Supporting Information

The Redox Mediated - Scanning Droplet Cell System for Evaluation of the Solid Electrolyte Interphase in Li-ion Batteries

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Section S1. The scanning droplet-cell system (SDCS)

The SDCS apparatus comprises seven components: i) an SDC head, which is the electrochemical probe; ii) a pumping system, which is connected to the head and fills it with electrolyte; iii) a positioning system, which moves the head in the X, Y and Z directions with a sub-µm precision; iv) a force sensor coupled to the SDC head to control the SDCS head force on the sample surface; v) a potentiostat, which controls the electrochemical cell; vi) an AD/DA converter; and a vii) a computer that controls each component of the SDCS.

The key element of the SDCS is its head. **Figure S1** shows a picture of the 3-D printed head developed in this work.

Prior to cell fabrication, the 3D-printing material stability in organic solvents was studied. Little pieces of the printed material were exposed to propylene carbonate (PC) and LP30 electrolyte for stability test. Those pieces remained stable in weight and shape for more than two weeks, and the electrolyte and PC stayed transparent, demonstrating the stability of the cell material against organic solvents.

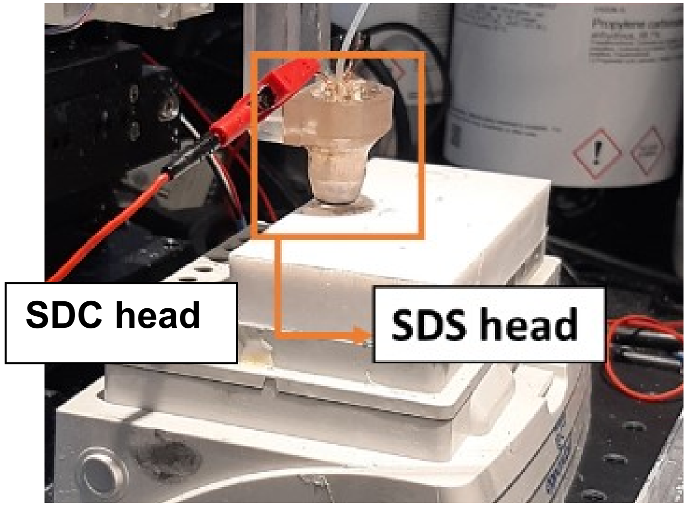

Figure S1. Picture of the 3-D printed head of the SDCS inside the Ar-filled glovebox.

Section S2. Cyclic voltammetry of redox mediators and Cu foil.

The redox potential of ferrocene, which is commonly used as redox mediator for scanning electrochemical miscroscopy, is very close to the oxidation potential of Cu as shown in **Figure S2**.

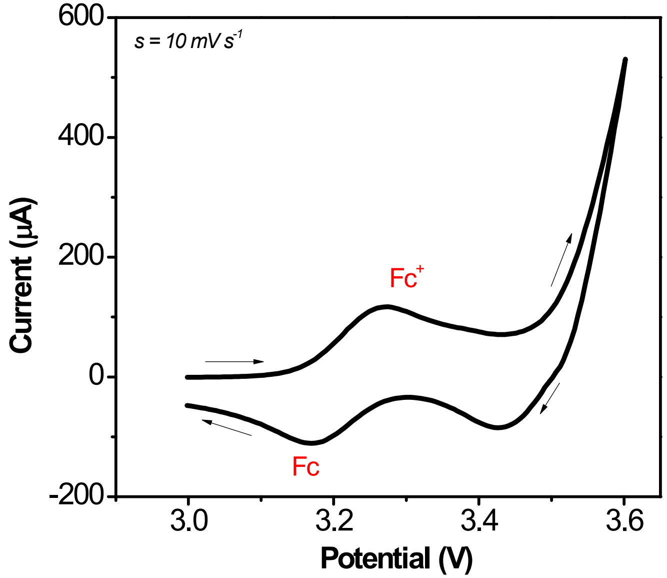

Figure S2. CV recorded on Cu substrate using ferrocene (Fc) as redox mediator at 10 mV s^{-1}.

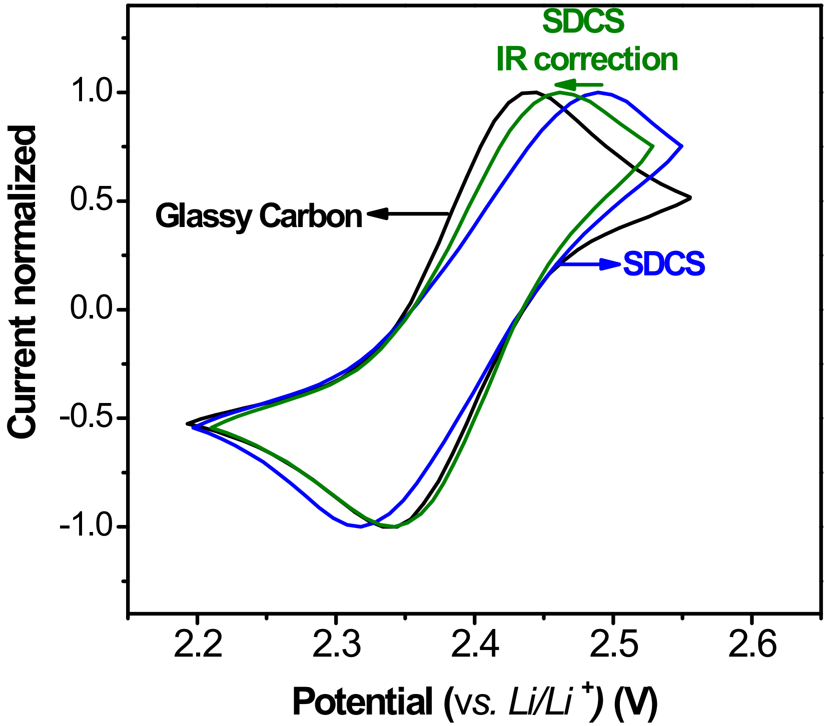

Figure S3. MVD CV recorded on Cu foil using a SDCS set up (blue), on Cu foil using a SDCS set up with a IR correction applied and using a 3-electrode cell whose working electrode is a glassy carbon.

Section S3. Conventional electrochemistry using the SDCS.

The SDCS can be used to perform classic electrochemical measurements such as linear sweep voltammetry for the SEI formation (**Figure S4**) and galvanostatic lithiation-delithiation measurements (**Figure S5**)

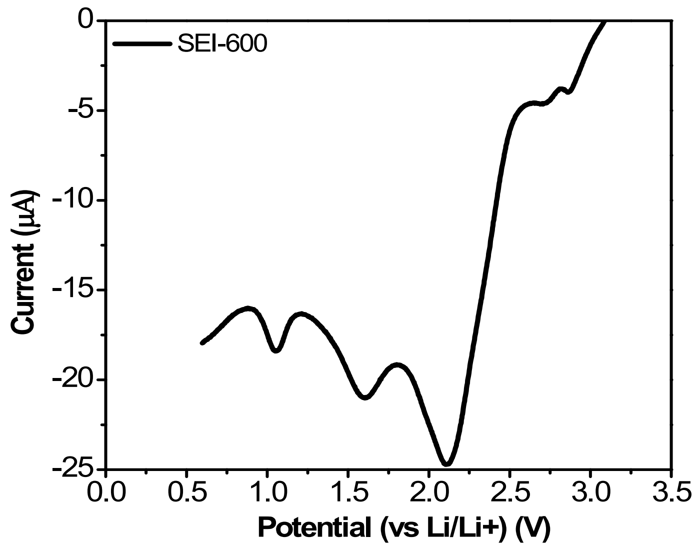

Figure S4. LSV from OCP to 600mV at 5mV s^{-1} recorded on Cu foil during SEI-600 formation.

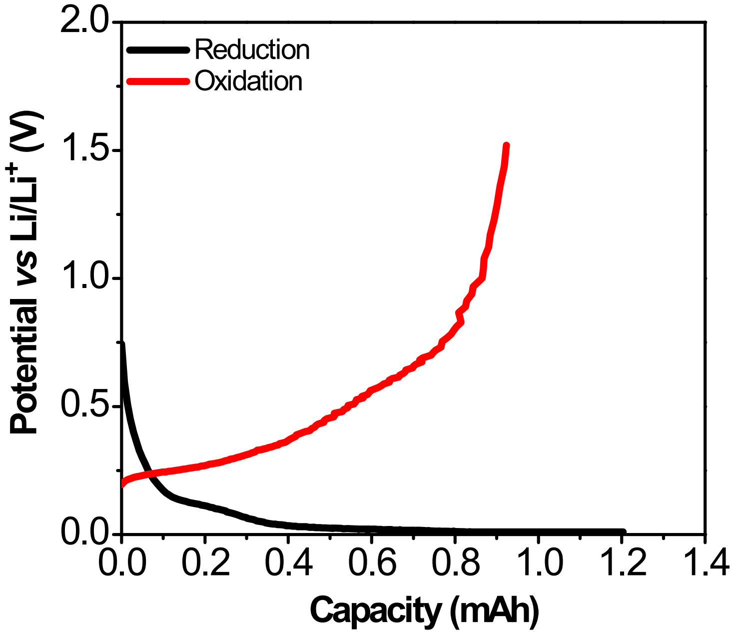

Figure S5. Galvanostatic reduction/lithiation and oxidation/delithiation at ±0.85 mA for a commercial Si-Gr electrode.

Section S4. Cyclic voltammetry and EIS measurements of 16 electrolyte formulations.

Cyclic voltammograms (CVs) recorded for 16 diferent electrolyte formulations are shown in **Figure S6**, and the corresponding EIS spectra in **Figure S7**.

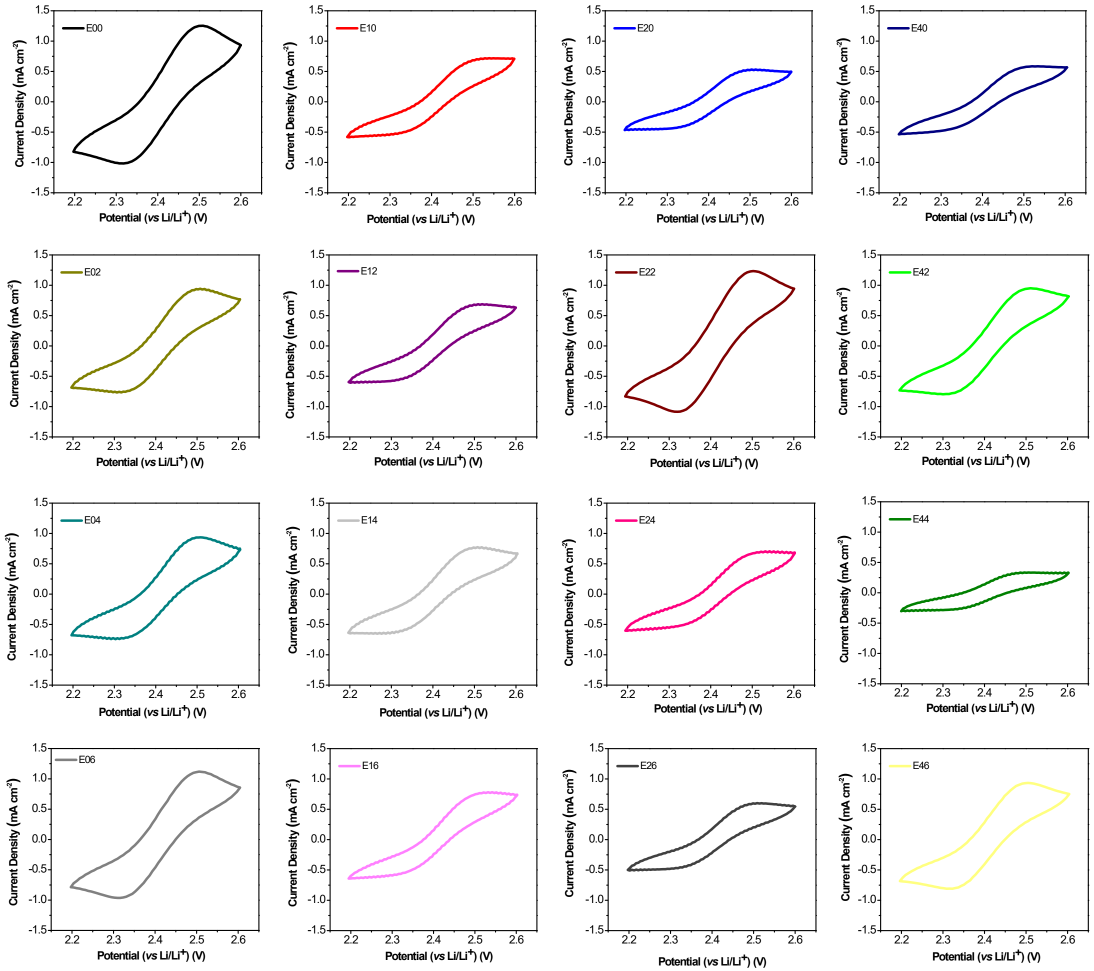

Figure S6. CVs recorded on Si-Gr electrodes after formation of an SEI at 10 mV using advanced electrolytes combining different VC-FEC proportions as additives added to the LP30 electrolyte.

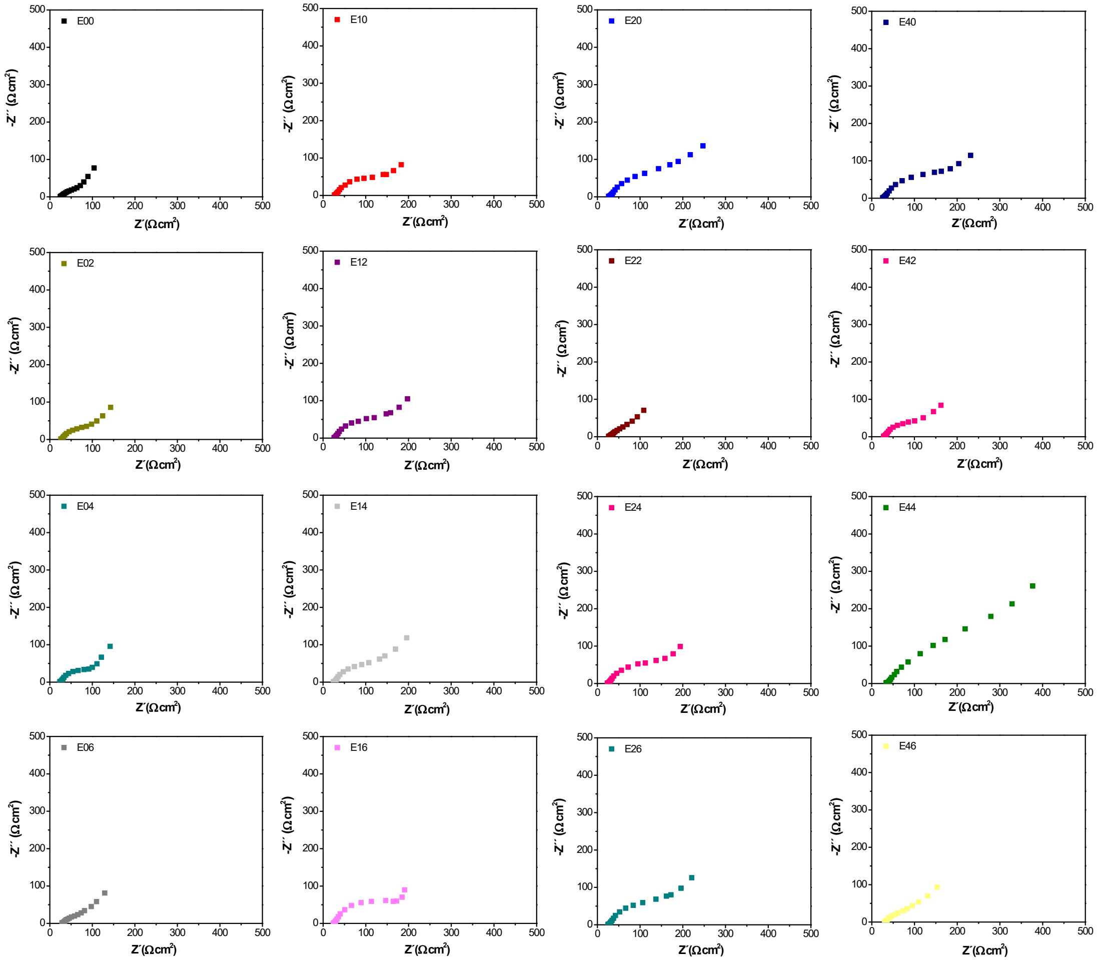

Figure S7. Nyquist plots obtained from EIS measurements recorded on Si-Gr electrodes after formation of the SEI at 10 mV using advance electrolytes combining different VC-FEC proportion as additive in LP30 electrolyte.

Section S5. Electrochemical Impendance Spectroscopy fitting for Cu and Si-Gr electrodes.

The EIS fitting was carried out using Zview impedance fitting software from the Nyquist plot and including the following variables: Frequency (Hz), Z´(Ω), - Z´´ (Ω), Z (Ω), - Phase (º), Time (s). The equivalent circurt appears as follows:

Where, Rb is the electrolyte resistance, Rsei+Rct is SEI and charge transfer resistance, Wo is Warburg element, CPE is constant phase element

Values of Rsei, Warburg and CEP with errors for Cu tests can be seen as follows:**Table S1**. EIS equivalent circuit parameters for Cu.

Test	X^2	STC	Rsei+Rct(+)	Rsei+Rct(Error)	Rsei+Rct(Error%)
SEI-Free	8.1E-05	3.3E-03	57	1.14E+00	1.99E+00
SEI-1400	1.1E-04	4.8E-03	188	3.58E+00	1.91E+00
SEI-1000	1.8E-04	6.1E-03	1325	2.65E+02	2.00E+01
SEI-800	4.4E-05	1.4E-03	1355	9.79E+01	7.22E+00
SEI-600	1.6E-03	6.3E-02	5931	5.07E+02	8.54E+00
SEI-200	1.7E-03	7.2E-02	9536	8.13E+04	8.52E+02

Test	CPEsei+CPEelectrode-T(+)	CPEsei+CPEelectrode-T(+)	CPEsei+CPEelectrode-T(Error)	CPEsei+CPEelectrode-T(Error%)	CPEsei+CPEelectrode-P(Error)
SEI-Free	1.3E-05	0.76	1.93E-06	1.47E+01	1.55E-02
SEI-1400	3.7E-06	0.80	3.31E-07	9.01E+00	9.06E-03
SEI-1000	1.1E-05	0.72	8.39E-07	7.90E+00	8.24E-03
SEI-800	8.7E-06	0.75	3.45E-07	3.98E+00	4.17E-03
SEI-600	4.2E-06	0.82	2.91E-07	7.25E+00	8.85E-03
SEI-200	4.9E-06	0.82	3.33E-07	6.80E+00	8.78E-03

Test	Wwarburg-R(+)	Wwarburg-T(+)	Wwarburg-R(Error)	Wwarburg-R(Error%)	Wwarburg-T(Error)	Wwarburg-T(Error%)	Wwarburg-P(Error)	Wwarburg-P(Error%)
SEI-Free	1E+03	1.1E+01	1.34E+02	1.33E+01	2.94E+00	2.77E+01	5.24E-03	1.02E+00
SEI-1400	4E+03	1.5E+01	3.11E+02	7.23E+00	2.61E+00	1.80E+01	3.70E-03	8.31E-01
SEI-1000	4E-04	1.0E-20	4.15E+01	1.03E+07	1.07E-20	1.07E+02	1.83E-02	1.35E+01
SEI-800	9E-05	3.7E-21	9.18E+00	1.02E+07	9.93E-16	2.67E+07	9.67E-03	5.07E+00
SEI-600	9E-05	1.4E-20	3.99E+01	4.08E+07	1.55E-14	1.12E+08	6.98E-02	3.83E+01
SEI-200	4E+00	7.0E-10	2.45E+05	4.96E+06	9.70E-05	1.38E+07	3.43E-02	1.91E+01

There was no diffusion element for SEI-200 since the high charge transfer resistance do not allows foring diffusion of species. Thus, the Warbugn element was removed and the fitting was improved (error of Rsei+Rct decreased from 80 % to 4 %). Thus, henceforth the equivalent circuit used appears as follows.

The fitting for SEI-200 was repeated with the new equivalente circuit.

Table S2. EIS equivalent circuit parameters for Cu SEI-200.

Test	X2	STC	Rsei+Rct(+)	Rsei+Rct(Error)	Rsei+Rct(Error%)	CPEsei +CPEelect -T(+)	CPEsei +CPEelect -P(+)	CPEsei +CPEelect -T(Error)	CPEsei +CPEelect -T(Error%)	CPEsei+ CPEelectr -P(Error)	CPEsei +CPEelect -P(Error%)
SEI-200	8.76E-03	4.03E-01	17600	7.75E+02	4.41	7.4E-06	7.7E-01	5.7E-07	7.8E+00	1.2E-02	1.5E+00

Using this equivalente circuit for the fitting the error pass from the 80% to 4.41%.

The results obtained for Si-Gr electrode at different potential can be seen in the following table using the equivalent circuit without Warbug element. It should be noted that the lowest 2 or 3 points in some cases were removed when the shape of the Nyquist plot indicated diffusion at lowest frequencies.

Table S2. EIS equivalent circuit parameters for Si-Gr at different SEI voltage formation.

Test	X2	STC	Rsei+ Rct(+)	Rsei+ Rct(Error)	Rsei+ Rct(Error%)	CPEsei +CPEelect -T(+)	CPEsei +CPEelect -P(+)	CPEsei +CPEelect -T(Error)	CPEsei +CPEelect -T(Error%)	CPEsei+ CPEelectr -P(Error)	CPEsei +CPEelect -P(Error%)
SEI-10	0.00021383	0.0081257	413.2	54.697	13.237	0.0025136	0.4669	0.00015861	6.3101	0.012949	2.7734
SEI-50	0.00028121	0.011811	838.5	116.11	13.847	0.0025774	0.45929	0.00010796	4.1887	0.010062	2.1908
SEI-100	0.0011881	0.026139	934.1	39.951	4.277	0.00032452	0.76434	1.65E-05	5.0943	0.014126	1.8481
SEI-200	0.0015642	0.037541	2911	115.8	3.978	0.00024353	0.80414	8.66E-06	3.5562	0.010733	1.3347
SEI-400	0.00067097	0.013419	4373	123.73	2.8294	0.00019105	0.82598	4.05E-06	2.1197	0.0074983	0.90781
SEI-Free	1.05E-06	1.46E-05	8.717	0.85479	9.806	0.0035955	0.4002	0.001065	29.62	0.036042	9.006

The results obtained for Si-Gr electrode using different VC-FEC combination as additive can be found as follows:

Table S2. EIS equivalent circuit parameters for SEI formed using different VC-FEC combination as additive.

Test	X2	STC	Rsei+ Rct(+)	Rsei+ Rct(Error)	Rsei+ Rct(Error%)	CPEsei +CPEelect -T(+)	CPEsei +CPEelect -P(+)	CPEsei +CPEelect -T(Error)	CPEsei +CPEelect -T(Error%)	CPEsei+ CPEelectr -P(Error)	CPEsei +CPEelect -P(Error%)
E00	0.00021383	0.0081257	413.2	54.697	13.237	0.0025136	0.4669	0.00015861	6.3101	0.012949	2.7734
E02	0.0005128	0.020512	387.7	24.557	6.334	0.0011544	0.58301	7.04E-05	6.1015	0.01407	2.4133
E04	0.000828	0.03312	343.7	19.36	5.6328	0.00084417	0.6267	6.06E-05	7.1744	0.016241	2.5915
E06	0.00011543	0.0020778	317.9	34.587	10.88	0.0017683	0.52671	0.00013538	7.6559	0.01793	3.4042
E10	0.00055161	0.023168	519.7	20.431	3.9313	0.0007361	0.61753	3.39E-05	4.6051	0.010895	1.7643
E12	0.00083889	0.035233	593.3	28.616	4.8232	0.00068779	0.61337	3.69E-05	5.3662	0.012495	2.0371
E14	0.00069246	0.027698	554.1	34.384	6.2054	0.000784	0.6204	4.45E-05	5.6783	0.01314	2.118
E16	0.0033634	0.15472	595.2	30.744	5.1653	0.0005361	0.65407	4.44E-05	8.2865	0.02012	3.0761
E20	0.00042938	0.017175	845.7	46.264	5.4705	0.0006541	0.6006	2.67E-05	4.078	0.0091714	1.527

E22	0.0001112	0.0035585	2000	300	40,27	0,0038157	0,44849	1,37E-04	3,5847	0,0092662	2,0661
E24	0.0018894	0.08691	763.5	48.191	6.3119	0.00097058	0.5744	5.61E-05	5.777	0.015048	2.6198
E26	0.00082885	0.02155	772.2	40.838	5.2885	0.00043189	0.71532	2.26E-05	5.2405	0.013326	1.8629
E40	0.0024159	0.11113	866.9	55.444	6.3957	0.00073157	0.56776	4.80E-05	6.5575	0.016047	2.8264
E42	0.00040712	0.0073282	393.2	36.397	9.2566	0.00075234	0.63631	0.000067333	8.9498	0.020972	3.2959
E44	0.00016592	0.0029866	1245	101.54	8.1558	0.00044212	0.64816	1.91E-05	4.3162	0.010054	1.5512
E46	0.00013087	0.0023557	433.8	53.728	12.385	0.0015221	0.55119	1.10E-04	7.2006	0.017069	3.0968