Evaluating the solid electrolyte interphase formed on silicon electrodes: a comparison of *ex situ* X-ray photoelectron spectroscopy and *in situ* neutron reflectometry

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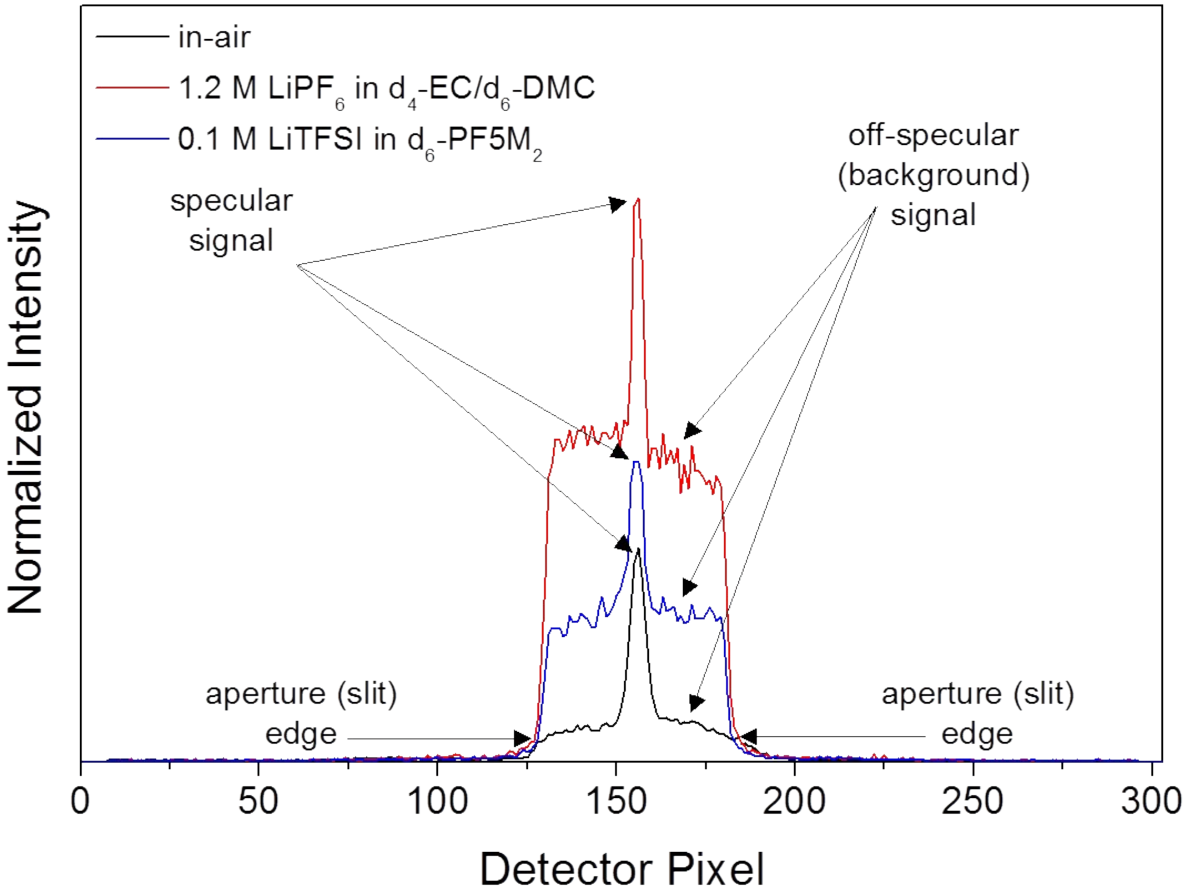

Figure S1. High-Q NR data before background subtraction. This data demonstrates the low background signal of the $PF5M_2$ electrolyte as compared to a deuterated EC/DMC electrolyte.[1]

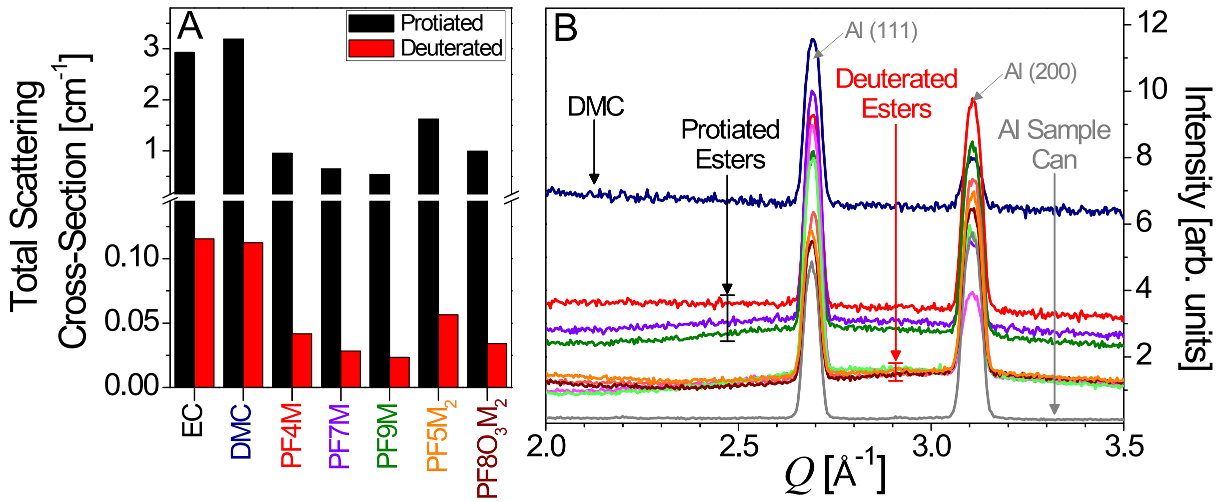

Figure S2. (A) Calculated total scattering cross-sections for a series of previously-investigated[2] deuterated and protiated perfluorocarboxylate esters as compared to deuterated and protiated ethylene carbonate (EC) and dimethyl carbonate (DMC). (B) Diffuse scattering profiles for deuterated and protiated perfluorocarboxylate esters as compared to protiated DMC, experimentally demonstrating the predicted low scattering cross-sections of the perfluorocarboxylate esters.

Energy-integrated diffuse neutron scattering profiles were collected on the University of Missouri Research Reactor (MURR) triple-axis spectrometer (TRIAX) using a 6-mm-diameter Al sample can. The incident wavelength was fixed at 2.36 Å (14.7 meV). Scattered neutrons were monitored from $2\theta = 44.0°$ ($Q = 1.99$ Å^{-1}) to $2\theta = 82.2°$ (3.50 Å^{-1}) at a step-size of 0.1° for 1×10^6 monitor counts (~2 min) per point.

Potentiostatic Voltage	Si Substrate SLD [10^{-6} Å^{-2}]	Interfacial Roughness [nm]	SiO_2 Thickness [nm]	SiO_2 SLD [10^{-6} Å^{-2}]	Interfacial Roughness [nm]	Cu Thickness [nm]	Cu SLD [10^{-6} Å^{-2}]	Interfacial Roughness [nm]	Si Electrode Thickness [nm]	Si Electrode SLD [10^{-6} Å^{-2}]	Interfacial Roughness [nm]	SEI Thickness [nm]	SEI SLD [10^{-6} Å^{-2}]	Interfacial Roughness [nm]	Electrolyte SLD [10^{-6} Å^{-2}]	χ^2
in-air	2.07 ± ?	0.399 ± ?	2.33 ± ?	2.67 ± ?	1.29 ± ?	7.5 ± ?	6.45 ± ?	0.68 ± ?	48.3 ± ?	1.9 ± ?	1.57 ± ?				0 (air)	2.2
OCV	*2.07*	*0.399*	*2.33*	*2.67*	*1.29*	*7.5*	*6.45*	0.02 ± 0.02	48.4 ± 0.1	2.02 ± 0.02	2.3 ± 0.1				4.78	2.0
1.1 V	*2.07*	*0.399*	*2.33*	*2.67*	*1.29*	*7.5*	*6.45*	0.03 ± 0.02	48.3 ± 0.1	2.09 ± 0.02	2.3 ± 0.1				4.78	1.8
0.7 V	*2.07*	*0.399*	*2.33*	*2.67*	*1.29*	*7.5*	*6.45*	0.06 ± 0.04	48.9 ± 0.1	*2.04*	2.5 ± 0.1	14.4 ± 3.2	4.5 ± 0.1	6.6 ± 1.7	4.78	2.3
0.4 V	*2.07*	*0.399*	*2.33*	*2.67*	*1.29*	*7.5*	*6.45*	0.02 ± 0.03	50.5 ± 0.5	*1.93*	3.0 ± 0.5	16.7 ± 6.4	4.5 ± 0.2	6.9 ± 2.4	4.78	7.0
0.08 V	*2.07*	*0.399*	*2.33*	*2.67*	*1.29*	*7.5*	*6.45*	0.01 ± 0.03	106.0 ± 0.3	*0.28*	9.7 ± 0.6	26.6 ± 2.1	4.7 ± 0.1	5.1 ± 2.0	4.78	2.9
2.0 V	*2.07*	*0.399*	*2.33*	*2.67*	*1.29*	*7.5*	*6.45*	0.03 ± 0.03	65.4 ± 1.1	*1.21*	10.1 ± 1.3	34.2 ± 7.2	4.3 ± 0.3	8.6 ± 2.0	4.78	4.1
0.08 V	*2.07*	*0.399*	*2.33*	*2.67*	*1.29*	*7.5*	*6.45*	0.01 ± 0.03	105.9 ± 0.7	*0.28*	11.2 ± 1.1	27.3 ± 2.3	4.3 ± 0.1	11.1 ± 2.6	4.78	3.0
2.0 V	*2.07*	*0.399*	*2.33*	*2.67*	*1.29*	*7.5*	*6.45*	0.02 ± 0.04	66.9 ± 0.6	*1.16*	10.4 ± 0.7	32.2 ± 1.5	4.3 ± 0.1	8.2 ± 1.4	4.78	3.2
0.08 V	*2.07*	*0.399*	*2.33*	*2.67*	*1.29*	*7.5*	*6.45*	0.43 ± 0.02	105.5 ± 0.7	*0.29*	11.2 ± 0.8	28.6 ± 4.0	4.3 ± 0.1	11.9 ± 2.5	4.78	3.9
2.0 V																

Table S1. Multilayer parameters determined from NR fits. Values in italics were not varied independently during fitting.

References:

1. G. M. Veith, M. Doucet, J. K. Baldwin, R. L. Sacci, T. M. Fears, Y. Wang and J. F. Browning, *The Journal of Physical Chemistry C*, 2015, **119**, 20339-20349.
2. T. M. Fears, R. L. Sacci, J. G. Winiarz, H. Kaiser, H. Taub and G. M. Veith, *Journal of Power Sources*, 2015, **299**, 434-442.