Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Taming Polysulfides in Sulfur-based Batteries via Electrolyte-soluble Thiomolybdate Additives

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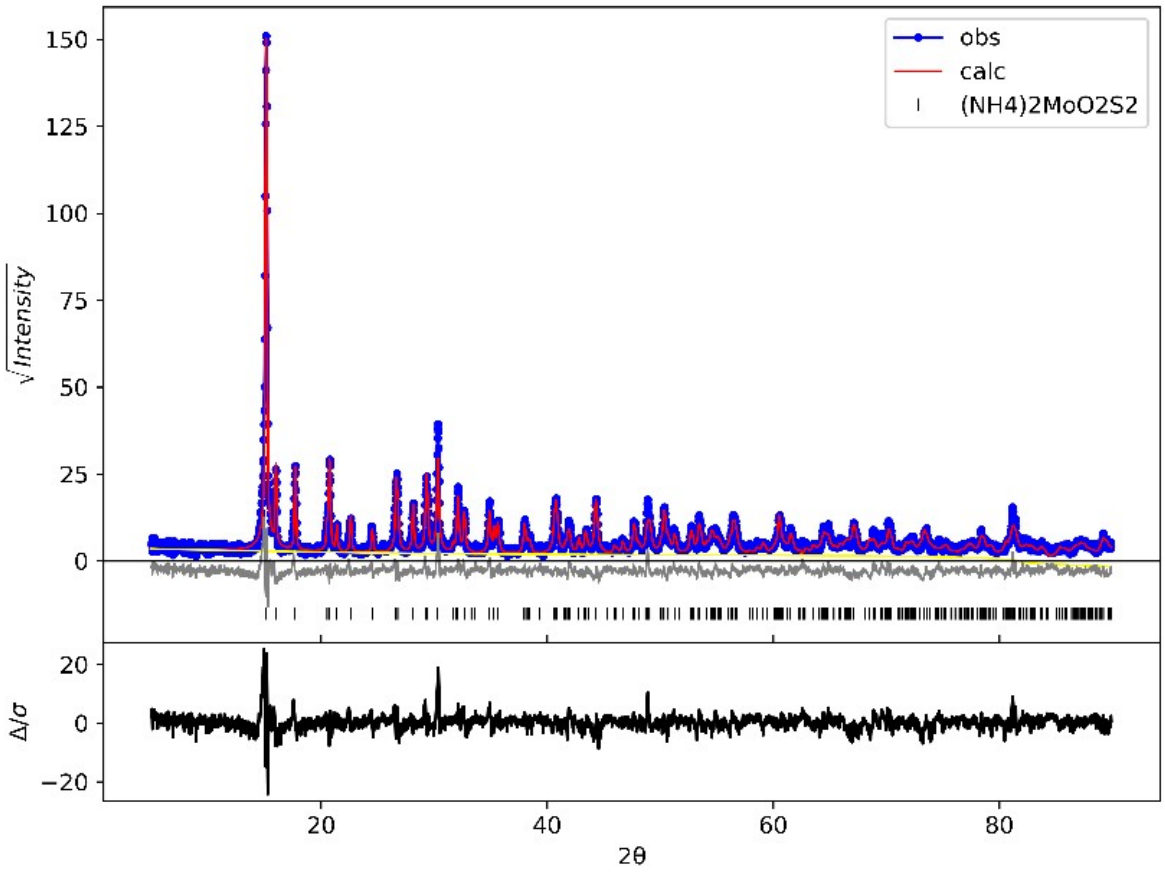

Figure S1. Pawley refinement on the powder XRD pattern of the crystalline $(NH_4)_2MoO_2S_2$, indicating the phase purity of the product.

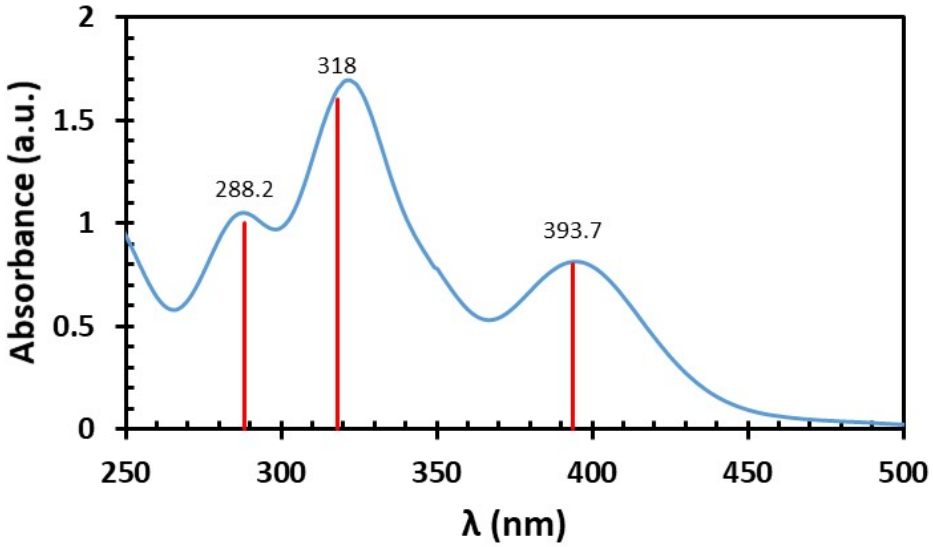

Figure S2. Optical absorption spectrum of an aqueous solution of $(NH_4)_2MoO_2S_2$ obtained through equation 1. The bars and numbers indicate previously reported absorption maxima for the pure $Mo_2O_2S_2$ dianion.

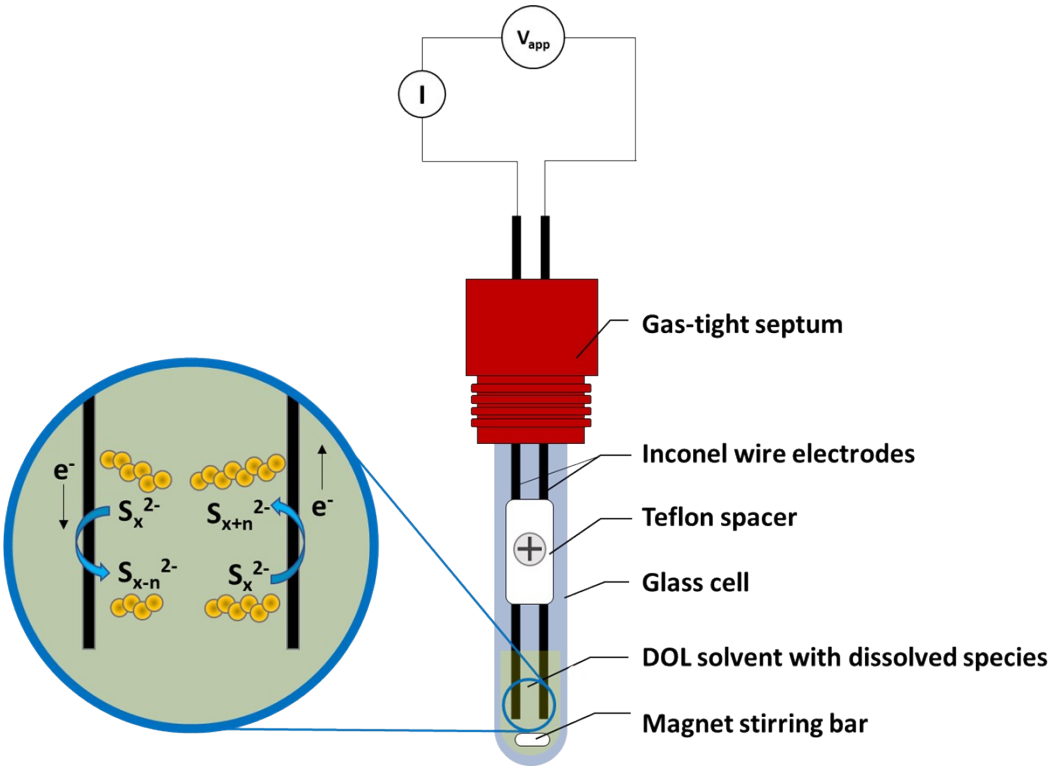

Figure S3. Schematic representation of the cell used for *in-situ* chronoamperometric analyses.

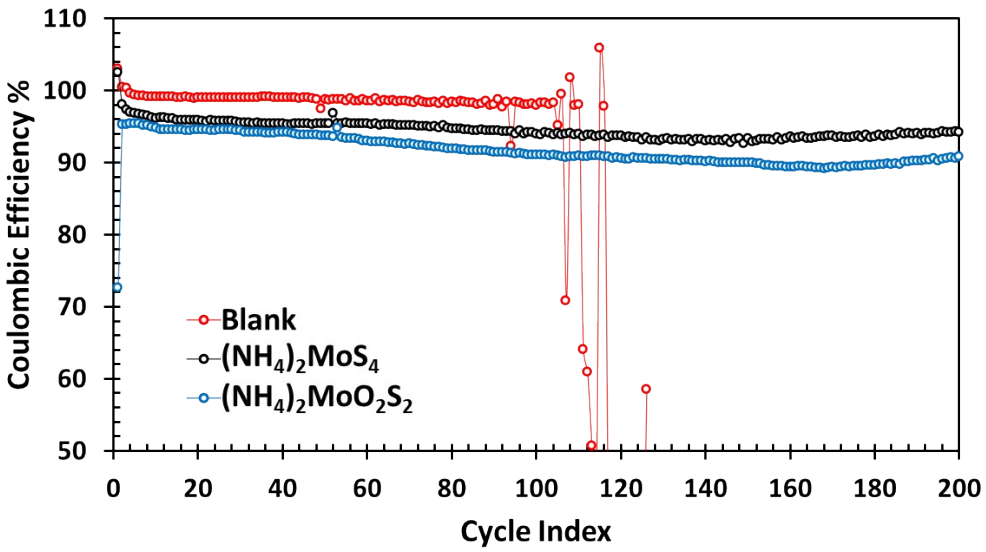

Figure S4. The effect of the thiomolybdate additives on the evolution of the coulombic efficiency in Li-S cells.

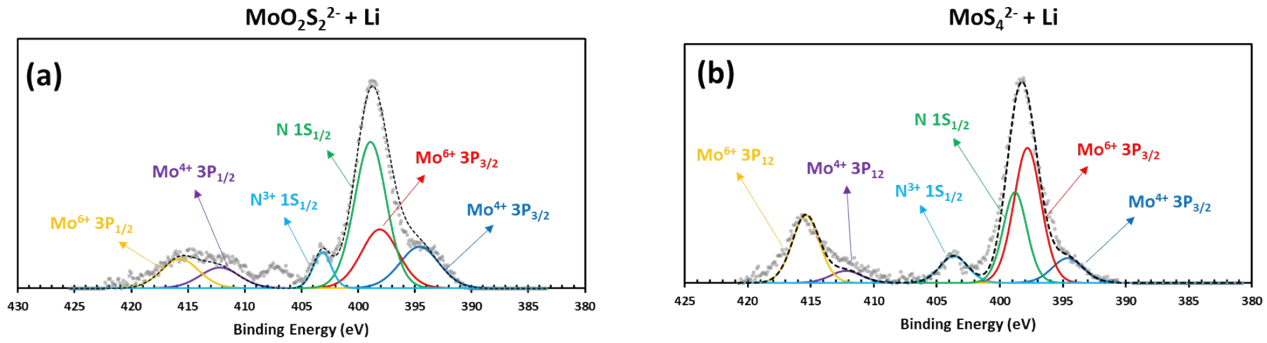

Figure S5. XPS data of Li anode exposed to $MoO_2S_2^{2-}$ (a) and MoS_4^{2-} (b) after 1,000 s of Ar-ion sputtering.

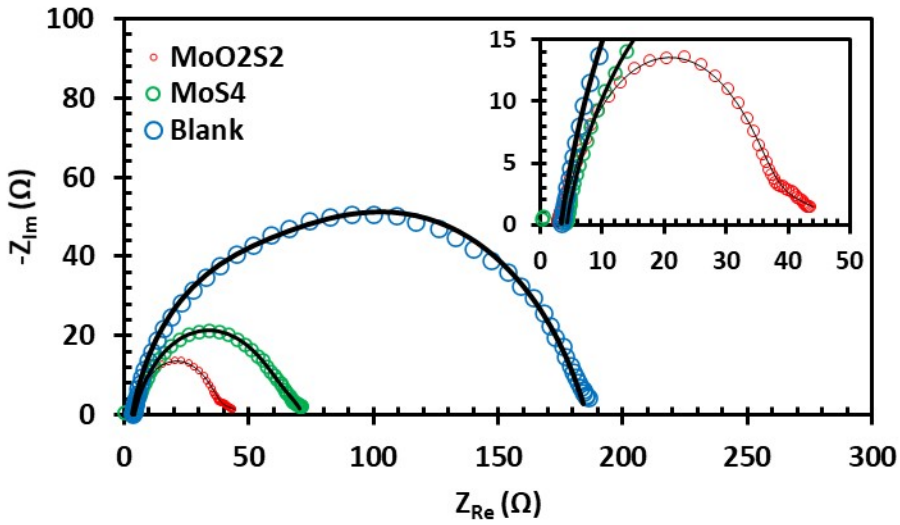

Figure S6. Electrochemical impedance spectra of pristine Li-S cells with various $MoX_2S_2^{2-}$ additives and that of the blank cell.

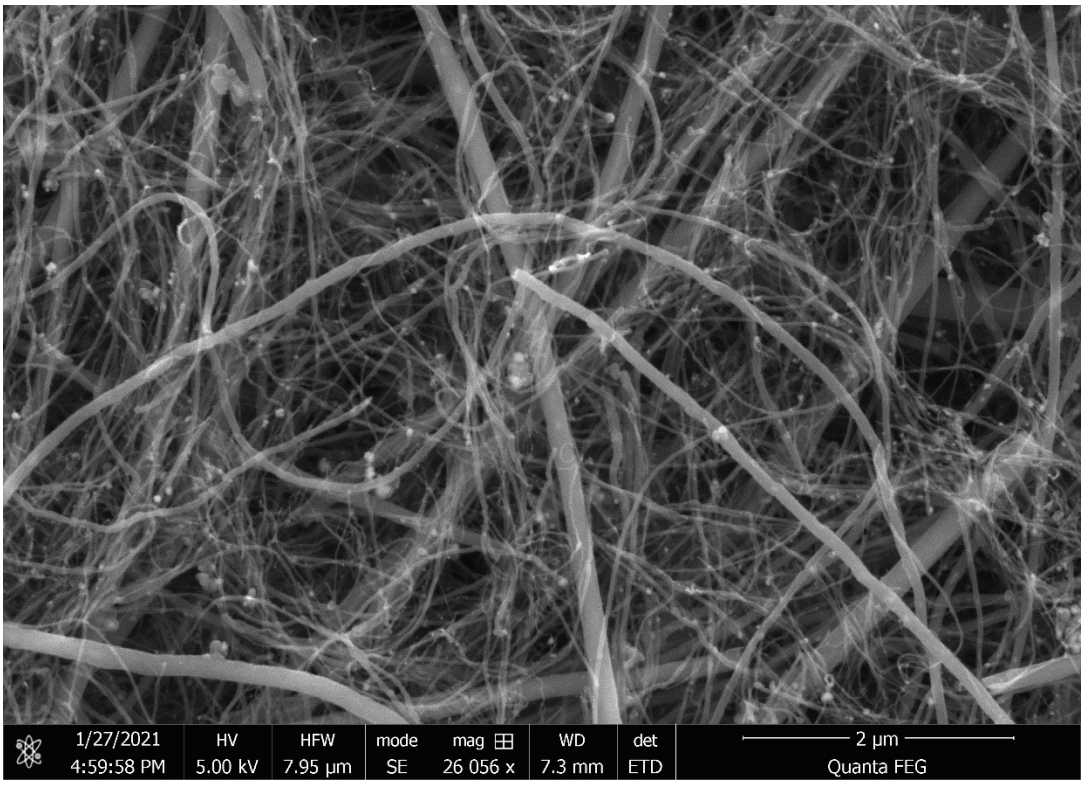

Figure S7. SEM image of the bucky paper carbon host used in this work for S cathode storage.

Table S1. Crystal data and structure refinement for compound A.

Empirical formula	$C_{10}H_{27}Mo_2N_3O_2S_8$
Formula weight	669.70
Temperature/K	100.02(11)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	20.6130(14)
b/Å	9.7726(4)
c/Å	12.3444(5)
α/°	90
β/°	92.710(5)
γ/°	90
Volume/Å^3	2483.9(2)
Z	4
ρ_{calc}g/cm^3	1.791
μ/mm^{-1}	1.693
F(000)	1344.0
Crystal size/mm^3	0.406 × 0.241 × 0.042
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.318 to 59.942
Index ranges	$-28 \leq h \leq 19$, $-13 \leq k \leq 13$, $-16 \leq l \leq 17$
Reflections collected	18094
Independent reflections	6193 [R_{int} = 0.0329, R_{sigma} = 0.0465]
Data/restraints/parameters	6193/0/235
Goodness-of-fit on F^2	1.088
Final R indexes [I>=2σ (I)]	R_1 = 0.0422, wR_2 = 0.0728
Final R indexes [all data]	R_1 = 0.0561, wR_2 = 0.0781
Largest diff. peak/hole / e Å^{-3}	1.33/-1.17

Table S2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for compound A. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{IJ} tensor.

Atom	**x**	**y**	**z**	**U_{eq}**
Mo1	7515.9(2)	5144.5(3)	4711.2(3)	12.29(8)
Mo2	8667.4(2)	6583.7(3)	4300.5(2)	10.98(8)
O1	7765.7(13)	3491(3)	4708(2)	19.2(6)
O2	9221.5(13)	5328(3)	4195(2)	16.7(6)
S1	6520.2(5)	5394.9(12)	3640.0(8)	23.2(2)
S2	5708.1(5)	5343.5(12)	4597.3(9)	24.9(2)
S3	6050.2(5)	4198.8(11)	5879.1(9)	25.0(2)
S4	6881.2(5)	5294.8(11)	6321.2(8)	20.2(2)
S5	8176.5(5)	6426.3(10)	5933.0(7)	15.84(19)
S6	9253.8(5)	8576.7(10)	4938.5(8)	19.5(2)
S7	8966.6(5)	8548.2(10)	3297.7(8)	18.2(2)
S8	7821.5(5)	6152.5(10)	3062.8(7)	15.86(19)
C1	6372(2)	1005(5)	4159(3)	26.1(10)
C2	7448(2)	-35(4)	4477(4)	26.2(10)
C3	6885(2)	979(4)	5978(3)	22.9(9)
C4	6488(2)	1148(4)	5167(5)	37.2(12)
C5	9116(2)	1184(4)	6687(3)	21.2(9)
C6	9312.5(19)	3592(4)	6326(3)	17.3(8)
C7	9525(2)	2689(4)	8155(3)	23.3(9)
C8	8405(2)	2921(4)	7422(3)	21.8(9)
C9	4982(2)	1518(4)	7008(4)	27.3(10)
C10	4731(2)	2358(5)	7868(4)	33.1(11)
N1	6800.3(16)	201(3)	4941(3)	17.8(7)
N2	9086.1(15)	2596(3)	7151(2)	13.8(6)
N3	5177(2)	853(4)	6341(4)	39.7(10)

Table S3. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for compound A. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo1	16.65(16)	8.92(14)	11.61(15)	0.11(12)	4.05(12)	1.07(12)
Mo2	15.45(16)	7.26(14)	10.19(15)	-0.92(12)	0.38(12)	0.98(12)
O1	22.6(15)	12.2(13)	23.6(15)	-0.5(11)	10.0(12)	0.8(11)
O2	19.6(14)	12.1(13)	18.7(14)	-1.2(11)	4.9(11)	0.8(11)
S1	17.7(5)	35.1(6)	16.8(5)	-2.2(4)	1.0(4)	-1.6(4)
S2	17.4(5)	33.3(6)	24.2(5)	-0.1(5)	3.8(4)	-2.1(4)
S3	25.2(6)	19.9(5)	30.7(6)	2.3(5)	10.5(5)	-1.5(4)
S4	21.4(5)	23.7(5)	15.9(5)	2.6(4)	6.0(4)	2.1(4)
S5	20.1(5)	17.7(5)	9.7(4)	-2.0(4)	0.4(4)	3.2(4)
S6	23.7(5)	14.3(5)	20.1(5)	-4.3(4)	-5.0(4)	-0.9(4)
S7	22.9(5)	12.9(4)	18.4(5)	2.9(4)	-3.0(4)	-3.7(4)
S8	19.5(5)	17.4(5)	10.7(4)	0.6(4)	0.3(4)	-5.2(4)
C1	27(2)	31(2)	20(2)	-0.3(19)	-4.1(18)	5.8(19)
C2	19(2)	25(2)	36(3)	-0.3(19)	11.0(19)	4.1(18)
C3	27(2)	22(2)	20(2)	5.2(18)	1.2(17)	2.6(18)
C4	31(3)	15(2)	67(4)	2(2)	12(2)	-4.4(19)
C5	34(2)	10.5(18)	20(2)	-3.3(16)	4.0(17)	-3.4(17)
C6	22(2)	14.2(18)	16.4(19)	5.4(15)	5.2(16)	0.1(15)
C7	36(3)	16.0(19)	17(2)	-0.4(17)	-6.7(18)	0.4(18)
C8	22(2)	22(2)	22(2)	-3.3(17)	8.2(17)	-3.8(17)
C9	22(2)	21(2)	38(3)	7(2)	-1(2)	-4.3(18)
C10	40(3)	24(2)	35(3)	0(2)	4(2)	4(2)
N1	17.0(17)	10.4(15)	26.4(18)	0.9(14)	5.2(14)	-0.4(13)
N2	17.9(17)	10.9(15)	12.8(15)	0.9(12)	3.8(12)	-0.4(12)
N3	31(2)	39(2)	49(3)	-6(2)	11(2)	0.4(19)

Table S4. Bond Lengths for compound A

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Mo1	Mo2	2.8253(5)	S3	S4	2.0714(15)
Mo1	O1	1.696(3)	S6	S7	2.0834(14)
Mo1	S1	2.4009(11)	C5	N2	1.496(5)
Mo1	S4	2.4351(10)	C6	N2	1.500(4)
Mo1	S5	2.3461(10)	C7	N2	1.502(5)
Mo1	S8	2.3726(10)	C8	N2	1.493(5)
Mo2	O2	1.685(3)	C1	N1	1.500(5)
Mo2	S5	2.3026(10)	C2	N1	1.496(5)
Mo2	S6	2.4052(10)	C3	N1	1.492(5)
Mo2	S7	2.3813(10)	C4	N1	1.499(5)
Mo2	S8	2.3022(10)	C9	C10	1.456(6)
S1	S2	2.0950(15)	C9	N3	1.138(6)
S2	S3	2.0364(16)			

Table S5. Values of various components used in the fitting of electrochemical impedance spectra of Figure 10

	Blank		**MoS_4^{2-}**		**$MoO_2S_2^{2-}$**	
	pristine	**cycled**	**pristine**	**cycled**	**pristine**	**cycled**
L1 (H)	2.94(9)E-7	2.48(2)E-7	2.81(7)E-7	1.29(6)E-7	3.01(9)E-7	4.86(8)E-7
R1 (Ω)	3.28(1)	3.97(7)	4.10(9)	6.46(4)	1.77(4)	1.10(8)
R2 (Ω)	1.39(7)E+2	42.8(1)	12.7(7)	9.98(9)	17.7(2)	9.8(8)
R3 (Ω)	42.6(3)	36.6(3)	55.0(1)	33.3(9)	28.4(1)	3.2(4)
CPE1-T	7.794(8)E-5	73.7(7)E-4	4.19(3)E-3	2.44(4)E-3	1.26(6)E-2	1.023(8)E-3
CPE1-P	0.73(5)	0.55(9)	0.56(2)	0.72(2)	0.28(8)	0.38(6)
CPE2-T	1.322(4)E-5	1.804(3)E-5	2.10(2)E-5	3.46(6)E-5	1.58(7)E-5	8.718(1)E-5
CPE2-P	0.88(2)	0.84(1)	0.79(8)	0.71(2)	0.89(1)	0.89(4)
$\Sigma(R_w^2)$	0.0311(3)	0.0082(2)	0.0146(2)	0.0179(4)	0.0177(3)	0.0112(1)