Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Understanding SEI evolutions during cycling test of anode-free lithium-metal batteries with LiDFOB salt

Naufal Hanif Hawari,[a,b] Huiqing Xie,[a] Achmad Prayogi,[b] Afriyanti Sumboja,[b,*] Ning Ding[a,*]

[a] Institute of Materials Research and Engineering, A*STAR (Agency for Science, Technology, and Research), 138634, Singapore;

[b] Material Science and Engineering Research Group, Faculty of Mechanical and Aerospace, Institut Teknologi Bandung, Jl. Ganesha 10, Bandung 40132, Indonesia;

* Correspondences: sumboja@itb.ac.id (A.S.), dingni@imre.a-star.edu.sg (N.D.)

S1. Plated lithium on Cu foil with different electrolyte

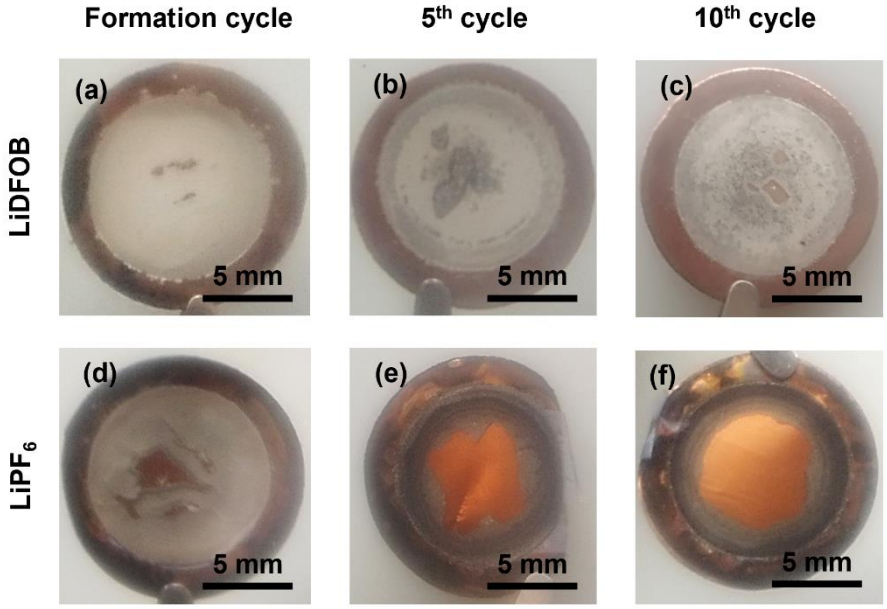

Figure S1. Plated Li metal on Cu foil after fully charging the NMC||Cu cells with the electrolyte comprised of 1M LiDFOB dissolved in EC:DEC (1:1, v/v) in the (a) formation cycle, (b) 5^{th} cycle, (c) 10^{th} cycle; and of 1M $LiPF_6$ in EC:DEC (1:1, v/v) in the (d) formation cycle, (e) 5^{th} cycle, (f) 10^{th} cycle.

S2. Fitting procedure of EIS data

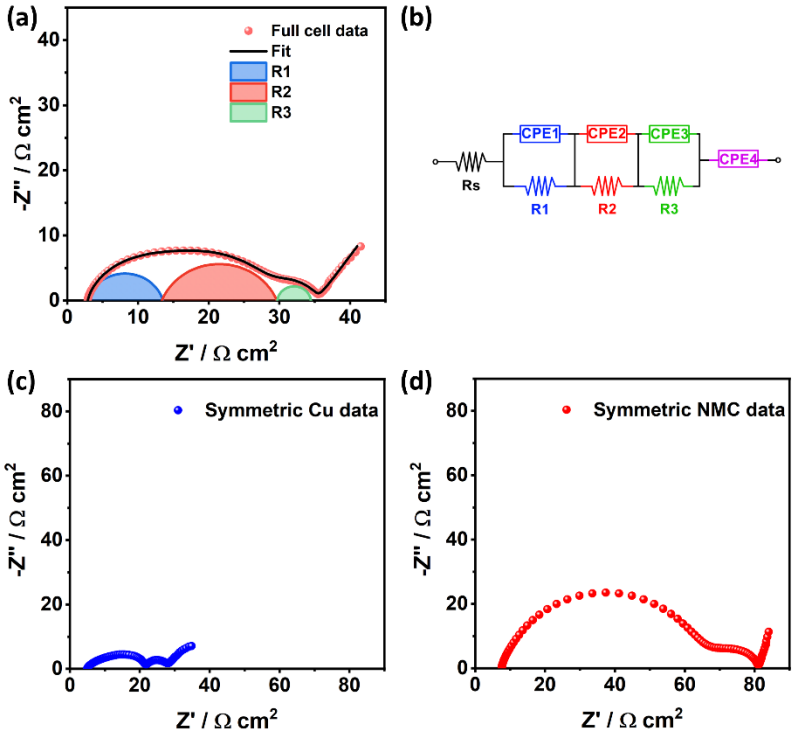

Figure S2. Nyquist plots of a fully charged NMC||Cu cell and the symmetric cells built from the electrodes retrieved from two NMC||Cu cells (1st charging after the formation cycle) with 1M LiDFOB electrolyte dissolved in EC:DEC (1:1, v/v). (a) impedance data fitting and (b) the equivalent circuit for fitting of the Nyquist plots of NMC||Cu cell. Representative's Nyquist plot of (c) Li plated Cu||Cu (i.e., anode) and (d) charged NMC||NMC (i.e., cathode) symmetric cell. R_s, R_1, R_2, and R_3 represents the resistance from electrolyte (R_s), SEI from anode ($R_{SEI\text{-}anode}$), cathode interphase electrolyte ($R_{CEI\text{-}cathode}$) and the charge transfer (R_{ct}), respectively.

The intersection of R_s at Z" = 0 is mainly from the resistance of electrolyte solution (partially attributed by the electric contact). Three distinct semi-circles are observed in the resulted Nyquist plot. Thus, we fitted the plot using three *R-CPE* circuits in series, followed by CPE as shown in **Figure S2b**. To better understand the cathode and anode contributions in the impedance spectra of AFLMBs, we used the electrodes obtained from two fully charged NMC||Cu cells and assembled the symmetric Li-Cu||Li-Cu (**Figure S2c**) and NMC||NMC cells (**Figure S2d**). The anode symmetric cell exhibits much smaller semicircles than the cathode symmetric cell. In comparison with the Nyquist plot of the full cell, the negative Li on Cu electrode contributes to high frequency (i.e., first semi-circles, R_1) which has lower and more suppressed semicircle. On the other hand, the cathode side contributes to the medium

frequency (i.e., second semi-circle, R_2) which has higher impedance value. R_3, at the low frequency, is from the charge transfer resistance, which varies with the electric field and cannot be deconvoluted based on the symmetric cell data.

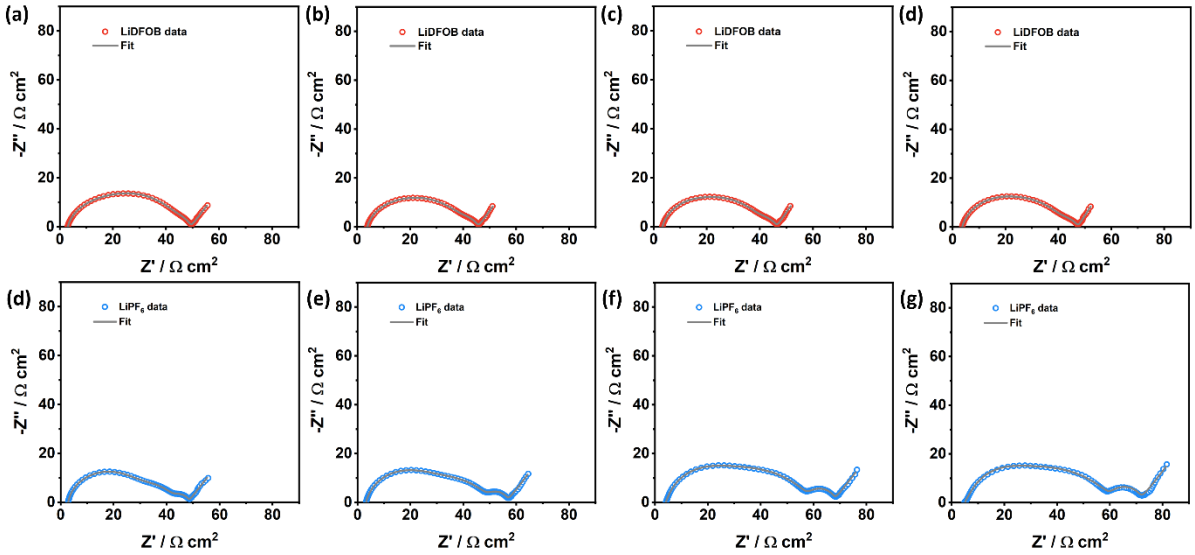

Figure S3. Fitted Nyquist plots of the fully charged NMC||Cu cells with (a-d) LiDFOB and (e-h) $LiPF_6$ electrolyte in the 1st, 5th, 10th, and 15th cycle.

S3. Fitting parameters of EIS data

Table S1. Fitting parameters of NMC||Cu cells with $LiPF_6$ and LiDFOB electrolyte

Parameters	Unit	$LiPF_6$				LiDFOB			
		1st cycle	5th cycle	10th cycle	15th cycle	1st cycle	5th cycle	10th cycle	15th cycle
OCV	V	4.4003	4.4009	4.3881	4.3521	4.3875	4.4156	4.4122	4.3918
R_s	Ω cm^2	2.77321	3.046202	3.918079	4.720776	2.907728	3.134938	3.234187	3.552734
$R_{SEI\text{-}anode}$	Ω cm^2	25.03836	18.94211	13.53541	8.848319	14.52677	15.36214	17.45225	20.95309
CPE_1 Y_0	$\Omega^{-1}s^{n_1}$	4.9328E-06	4.5439E-06	3.055E-06	1.8128E-06	2.056E-05	5.626E-05	1.5304E-05	1.5199E-05
CPE_1 n		0.90251	0.93845	1.0096	1.1	0.8451	0.84701	0.85958	0.85127
$R_{CEI\text{-}cathode}$	Ω cm^2	15.24231	28.35948	41.68237	47.93122	24.46299	18.20735	17.26686	15.25023
CPE_2 Y_0	$\Omega^{-1}s^{n_2}$	0.00025	0.00021488	0.00011887	0.00011297	4.666E-05	1.656E-05	6.4271E-05	8.9333E-05
CPE_2 n		0.7621	0.66727	0.6668	0.63829	0.84834	0.85726	0.84507	0.83376
R_{ct}	Ω cm^2	5.026324	5.951782	8.126333	9.417023	7.395077	8.320535	8.364621	7.55062
CPE_3 Y_0	$\Omega^{-1}s^{n_3}$	0.0065393	0.0073946	0.0072711	0.0075733	0.002397	0.0026729	0.003171	0.0039061
CPE_3 n		0.91512	1.0018	1.0174	1.0224	0.7543	0.72728	0.71266	0.71909
CPE_4 Y_0	$\Omega^{-1}s^{n_4}$	0.48732	0.43816	0.40611	0.33804	0.57854	0.6428	0.67363	0.73152
CPE_4 n		0.60604	0.60768	0.60985	0.60786	0.61136	0.63142	0.64332	0.6634
χ^2		0.0031947	0.0031838	0.0036525	0.025055	0.010569	0.0092195	0.0070283	0.0033764

S4. Solution resistance and charge transfer resistance growth

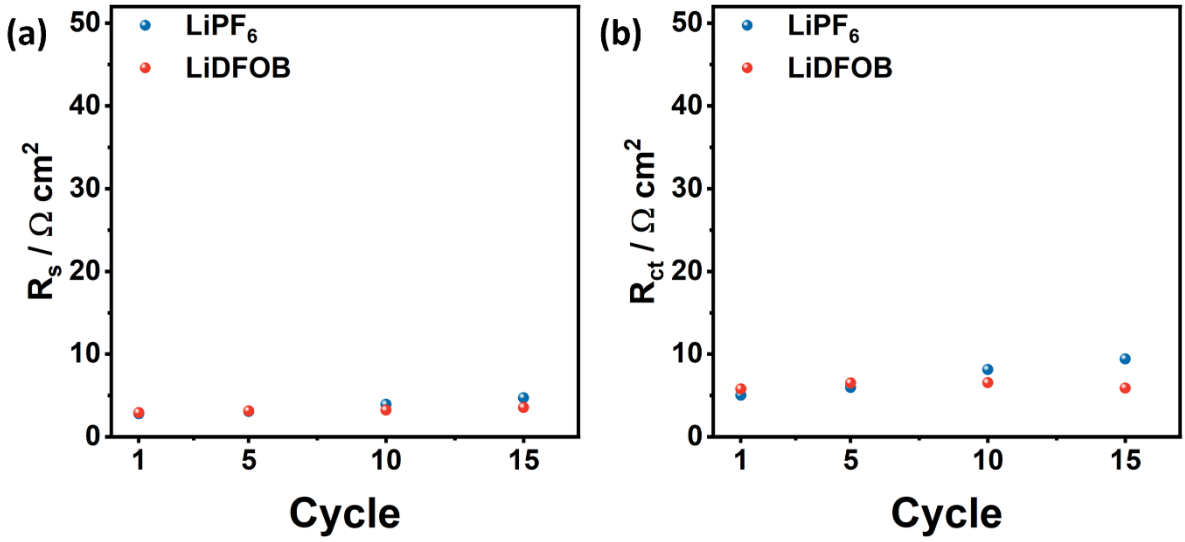

Figure S4. (a) Solution resistance (R_s) and (b) Charge transfer resistance (R_{ct}) growth of NMC||Cu cell with LiDFOB and $LiPF_6$ based electrolyte within 15 cycles.