Supporting Information:

Unifying the Clustering Kinetics of Lithium Polysulfides with the Nucleation Behavior of Li_2S in Lithium-Sulfur Batteries

Abhay Gupta and Arumugam Manthiram*

Materials Science & Engineering Program and Texas Materials Institute, The University of Texas at Austin, Austin, TX 78712, United States

Table of Contents

*Corresponding authors:
manth@austin.utexas.edu (A. Manthiram)

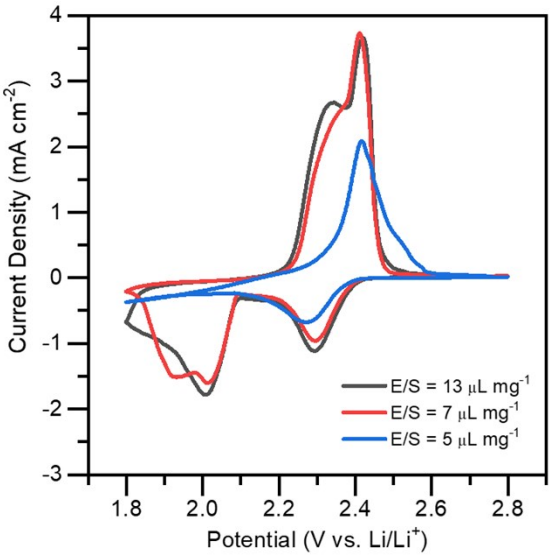

Figure S1. Cyclic voltammograms of Li-S cells with E/S ratios varying from 13 to 5 µL mg^{-1}.

Table S1. Calculated Lithium Polysulfide Diffusion Coefficients

T (°C)	T (K)	i_p (mA cm^{-2})	i_p/electroactive area (A cm^{-2})	D (cm^2 s^{-1})
25	298	-2.895	-1.60E-06	1.77E-11
0	273	-1.388	-7.66E-07	3.72E-12
-10	263	-0.935	-5.16E-07	1.63E-12
-20	253	-0.51	-2.81E-07	4.66E-13

Supporting Discussion

The fall in polysulfide diffusion coefficient can be fitted with an Arrhenius plot, as shown in **Figure R1**. From this analysis, an activation energy of 44 kJ mol^{-1} is found. This is a much steeper activation energy than what has been previously found for the change in diffusion coefficient with temperature from past work. In one of these past works, a ΔE_a on the order of 12 kJ mol^{-1} is found for the various salt and solvent species that exist in the DOL/DME system.[1] This activation energy reflects the diffusional activity from random vibrational motion. While this would certainly play a role in subverting the diffusion coefficient of polysulfides at low temperatures, we see that this on its own does not explain the majority of the losses seen in the data shown here. This reinforces the conclusion that the decline in diffusion coefficient stems predominantly from ion coordination behavior; this decline is anomalously high compared to the decline in diffusion coefficient for other electrolyte components in the DOL/DME system.

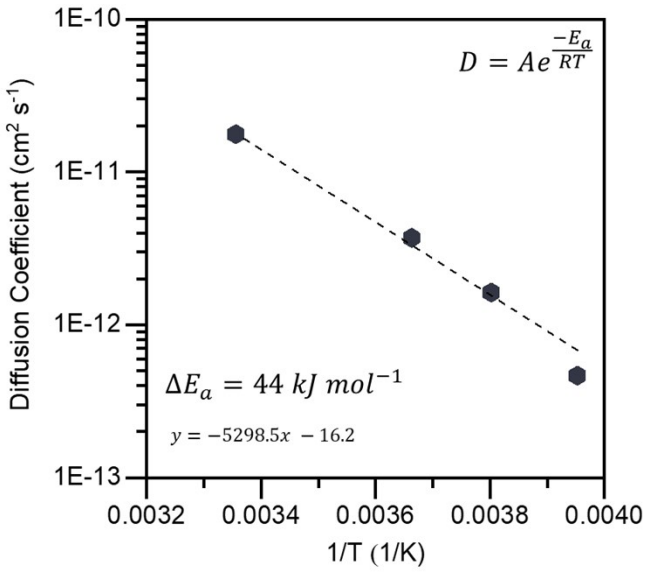

Figure S2. An Arrhenius plot modelling the fall in diffusion coefficient of polysulfides with temperature; an activation energy of 44 kJ mol^{-1} is found.

Table S2. Partial charge analysis on various sized Li_2S_4 clusters, with interior sulfur atoms in bold

Li_2S_4			$(Li_2S_4)_2$			$(Li_2S_4)_4$		
Atom	**Position**	**Charge**	**Atom**	**Position**	**Charge**	**Atom**	**Position**	**Charge**
S	1	-0.76334	S	1	-0.74688	S	1	-0.78794
S	**2**	**-0.12827**	**S**	**2**	**-0.11121**	**S**	**2**	**-0.08499**
S	**3**	**-0.12825**	**S**	**3**	**-0.12159**	**S**	**3**	**-0.0994**
S	4	-0.76333	S	4	-0.74707	S	4	-0.79136
Li	5	0.89158	Li	5	0.85594	Li	5	0.90741
Li	6	0.89161	Li	6	0.87081	Li	6	0.9015
			S	7	-0.74688	S	7	-0.81141
			S	**8**	**-0.11121**	**S**	**8**	**-0.08362**
			Li	9	0.85594	Li	9	0.8995
			Li	10	0.87081	Li	10	0.79501
			S	**11**	**-0.12159**	**S**	**11**	**-0.09588**
			S	12	-0.74706	S	12	-0.74884
						S	13	-0.81141
						S	**14**	**-0.08362**
						Li	15	0.9015
						Li	16	0.89951
						S	**17**	**-0.09588**
						Li	18	0.79502
						S	19	-0.79135
						S	**20**	**-0.08499**
						S	21	-0.74885
						S	22	-0.78793
						S	**23**	**-0.0994**
						Li	24	0.90741
Average interior S charge		-0.12826	**Average interior S charge**		-0.1164	**Average interior S charge**		-0.09097

Table S3. Replications of Chronoamperometry Experiments

T (°C)	25	0	-20
	N_0k^2 (s^{-2})	N_0k^2 (s^{-2})	N_0k^2 (s^{-2})
Trial 1	4.68937E-07	1.00665E-07	2.05967E-09
Trial 2	9.34752E-07	4.92756E-08	1.81964E-09
Trial 3	2.66719E-07	2.99135E-08	3.06583E-09
Trial 4	–	5.92885E-08	–
Trial 5	–	9.05004E-08	–
Average	**5.57E-07**	**6.59E-08**	**2.32E-09**
Standard Dev.	**2.80E-07**	**2.59E-08**	**5.40E-10**

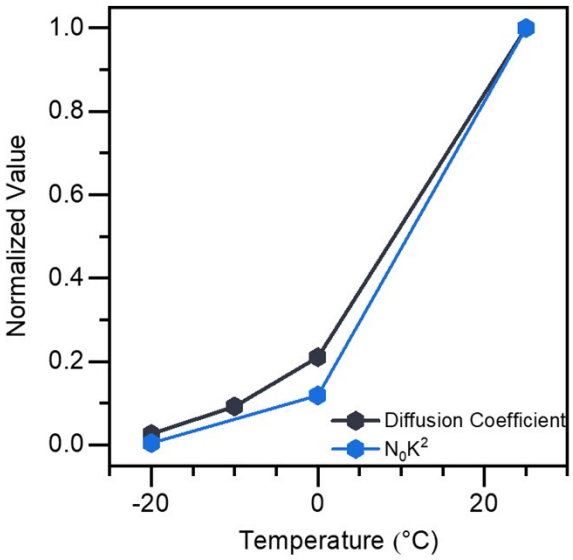

Figure S3. The decline in diffusion coefficient and N_0K^2 with temperature, normalized to the respective values at 25 °C.

References

1 C. Park, M. Kanduč, R. Chudoba, A. Ronneburg, S. Risse, M. Ballauff and J. Dzubiella, *J. Power Sources*, 2018, **373**, 70–78.