Electronic Supplementary Information

Operando and Ex-situ Raman Spectroscopies for Evaluating Carbon Structural Changes in Anode-Free-Type Sulfide-Based All-Solid-State Li Battery

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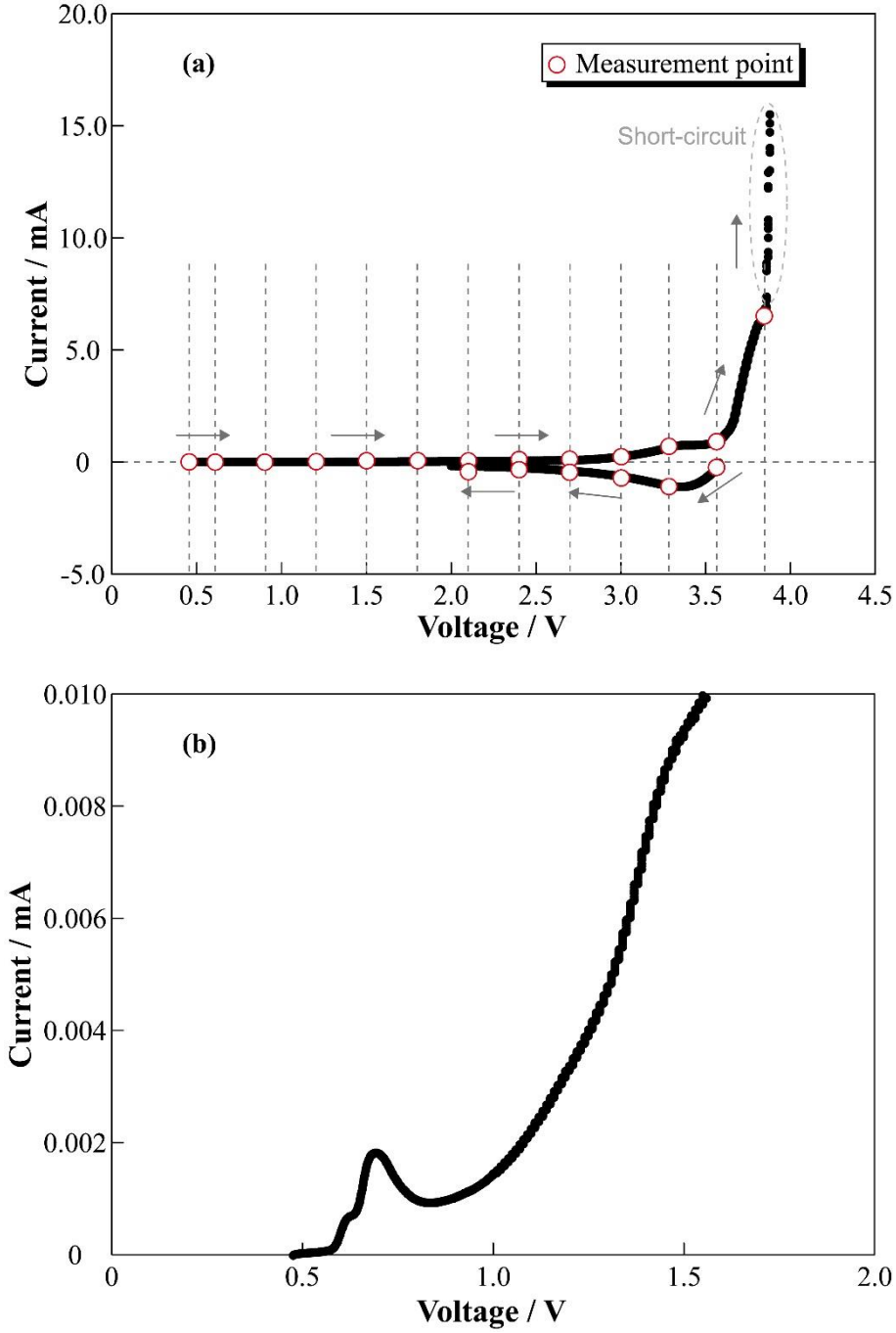

Fig. S1. The electrochemical profiles for CV measurement in the range of 0–4.5 V (a) and 0–2.0 V during *Operando* Raman spectroscopy.

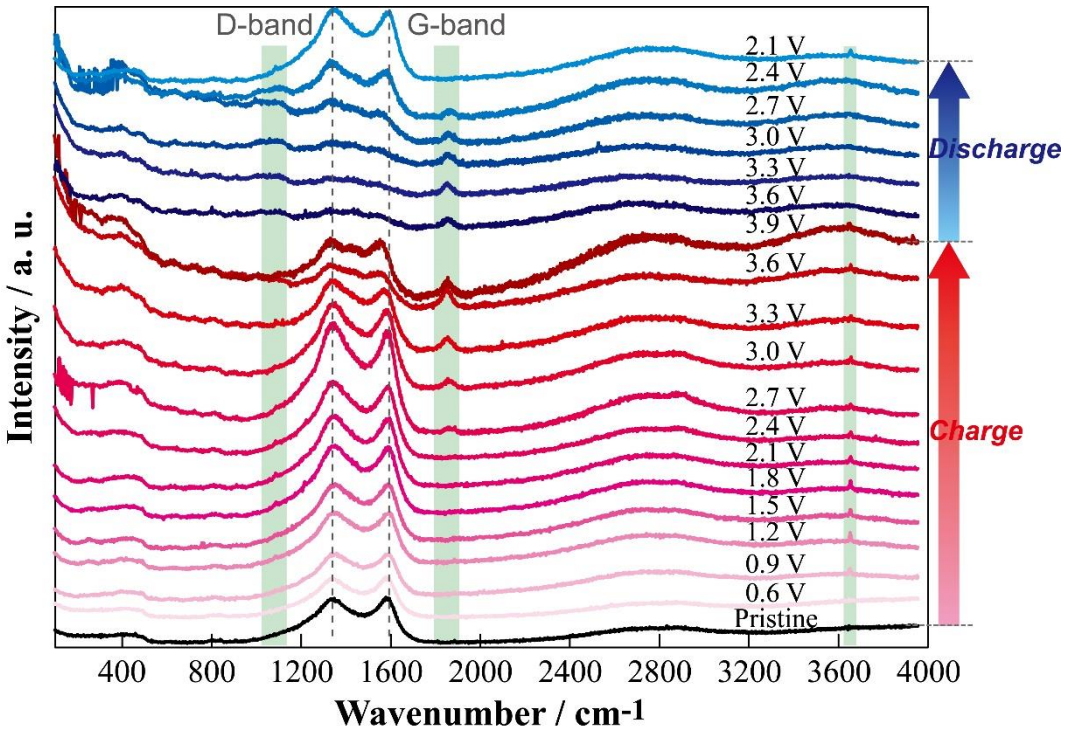

Fig. S2 The Raman spectra acquired from point 2 in the cross-sectional AF-ASSB with the Ag/C layer every 0.3 V during charge-discharge processes in the *Operando* Raman spectroscopy at room temperature.

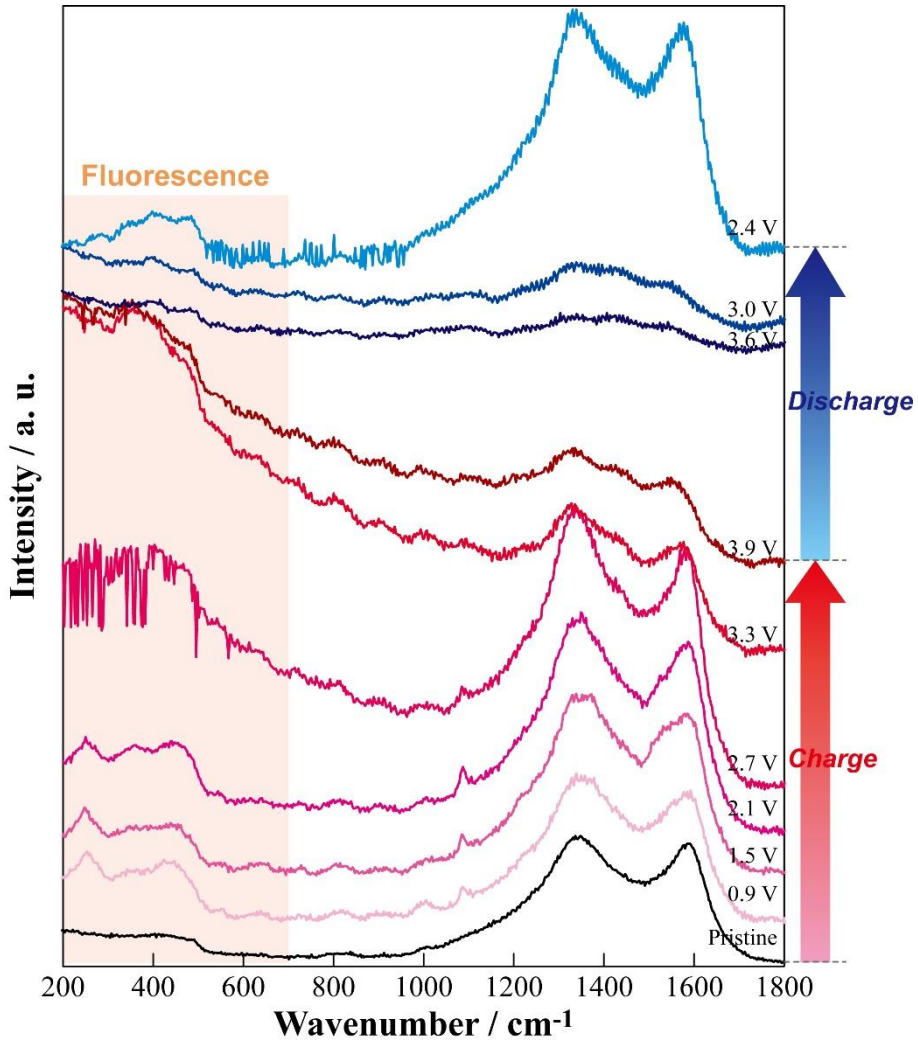

Fig. S3 The Raman spectra in the range of 200–1800 cm^{-1} at point 1 during the *Operando* Raman spectroscopy. The fluorescence signal is indicated as orange region in the lower wavenumber.

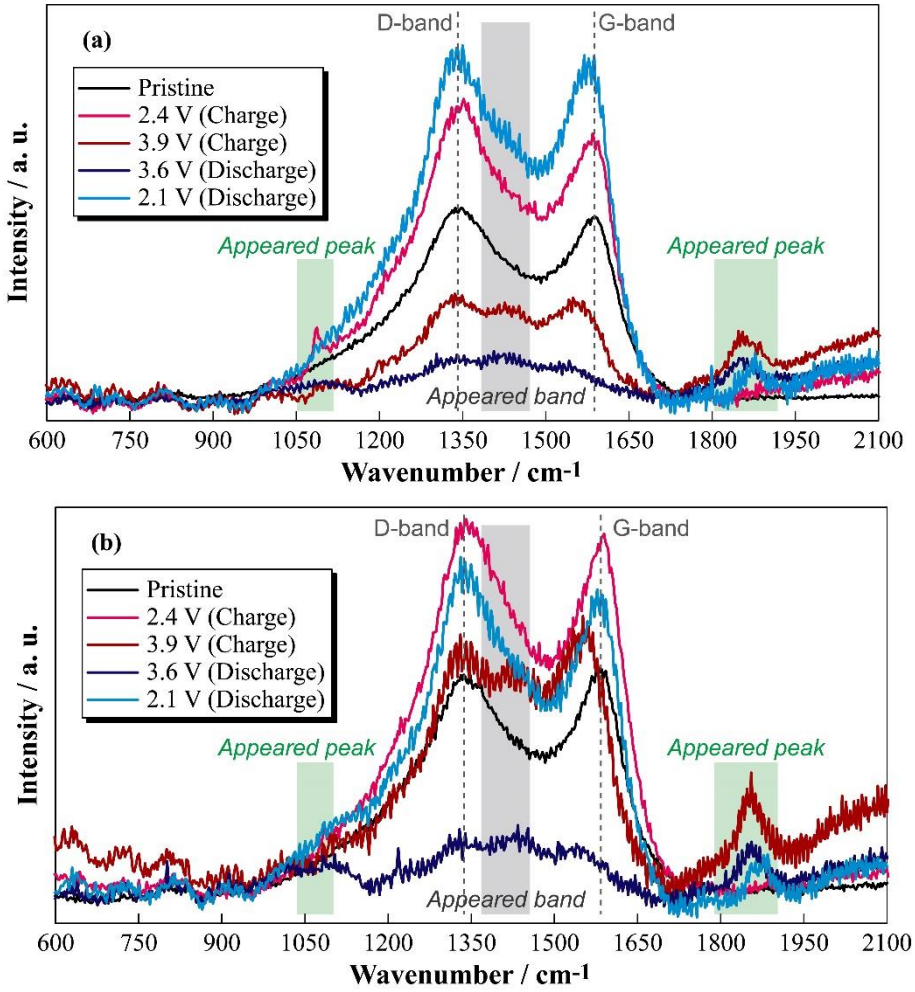

Fig. S4. The baseline corrected Raman spectra in the range of 600–2100 cm^{-1} acquired from point 1 (a) and point 2 (b) in the Ag/C layer during *Operando* Raman spectroscopy.

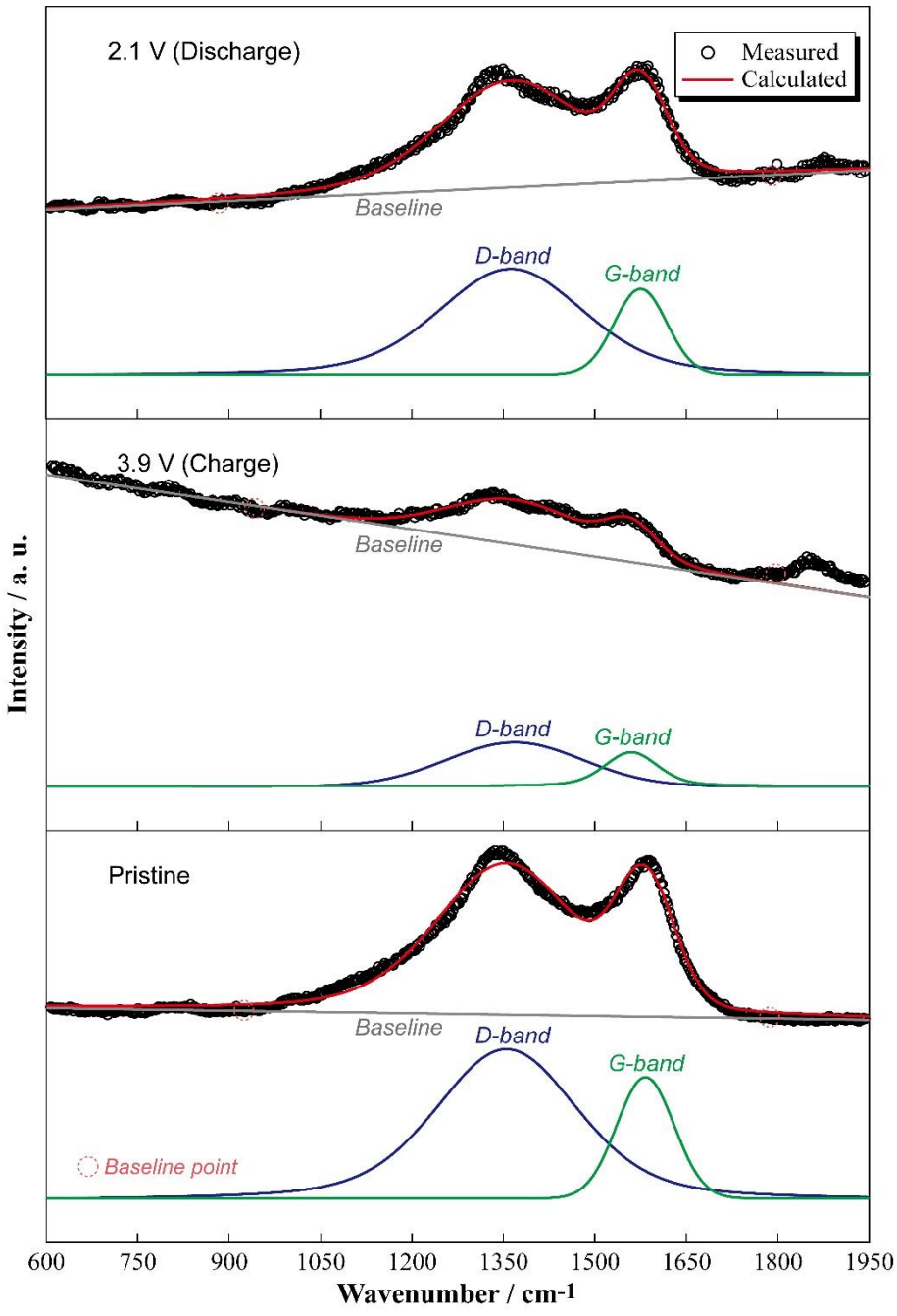

Fig. S5. The curve fitted Raman spectra in the range of 600–1950 cm^{-1} at a pristine, 3.9 (charge) and 2.1 (discharge) V acquired from the Ag/C layer during *Operando* Raman spectroscopy in point 1.

D- and G-bands in carbon materials[s1-s4]

In almost carbon materials, Raman spectra exhibit the D- and G-bands around 1360 and 1580 cm^{-1}, respectively. For example, graphite with ideal structure consisting of sp^2 orbital (e.g. Highly oriented pyrolytic graphite; HOPG) has quite intense peak approximately 1580 cm^{-1}, derived from the symmetric motion (lattice vibration) of C atoms inner graphene plane (E_{2g}), namely as G-band. With increasing the defects (correspondence to sp^3 orbital), Raman spectrum appear the new peak approximately 1360 cm^{-1}, due to induce the disordered structure and lattice vibration inside and edge of the graphene plane, close to the diamond-like structure and phonon state (T_{2g}). In addition, disordered structure also induces the D2-band around 1620 cm^{-1} with a weak shoulder on the G-band, corresponding to the symmetric motion of graphitic lattice (E_{2g}). The amorphous carbon with the soot (organic molecule, fragment or functional group) have been proposed the existence of the D3-band around 1500 cm^{-1}, originated from the distribution of amorphous phase in the disturbed graphitic lattice. In case of existence peak around 1200 cm^{-1} with a shoulder on D-band, namely as D4-band, this may attribute to flame soot and tentatively originating from the sp^2-sp^3 bonds or C–C and C=C stretching vibrations of polyene-like structures. Thus, the D-bands and G-band plays role as index of disorder and defects in the carbon materials. However, these D2-, D3-, and D4-bands are often quite weak Raman active and hidden in the intense and broad D-band. In particular, Raman spectra in this *Operando* measurement is lower S/N ratio and weak intensity due to their short acquisition time and porously Ag/C layer in the cross-section. Indeed, the D2-, D3-, and D4-band was not clear observed, even though the use of the amorphously CB with much defects. From this reason, the curve fitting calculation in this study was performed as 2 components of D- and G-bands only.

From the feature of D-band, intensity ratio (D-band/G-band) is sometimes used as a *R* value reflecting the structural regularity and amount of defect in the carbon materials. The *R* values was reported to corelate on the crystallite size (L_a) measured by the XRD. Although the *R* value is sensitive for the sample surface and excitation wavelength, this may increase with decreasing the L_a. Therefore, various hypothesis is related on the Raman spectrum in the carbon material, however peak shape

(aspect ratio) and *R* value defined in following Fig. S5 is expected to indicate the structural changes in the CB during the charge-discharge.

References

S1 A. Ferrari, J. Robertson, *Phys. Rev. B*, 2000, **61**, 14095-14107.

S2 A. Ferrari, *Solid State Commun.*, 2007, **143**, 47-45.

S3 A. Sadezky, H. Muckenhuber, H. Grothe, H., R. Niessner, U. Pöschl, *Carbon*, 2005, **43**, 1731-1742.

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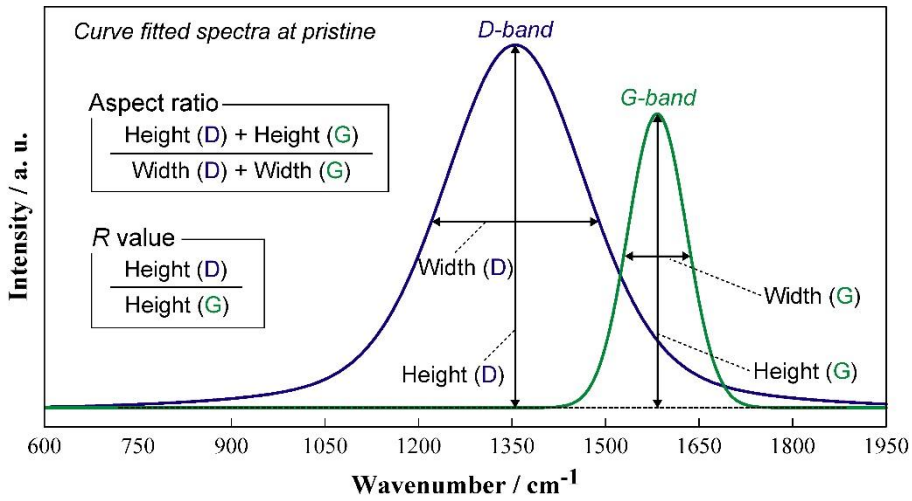

Fig. S6 Schematic image of definition in an aspect ratio and *R* value in this study.

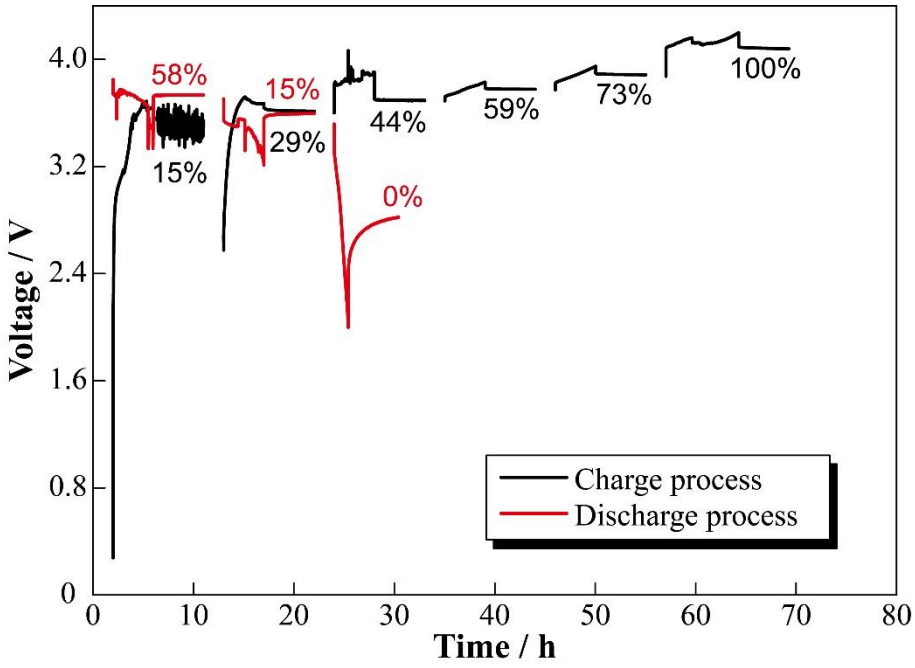

Fig. S7. The charge-discharge profile in the *ex-situ* Raman spectroscopy (percentages indicate SOCs). The curve and flat regions in the voltage profiles are constant-current charge-discharge and open-circuit periods, respectively.

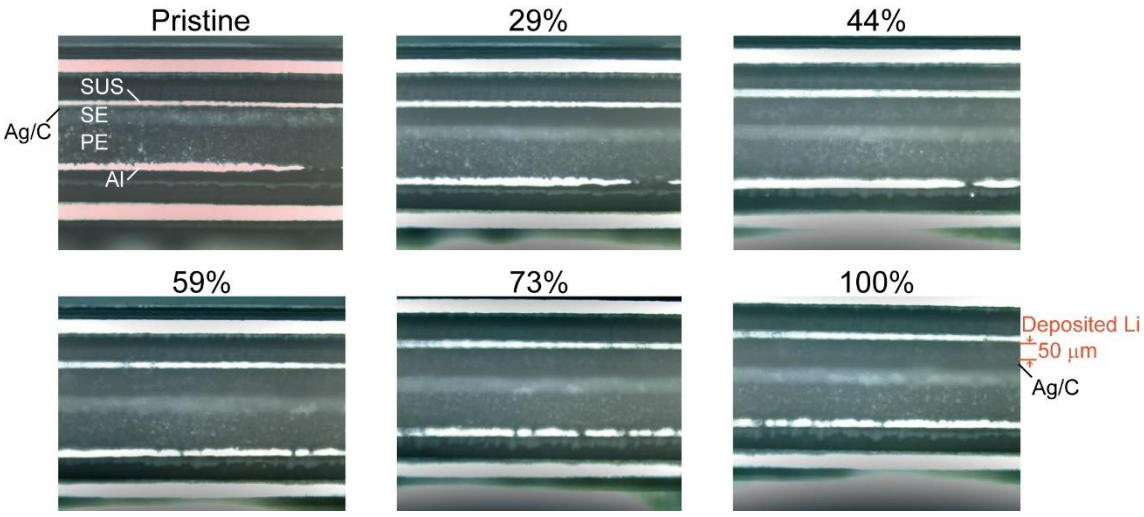

Fig. S8. The microscopic images from the cross-sectional AF-ASSB with Ag/C layer in the *ex-situ* Raman spectroscopy, indicating clear deposited Li layer between Ag/C layer and SUS current collector.

Table S1 Calculated parameters in curve fitting analysis based on *pseudo*-Voigt function at point 1

	D-band				G-band			
	Height / -	Position / cm^{-1}	Width / cm^{-1}	Lorentz ratio / -	Height / -	Position / cm^{-1}	Width / cm^{-1}	Lorentz ratio / -
Pristine	379.3	1355.1	158.4	0.35	303.2	1582.9	66.4	0
0.6 V (Charge)	184.2	1358.1	144.4	0.44	150.2	1583.9	70.4	0
0.9 V (Charge)	446.5	1360.7	155.2	0.26	339.2	1581.0	68.7	0
1.2 V (Charge)	503.4	1360.0	148.4	0.28	403.1	1581.0	66.5	0
1.5 V (Charge)	550.8	1361.0	156.7	0.17	428.0	1577.5	68.3	0
1.8 V (Charge)	600.0	1359.0	144.2	0.39	459.8	1580.1	67.4	0
2.1 V (Charge)	627.7	1359.2	151.2	0.25	494.0	1579.3	66.0	0
2.4 V (Charge)	578.8	1359.0	158.7	0.22	443.2	1580.2	64.4	0
2.7 V (Charge)	710.6	1360.3	156.2	0.12	575.8	1577.2	60.8	0
3.0 V (Charge)	444.1	1362.2	141.7	0.37	362.5	1575.4	61.2	0
3.3 V (Charge)	262.44	1365.9	126.3	0.13	235.5	1565.9	64.8	0
3.6 V (Charge)	114.7	1368.8	106.1	0	109.84	1558.8	73.5	0
3.9 V (Charge)	202.6	1368.5	157.3	0	157.1	1559.6	59.4	0.31
3.6 V (Discharge)	90.7	1379.8	152.3	1	24.5	1540.5	45.5	0
3.3 V (Discharge)	115.9	1381.7	141.1	0.87	36.7	1541.9	58.8	0
3.0 V (Discharge)	173.5	1379.9	150.0	0.81	52.0	1547.8	59.2	0
2.7 V (Discharge)	195.7	1375.5	138.6	1	86.9	1556.3	60.8	0
2.4 V (Discharge)	550.6	1365.2	152.9	0.43	385.9	1572.0	62.2	0
2.1 V (Discharge)	686.8	1362.4	163.0	0.29	550.3	1575.0	60.6	0

Table S2 Calculated parameters in curve fitting analysis based on *pseudo*-Voigt function at point 2

	D-band				G-band			
	Height / -	Position / cm^{-1}	Width / cm^{-1}	Lorentz ratio / -	Height / -	Position / cm^{-1}	Width / cm^{-1}	Lorentz ratio / -
Pristine	215.6	1349.5	157.7	0.31	191.1	1579.5	67.2	0
0.6 V (Charge)	188.6	1350.2	160.5	0.26	171.3	1580.2	66.7	0.04
0.9 V (Charge)	212.3	1356.4	156.6	0.10	183.6	1581.9	75.5	0
1.2 V (Charge)	267.3	1361.1	165.2	0.21	218.0	1586.3	68.1	0
1.5 V (Charge)	303.0	1362.4	164.1	0.29	240.4	1585.9	66.7	0
1.8 V (Charge)	347.7	1361.2	167.7	0.15	283.4	1587.0	65.9	0
2.1 V (Charge)	355.9	1358.9	163.7	0.20	291.0	1585.4	65.6	0
2.4 V (Charge)	367.0	1356.3	160.7	0.13	315.3	1583.4	66.3	0.11
2.7 V (Charge)	486.8	1358.4	161.0	0	419.3	1582.2	61.4	0
3.0 V (Charge)	387.0	1361.0	154.2	0.19	323.0	1579.0	63.3	0
3.3 V (Charge)	288.7	1367.6	152.3	0.08	238.2	1572.1	64.5	0.04
3.6 V (Charge)	148.1	1375.7	141.2	0.19	110.7	1556.6	71.3	0
3.9 V (Charge)	248.7	1375.6	163.1	0.36	184.9	1555.5	57.7	0
3.6 V (Discharge)	55.9	1385.3	157.0	1	20.6	1544.3	39.3	0
3.3 V (Discharge)	44.8	1385.8	153.4	1	12.4	1541.6	30.8	0
3.0 V (Discharge)	62.5	1361.1	214.7	1	9.4	1540.4	27.2	0
2.7 V (Discharge)	112.6	1365.8	142.0	1	61.3	1550.0	70.9	0
2.4 V (Discharge)	218.6	1358.7	137.0	1	123.6	1569.4	65.1	0
2.1 V (Discharge)	331.9	1357.2	139.2	0.71	245.5	1575.7	58.3	0

Table S3 Calculated parameters in curve fitting analysis based on *pseudo*-Voigt function, as representative 3 data used for curve fitting analysis

	D-band				G-band			
	Height / -	Position / cm^{-1}	Width / cm^{-1}	Lorentz ratio / -	Height / -	Position / cm^{-1}	Width / cm^{-1}	Lorentz ratio / -
Pristine	93.6 185.7 173.7	1355.4 1350.0 1355.8	180.1 168.9 172.3	0.14 0.37 0.27	81.1 155.2 151.9	1580.5 1575.9 1580.9	63.5 65.0 64.1	0 0 0
15% (Charge)	132.4 113.7 116.0	1353.5 1357.2 1353.3	159.4 133.5 129.2	1 0.88 0.84	81.9 86.6 95.0	1581.8 1586.7 1583.8	66.0 72.4 63.8	0 0.01 0
29% (Charge)	93.4 159.2 89.8	1360.0 1360.2 1357.2	156.0 156.0 133.5	0.39 0.16 0.36	84.8 149.4 83.4	1588.4 1586.7 1583.4	65.4 66.0 68.7	0 0 0
44% (Charge)	226.0 243.0 276.4	1357.8 1353.4 1355.8	149.8 146.6 140.6	0.28 0.55 0.42	214.0 208.5 244.2	1584.4 1587.6 1585.7	65.2 66.4 66.9	0 0 0
59% (Charge)	131.0 152.2 128.5	1359.9 1357.1 1359.1	147.4 146.6 135.2	0.13 0.32 0.64	127.7 138.3 110.9	1587.9 1587.7 1587.5	66.1 68.8 67.9	0 0 0
73% (Charge)	121.8 197.3 172.0	1359.0 1355.8 1357.9	149.2 142.7 138.7	0.35 0.38 0.49	110.7 176.7 150.7	1589.2 1586.9 1587.0	66.3 66.9 67.1	0 0 0
100% (Charge)	410.3 427.7 215.6	1348.3 1346.6 1348.3	117.3 95.2 120.7	0.43 1 0.28	386.7 349.7 200.9	1582.9 1583.0 1584.6	65.9 66.3 66.2	0 0.02 0
58% (Discharge)	169.0 106.4 163.1	1360.5 1359.2 1360.2	186.4 133.2 148.5	0.15 0.63 0.32	148.9 106.4 141.2	1582.7 1586.8 1586.9	59.8 66.9 64.2	0 0 0
15% (Discharge)	242.1 124.2 68.7	1370.3 1376.7 1371.6	160.4 154.0 156.6	0.32 0.62 0.27	193.0 79.0 53.4	1587.0 1592.0 1596.4	65.3 65.8 58.8	0.30 0 0
0% (Discharge)	135.9 126.6 151.7	1368.6 1366.3 1364.7	200.8 150.2 162.9	0.52 0.71 0.73	74.3 97.0 106.0	1587.3 1589.5 1589.1	70.1 65.4 62.6	0 0 0