Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information for: Electron passivation in CaF_2 on calcium metal anodes

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S1 Effects of straining Ca electrodes on electron transport

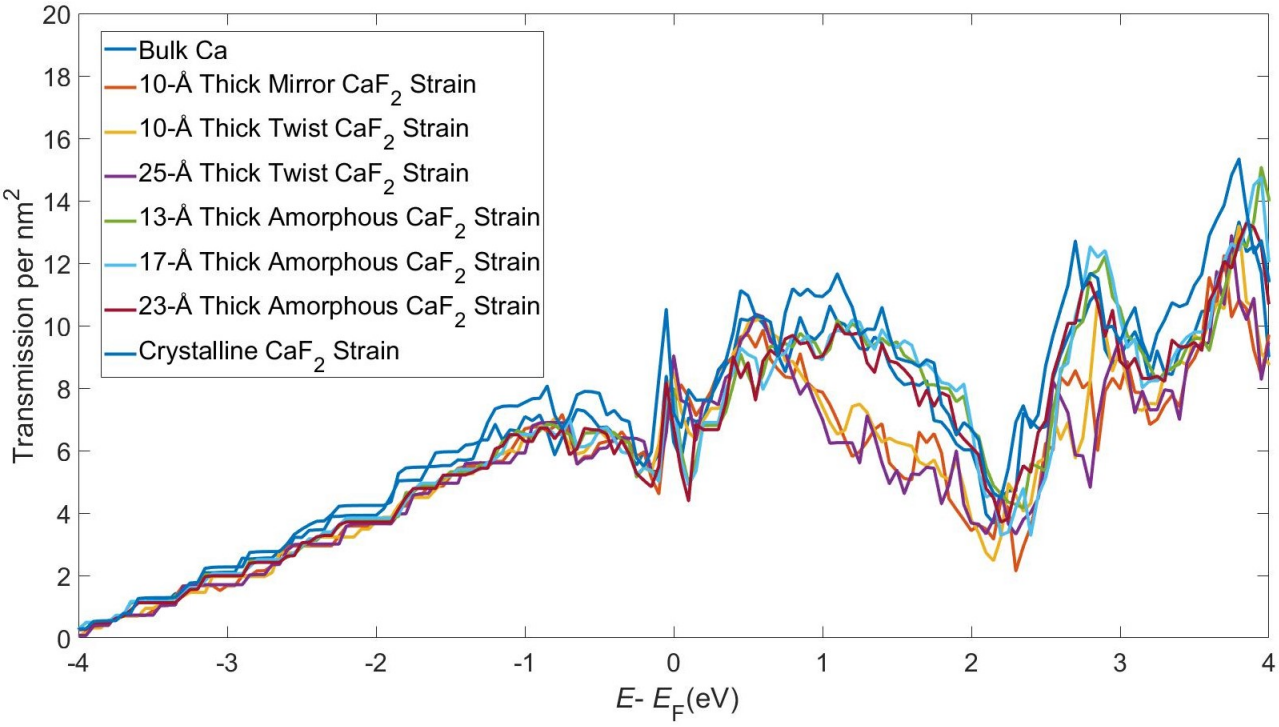

Figure S1: Transmission for different pure Ca systems that are strained to adopt the crystalline, amorphous, or polycrystalline CaF_2 lattice constants or fully relaxed to adopt the Ca crystal structure.

The Ca electrodes had to be strained in order to accommodate lattice mismatch between the CaF_2 systems. The transmission spectra of each strained Ca cell are plotted in Fig. S1. From these calculated data, it is evident that lattice strain does not significantly impact transmission calculations.

S2 Amorphous structures generated by the liquid quench technique

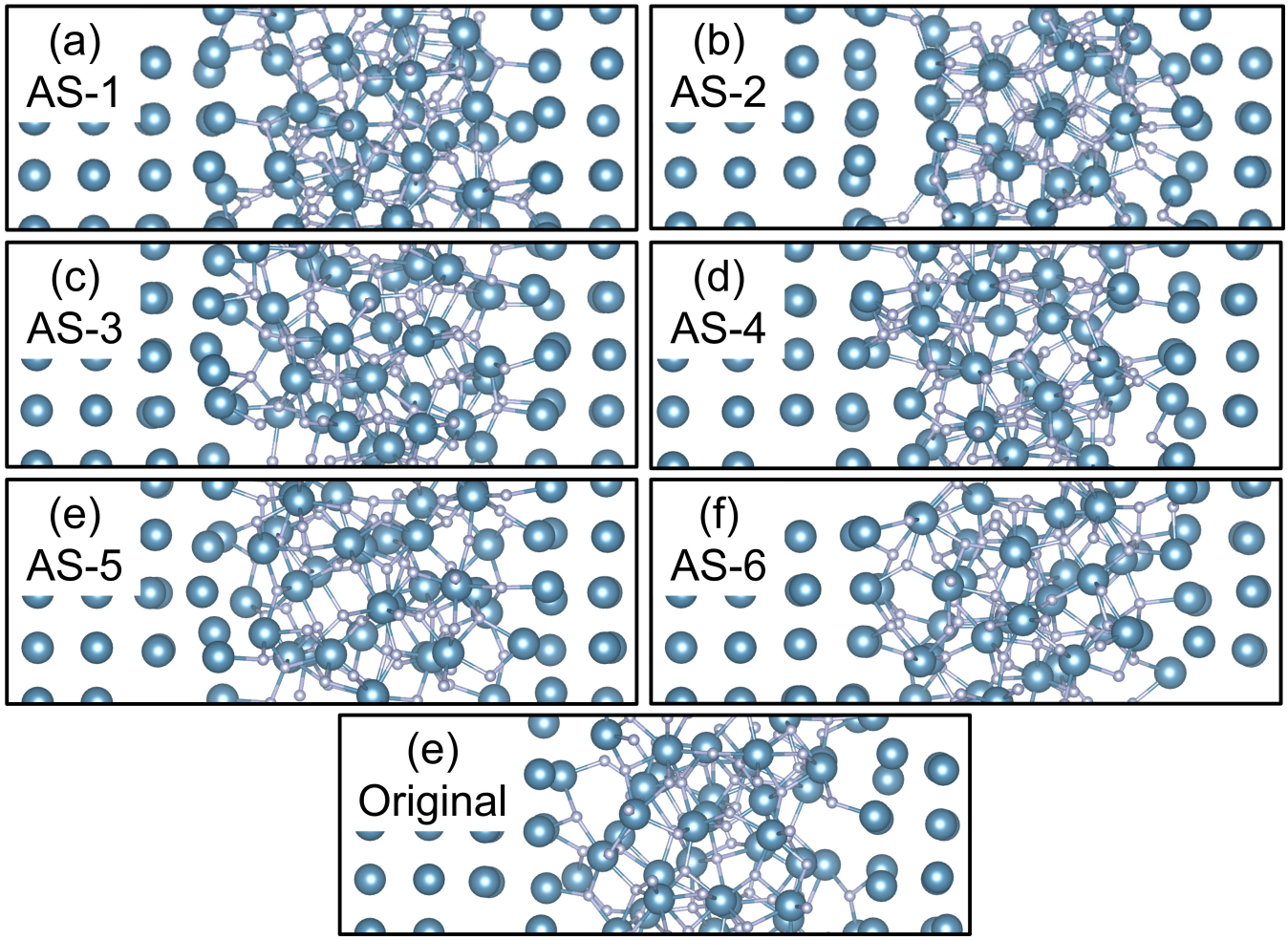

Figure S2: Atomic structures of (a) AS-1, (b) AS-2, (c) AS-3, (d) AS-4, (e) AS-5, (f) AS-6, and (e) original amorphous CaF_2.

The structures in Fig. S2 were were generated via the following process. First, a cell of crystalline CaF_2 was heated to 2700 K. Structures were then obtained from different time steps in the equilibration process, and then allowed to cool to 300 K at a rate of 1 K/fs and equilibrate at 300 K for 10 ps. Atomic Structure 1 (AS-1) was allowed to equilibrate at 2700 K for 3 ps, AS-2 was allowed to equilibrate at 2700 K for 6 ps, and AS-3 was allowed to equilibrate at 2700 K for 9 ps. AS-4 was allowed to equilibrate at 2700 K for 5 ps, AS-5

was allowed to equilibrate at 2700 K for 8 ps, and AS-6 was allowed to equilibrate at 2700 K for 8 ps. The original structure was allowed to equilibrate for 10 ps.

S3 CaF_2 Band Gap Information

Table S1: The band gap of the CaF_2 systems are shown in the table below.

Species	Band Gap (eV)
Crystalline CaF_2	7.20
48 atom Amorphous CaF_2	6.72
96 atom Amorphous CaF_2	6.84
144 atom Amorphous CaF_2	6.94
Mirror GB CaF_2	6.00
Twist GB CaF_2	6.18

S4 Effects of grain boundaries on the DOS of CaF_2

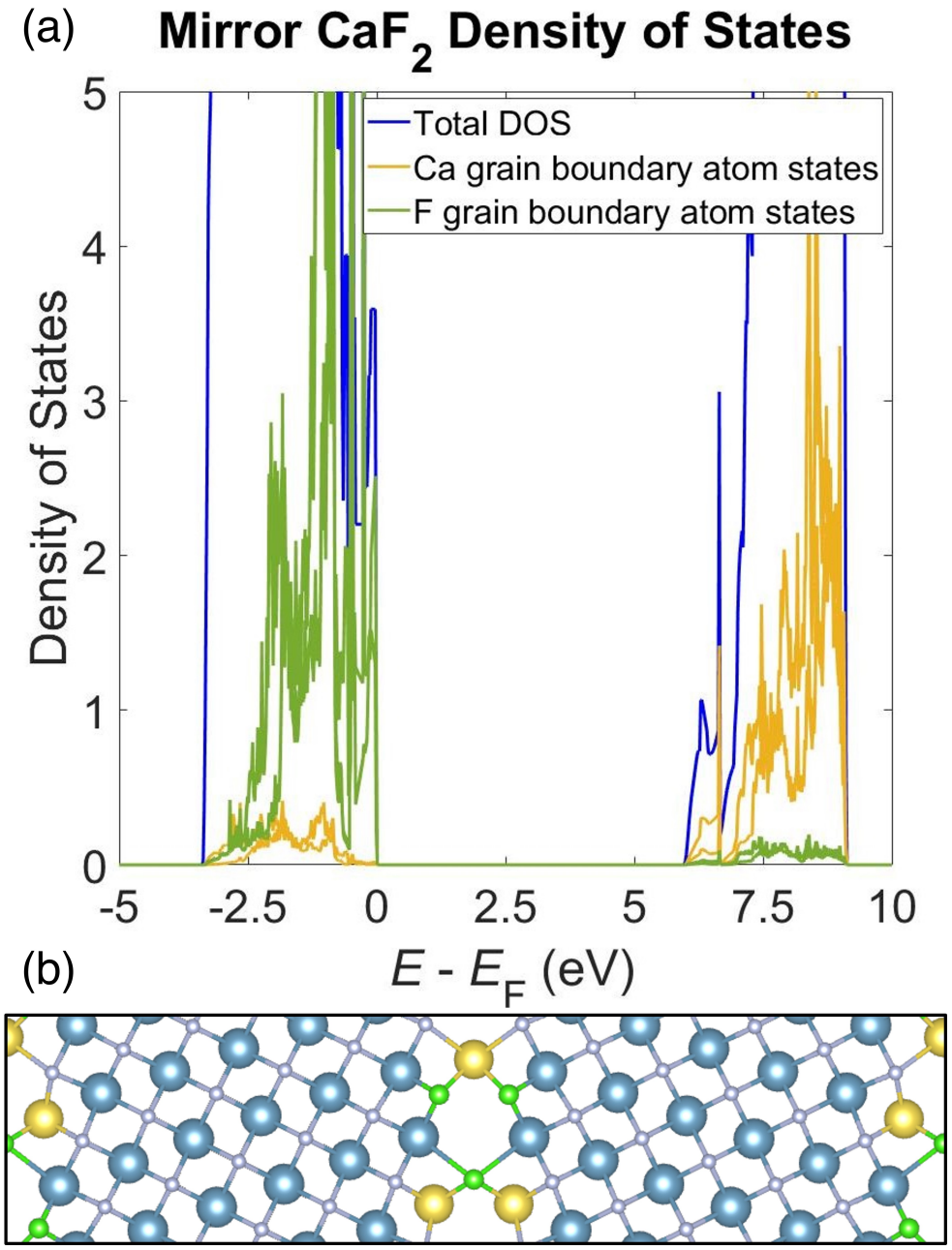

Figure S3: Density-of-states for the mirror polycrystalline system. (a) density of states plot for the mirror system with grain boundary atom states plotted; (b) atoms responsible for the states narrowing the band gap are highlighted. Atoms contributing to the lowering of the conduction band are highlighted in yellow, and those responsible for the increase of states in the valence band are shown in green.

Figure S3 contains density-of-states data projected on to grain boundary atoms in the

mirror CaF_2 system. The density of states for the Ca atoms present in the grain boundary are shown in yellow, and those of the F atoms present in the grain boundary are plotted in green. It is evident from the graph that in the conduction band the Ca atoms in the grain boundary introduce states closer to the Fermi energy. In the valance band, F atoms introduce states just below the Fermi energy. Together, these contribute to the narrowing of the band gap in mirror CaF_2.

S5 Scattering state plots in crystalline CaF_2

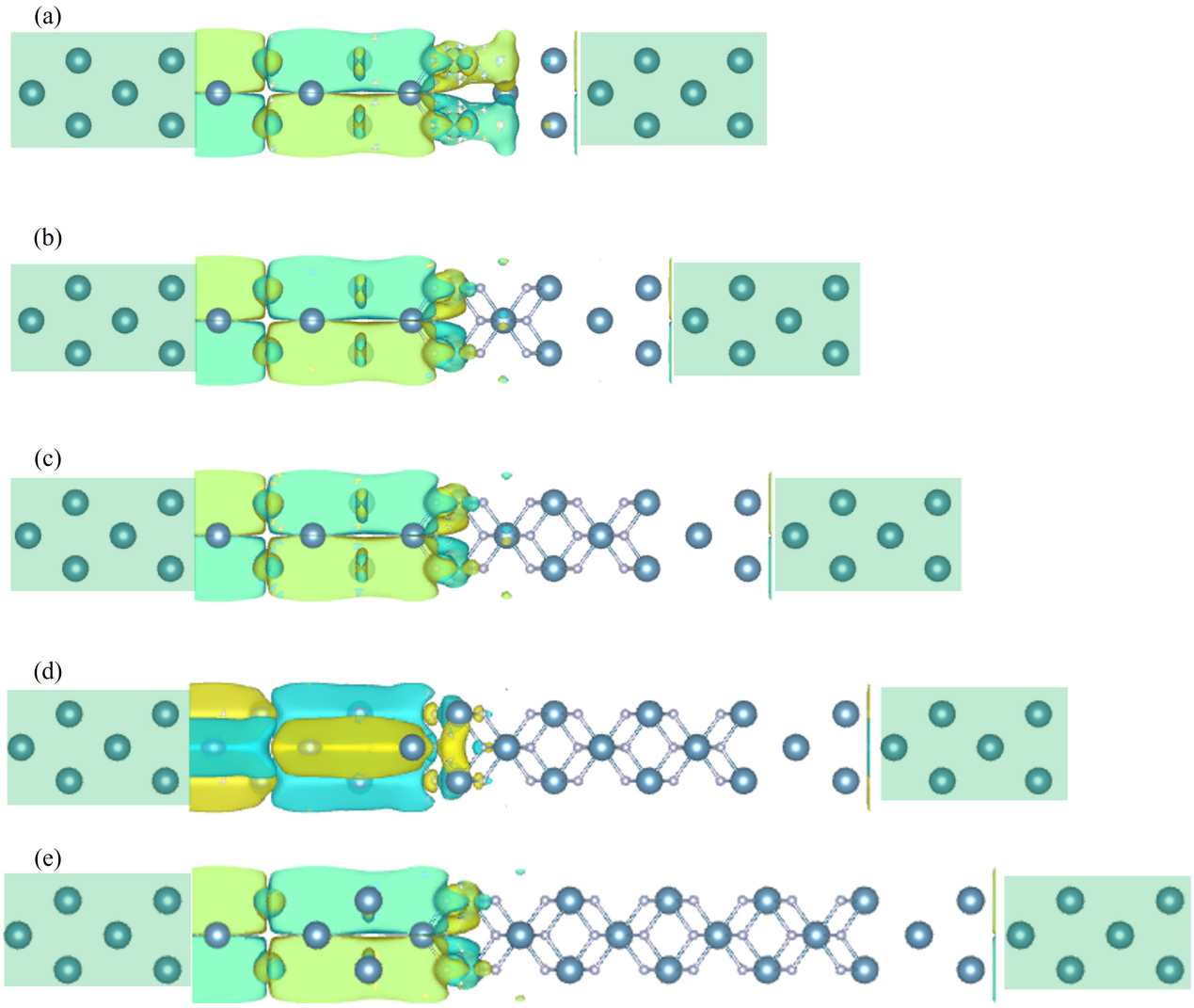

Figure S4: Scattering states of crystalline CaF_2 are plotted. Scattering state plot of (a) CaF_2 (8.8 Å), (b) CaF_2 (14.3 Å), (c) CaF_2 (19.9 Å), (d) CaF_2 (25.4 Å), and (e) CaF_2 (30.9 Å) at E_F. Note that the scattering-state wavefunctions of CaF_2 (8.8 Å) almost reach the right electrode, which does not occur in thicker systems.

S6 Amorphous structure scattering state plots

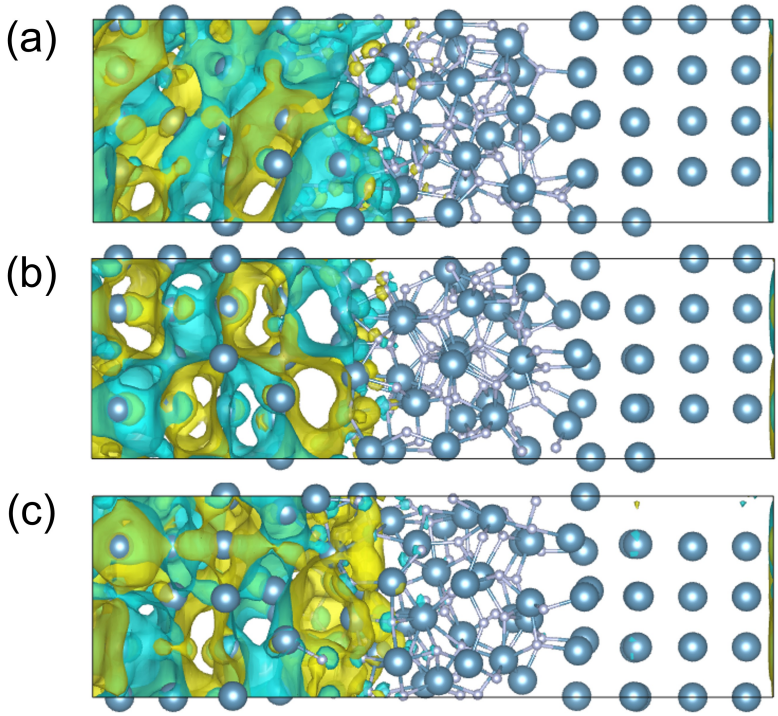

Figure S5: Scattering state plots of (a) AS-1, (b) AS-2, and (c) AS-3 obtained at the Fermi energy, plotted at an isosurface value of .

The scattering state plots in Fig. S5 were obtained at the Fermi energy of each system. AS-1 and and AS-3, shown in Fig. S5(a) and (c), respectively, have relatively dense wave functions coming from the the left electrode into CaF_2. However, AS-2, shown in Fig. S5(b), has large gaps in the electronic wave function between the electrode and CaF_2, due to the increased electrode-CaF_2 distance, explaining the decrease in the transmission function of AS-2. These results highlight how the transmission function can change during an AIMD trajectory. AS-2 can be considered an outlier, as the other atomic structures as well as the original amorphous structure all produced largely similar results.

S7 CaF_2 Conductance Values

Table S2: The low-bias conductance of each CaF_2 system is shown in the table below.

Species	Thickness	Conductance
Crystalline CaF_2	8.70 Å	1.843×10^{-1} G_0/nm^2
Crystalline CaF_2	14.30 Å	3.280×10^{-4} G_0/nm^2
Crystalline CaF_2	19.80 Å	7.730×10^{-6} G_0/nm^2
Crystalline CaF_2	25.40 Å	2.432×10^{-7} G_0/nm^2
Crystalline CaF_2	30.90 Å	6.258×10^{-9} G_0/nm^2
Amorphous CaF_2	12.90 Å	1.547×10^{-1} G_0/nm^2
Amorphous CaF_2	16.56 Å	7.200×10^{-3} G_0/nm^2
Amorphous CaF_2	22.87 Å	3.427×10^{-4} G_0/nm^2
Mirror GB CaF_2	8.54 Å	5.220×10^{-2} G_0/nm^2
Twist Parallel CaF_2	13.22 Å	9.030×10^{-3} G_0/nm^2
Twist Parallel CaF_2	21.04 Å	2.598×10^{-6} G_0/nm^2
Twist Perpendicular CaF_2	25.44 Å	9.430×10^{-8} G_0/nm^2

S8 Information on the size of each system

Table S3: The number of atoms in and lattice parameters of the simulation cell of each system are presented in the table below.

System	Number of Atoms	a (Å)	b (Å)	c (Å)
Unstrained Ca Electrode	16	5.523	5.523	22.092
CaF_2 (8.8 Å)	20	5.504	5.504	23.011
CaF_2 (14.3 Å)	32	5.504	5.504	28.521
CaF_2 (19.9 Å)	44	5.504	5.504	34.043
CaF_2 (25.4 Å)	56	5.504	5.504	39.618
CaF_2 (30.9 Å)	68	5.504	5.504	45.225
a-CaF_2 (12.9 Å)	112	10.551	10.792	30.524
a-CaF_2 (16.5 Å)	160	10.757	10.438	36.824
a-CaF_2 (22.8 Å)	208	10.792	10.764	42.022
Original a-CaF_2	160	10.757	10.438	36.824
AS-1 a-CaF_2	160	10.778	10.738	36.186
AS-2 a-CaF_2	160	10.703	10.693	36.512
AS-3 a-CaF_2	160	10.705	10.741	36.270
AS-4 a-CaF_2	160	10.743	10.722	36.024
AS-5 a-CaF_2	160	10.694	10.770	36.124
AS-6 a-CaF_2	160	10.734	10.741	36.124
Mirror Parallel (9 Å)	456	17.368	36.115	21.933
Mirror Parallel (16 Å)	696	17.368	36.115	27.877
Mirror Parallel (20 Å)	936	17.368	36.115	33.431
Twist Parallel (13 Å)	384	17.539	22.499	26.242
Twist Parallel (20 Å)	672	17.539	22.499	39.661
Twist Perpendicular (28 Å)	624	17.539	17.539	43.897

Table S3 contains data on the number of atoms in each simulation cell and the corresponding lattice parameters. All cells are orthorhombic in nature. The buffer layers of the Ca metal electrodes are included in the cell parameters and number of atoms for each system.