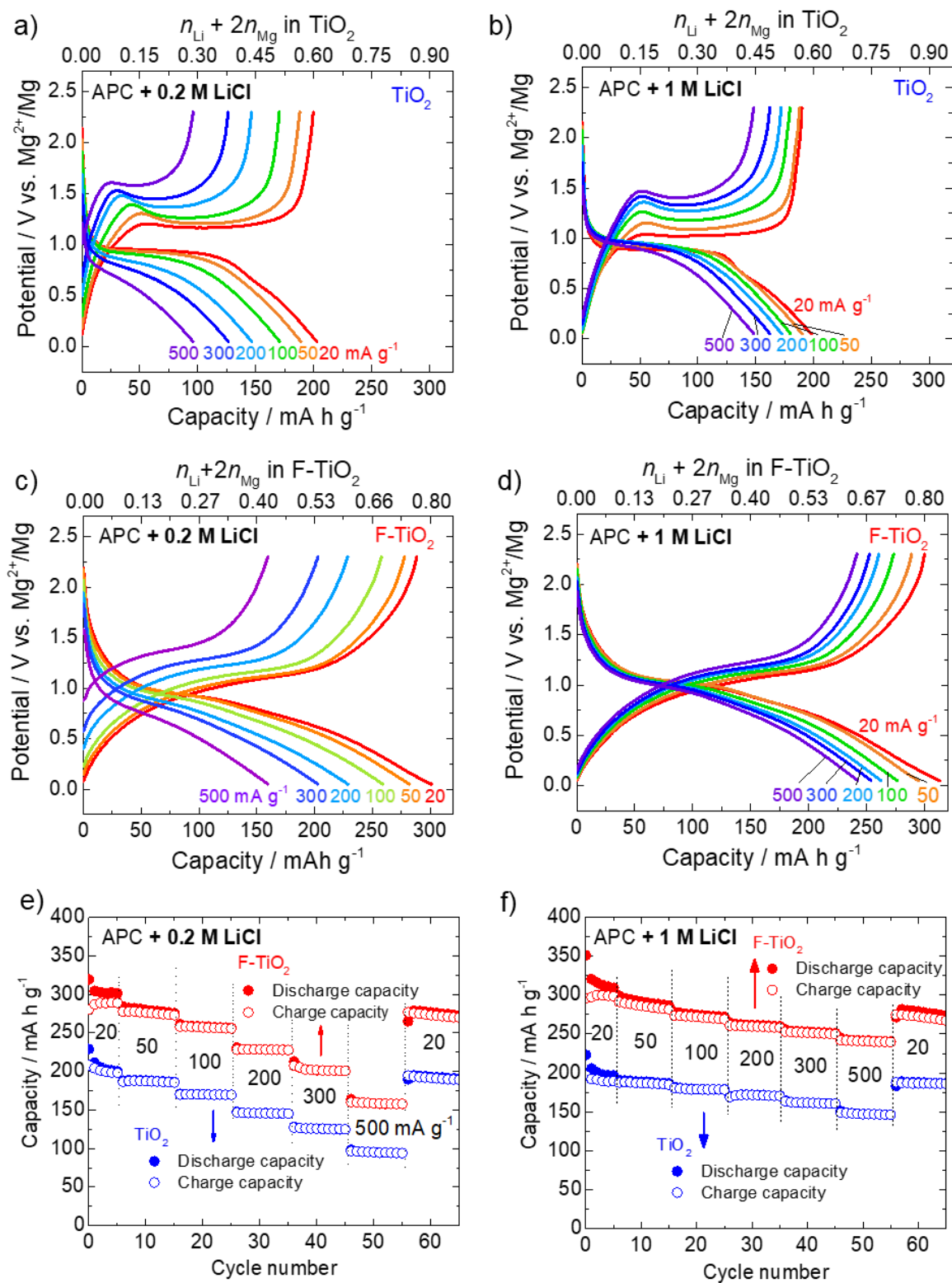


Figure S2. Discharge-charge profiles of (a) Mg/TiO_2 and (b) $\text{Mg}/\text{Ti}_{0.78}\square_{0.22}\text{O}_{1.12}\text{F}_{0.40}(\text{OH})_{0.48}$ cells with APC + 0.2-1 M LiCl at different current densities of 20, 50, 100, 200, 300, 500 mA g^{-1} .

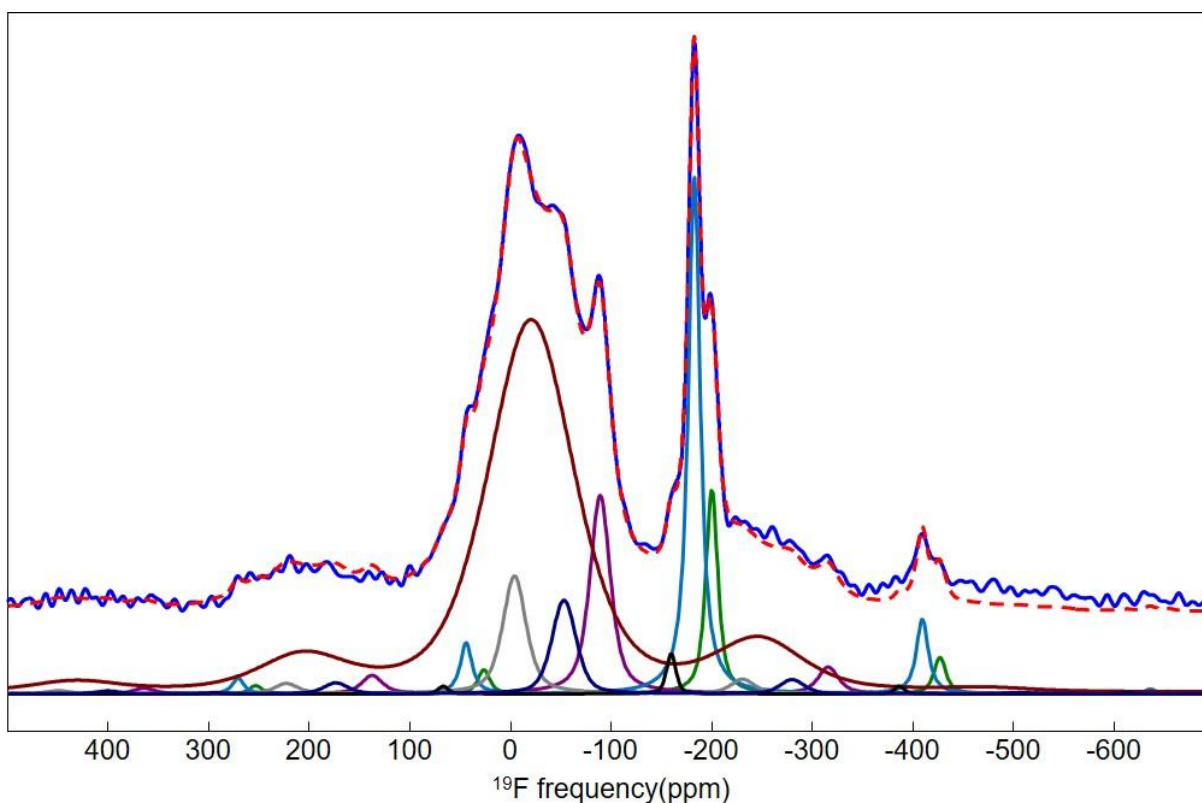


Figure S3. Experimental (in blue) and fitted (in dashed red) ^{19}F solid-state MAS (64 kHz) NMR spectra of the electrochemically charged electrode using hybrid electrolyte 0.2 M APC + 0.2 M LiCl. The individual resonances used for the fit are shown below (see **Table S1**).

Table S1. Isotropic chemical shifts (δ_{iso} , ppm), line widths (LW, ppm), relative intensities (I, %) and tentative and partial assignment of the NMR resonances used for the fit of the ^{19}F MAS (64 kHz) NMR spectrum of the electrochemically charged electrode using hybrid electrolyte 0.2 M APC + 0.2 M LiCl. Weighted average isotropic chemical shift value ($\langle\delta_{\text{iso}}\rangle$, ppm).

δ_{iso}	LW	I	Assignment
-3.7	27.6	5.6	$\text{F-Ti}^{\text{IV}}_2\text{□}$, $\text{F-Ti}^{\text{IV}}\text{Mg□}$, $\text{F-Ti}^{\text{III}}\text{□}_2$,...
-20.3	100.9	60.5	
-53.0	28.3	4.5	...
-88.9	24.1	8.5	$\text{F-Ti}^{\text{IV}}_3$, $\text{F-Ti}^{\text{IV}}\text{Ti}^{\text{III}}\text{□}$, $\text{F-Ti}^{\text{IV}}_2\text{Mg}$, $\text{F-Ti}^{\text{III}}\text{Mg}$,...
-159.5	11.3	0.9	$\text{F-Ti}^{\text{IV}}_2\text{Ti}^{\text{III}}$, $\text{F-Ti}^{\text{III}}_2\text{□}$, $\text{F-Ti}^{\text{IV}}\text{Ti}^{\text{III}}\text{Mg}$, $\text{F-Ti}^{\text{IV}}\text{Mg}_2$,...
-182.4	14.0	14.4	
-199.9	14.3	5.7	$\text{F-Ti}^{\text{IV}}\text{Ti}^{\text{III}}_2$, $\text{F-Ti}^{\text{III}}_2\text{Mg}$, $\text{F-Ti}^{\text{III}}\text{Mg}_2$,...
	$\langle\delta_{\text{iso}}\rangle$	-61	

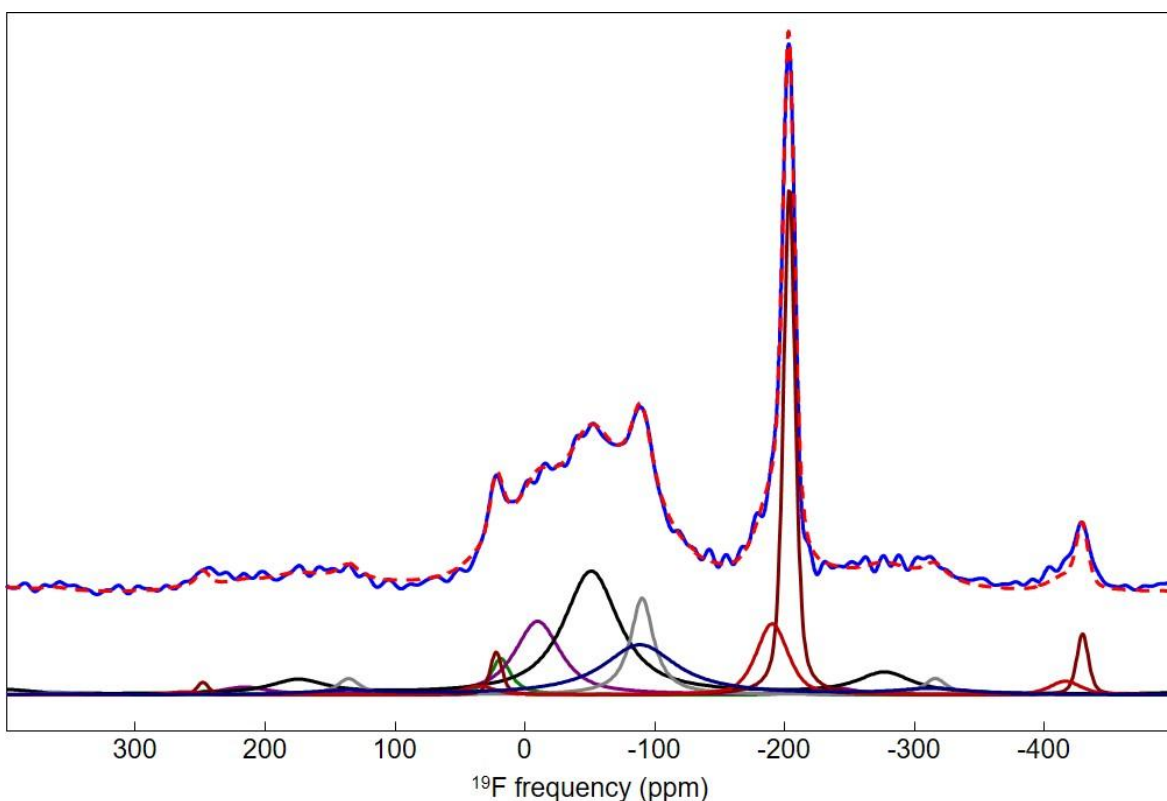


Figure S4. Experimental (in blue) and fitted (in dashed red) ^{19}F solid-state MAS (64 kHz) NMR spectra of the electrochemically discharged electrode using hybrid electrolyte 0.2 M APC + 0.2 M LiCl. The individual resonances used for the fit are shown below (see **Table S2**).

Table S2. Isotropic chemical shifts (δ_{iso} , ppm), line widths (LW, ppm), relative intensities (I, %) and tentative and partial assignment of the NMR resonances used for the fit of the ^{19}F MAS (64 kHz) NMR spectrum of the electrochemically discharged electrode using hybrid electrolyte 0.2 M APC + 0.2 M LiCl. Weighted average δ_{iso} value ($\langle\delta_{\text{iso}}\rangle$, ppm).

δ_{iso}	LW	I	Assignment
19.0	18.4	3.1	F-Ti ^{IV} ₂ □, F-Ti ^{IV} Mg□, F-Ti ^{III} □ ₂ ...
-9.4	41.7	12.9	
-50.7	51.1	28.9	...
-88.2	69.3	15.1	F-Ti ^{IV} ₃ , F-Ti ^{IV} Ti ^{III} □, F-Ti ^{IV} ₂ Mg, F-Ti ^{III} Mg□,...
-89.9	21.4	10.5	
-190.1	28.7	8.6	F-Ti ^{IV} ₂ Ti ^{III} , F-Ti ^{III} ₂ □, F-Ti ^{IV} Ti ^{III} Mg, F-Ti ^{IV} Mg ₂ ...
-203.4	10.8	21.0	F-Ti ^{IV} Ti ^{III} ₂ , F-Ti ^{III} ₂ Mg, F-Ti ^{III} Mg ₂ ...
$\langle\delta_{\text{iso}}\rangle$		-97	

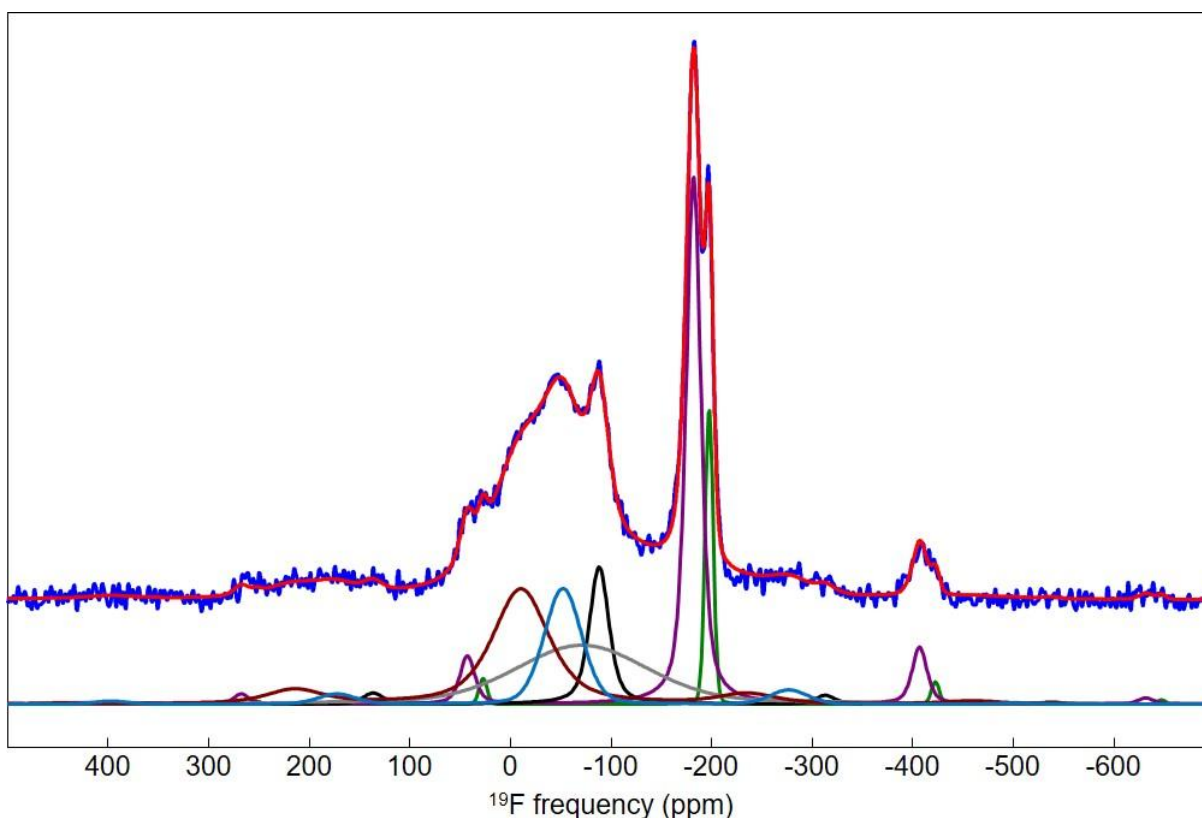


Figure S5. Experimental (in blue) and fitted (in dashed red) ^{19}F solid-state MAS (64 kHz) NMR spectra of the electrochemically charged electrode using hybrid electrolyte 0.2 M APC + 1 M LiCl. The individual resonances used for the fit are shown below (see **Table S3**).

Table S3. Isotropic chemical shifts (δ_{iso} , ppm), line widths (LW, ppm), relative intensities (I, %) and tentative and partial assignment of the NMR resonances used for the fit of the ^{19}F MAS (64 kHz) NMR spectrum of the electrochemically charged electrode using hybrid electrolyte 0.2 M APC + 1 M LiCl. Weighted average δ_{iso} value ($\langle\delta_{\text{iso}}\rangle$, ppm).

δ_{iso}	LW	I	Assignment
-10.7	66.1	23.1	F-Ti ^{IV} ₂ □, F-Ti ^{IV} Mg□, F-Ti ^{III} □ ₂ ...
-52.5	43.8	13.4	...
-71.3	155.1	19.9	F-Ti ^{IV} ₃ , F-Ti ^{IV} Ti ^{III} □, F-Ti ^{IV} ₂ Mg, F-Ti ^{III} Mg□,...
-88.5	23.1	9.0	
-182.3	17.5	27.9	F-Ti ^{IV} ₂ Ti ^{III} , F-Ti ^{III} ₂ □, F-Ti ^{IV} Ti ^{III} Mg, F-Ti ^{IV} Mg ₂ ,...
-197.9	9.4	6.8	F-Ti ^{IV} Ti ^{III} ₂ , F-Ti ^{III} ₂ Mg, F-Ti ^{III} Mg ₂ ,...
$\langle\delta_{\text{iso}}\rangle$		-96	

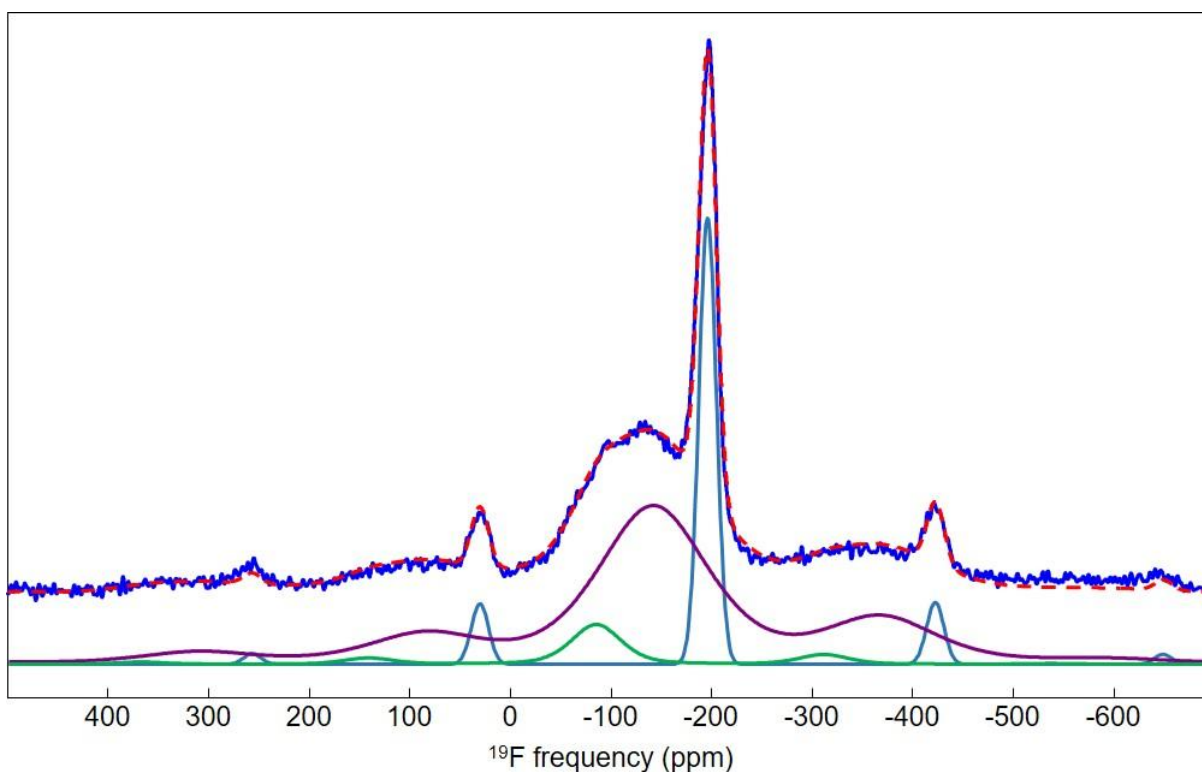


Figure S6. Experimental (in blue) and fitted (in dashed red) ^{19}F solid-state MAS (64 kHz) NMR spectra of the electrochemically discharged electrode using hybrid electrolyte 0.2 M APC + 1 M LiCl. The individual resonances used for the fit are shown below (see **Table S4**).

Table S4. Isotropic chemical shifts (δ_{iso} , ppm), line widths (LW, ppm), relative intensities (I, %) and tentative and partial assignment of the NMR resonances used for the fit of the ^{19}F MAS (64 kHz) NMR spectrum of the electrochemically discharged electrode using hybrid electrolyte 0.2 M APC + 1 M LiCl. Weighted average δ_{iso} value ($\langle\delta_{\text{iso}}\rangle$, ppm).

δ_{iso}	LW	I	Assignment
-85.6	58.6	7.8	F-Ti ^{IV} ₃ -F, F-Ti ^{IV} Ti ^{III} □, F-Ti ^{IV} ₂ Mg, F-Ti ^{III} Mg□, ...
-142.2	129.2	69.3	F-Ti ^{III} ₂ □, F-Ti ^{IV} ₂ Ti ^{III} , F-Ti ^{III} ₂ □, F-Ti ^{IV} Ti ^{III} Mg, F-Ti ^{IV} Mg ₂ ...
-196.3	20.3	22.9	F-Ti ^{IV} Ti ^{III} ₂ , F-Ti ^{III} ₂ Mg, F-Ti ^{III} Mg ₂ ...
$\langle\delta_{\text{iso}}\rangle$		-150	

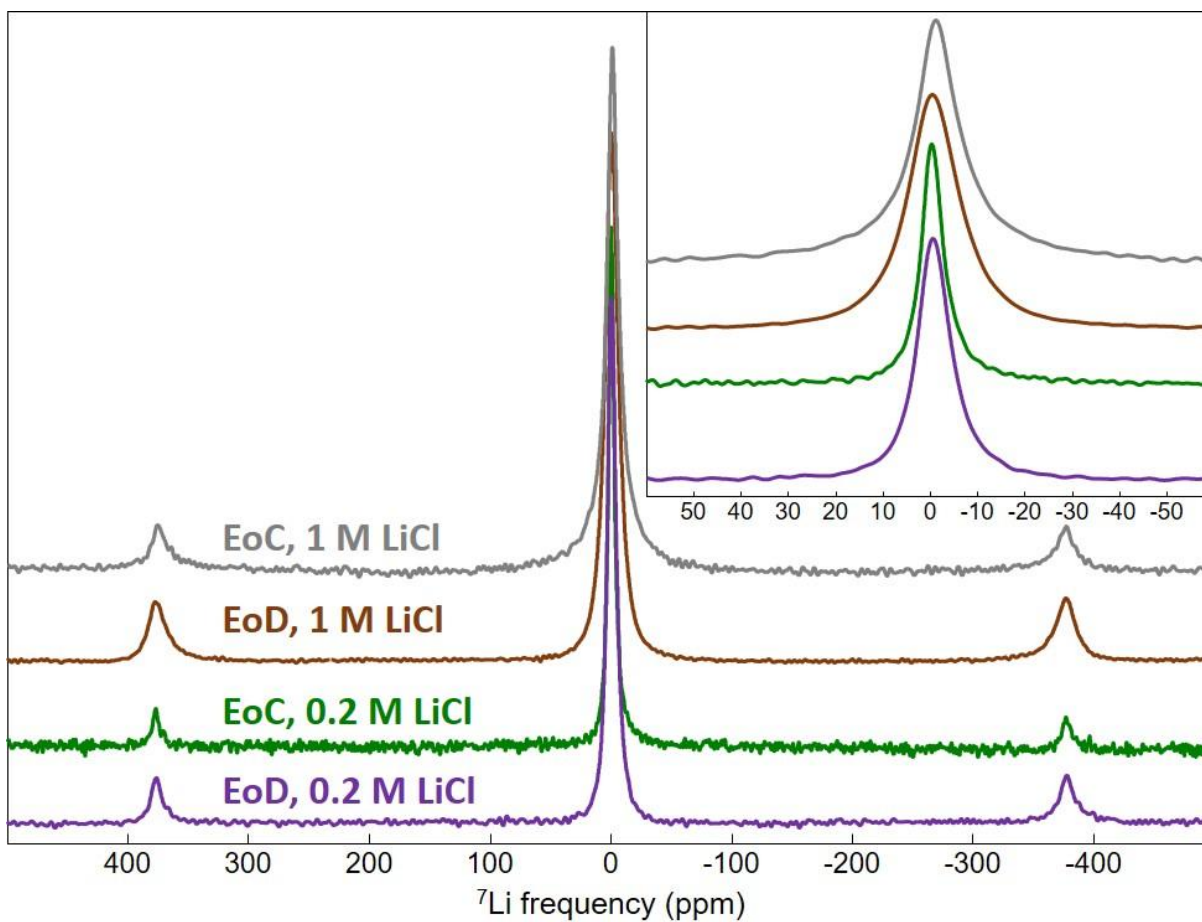


Figure S7. Normalized ^7Li MAS (44 kHz) NMR spectra of the electrochemically discharged (EoD) and charged (EoC) electrodes using hybrid electrolyte 0.2 M APC + 0.2 M LiCl and 1 M LiCl. Expansions of the central lines are shown in the inset.

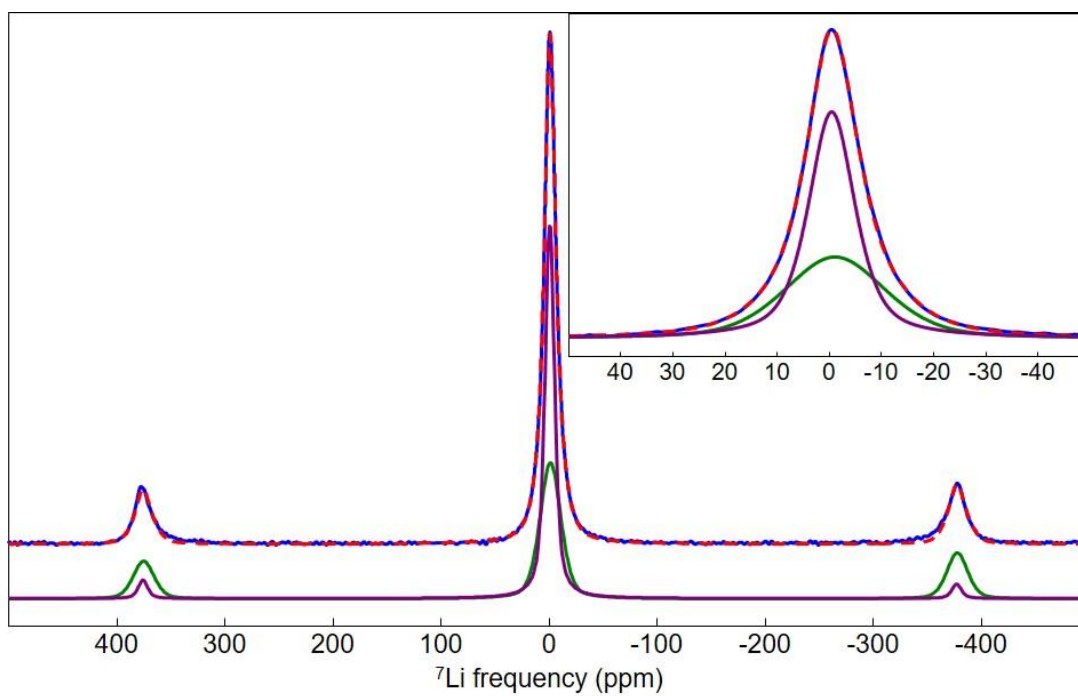


Figure S8. Experimental (in blue) and fitted (in dashed red) ${}^7\text{Li}$ solid-state MAS (44 kHz) NMR spectra of the electrochemically discharged electrode using hybrid electrolyte 0.2 M APC + 1 M LiCl. The individual resonances used for the fit are shown below (see **Table S5**). Expansions of the central lines are shown in the inset.

Table S5. Isotropic chemical shifts (δ_{iso} , ppm), line widths (LW, ppm) and relative intensities (I, %) of the NMR resonances used for the fit of the ^7Li MAS (44 kHz) NMR spectra of the electrochemically charged and discharged electrode using hybrid electrolyte 0.2 M APC + 0.2 M and 1 M LiCl. Weighted average δ_{iso} ($\langle\delta_{\text{iso}}\rangle$, ppm) and LW ($\langle\text{LW}\rangle$, ppm) values.

Sample	δ_{iso}	LW	I
EoC 0.2 M LiCl	-3.2	12.9	28.5
	-0.2	5.0	71.5
$\langle\delta_{\text{iso}}\rangle/\langle\text{LW}\rangle$	-1.1	7.2	
EoD 0.2 M LiCl	-2.5	19.0	30.6
	-0.6	7.6	69.4
$\langle\delta_{\text{iso}}\rangle/\langle\text{LW}\rangle$	-1.2	11.1	
EoC 1 M LiCl	-2.0	23.1	64.5
	-1.1	8.3	35.5
$\langle\delta_{\text{iso}}\rangle/\langle\text{LW}\rangle$	-1.7	17.9	
EoD 1 M LiCl	-1.1	22.8	52.8
	-0.5	10.6	47.2
$\langle\delta_{\text{iso}}\rangle/\langle\text{LW}\rangle$	-0.8	17.0	