Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information

Electrochemically activated solid synthesis: A novel solid-state synthetic method demonstrated by low-temperature and ambient pressure formation of $Sc_{2/3}WO_4$

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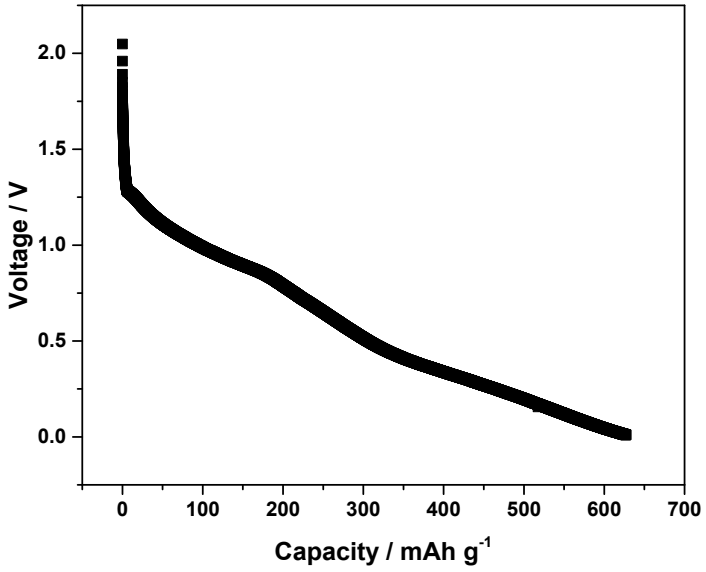

Figure S1 The full discharge curve of 100% Li discharged $Sc_2W_3O_{12}$. The recorded capacity was 627(1) mAh g^{-1}.

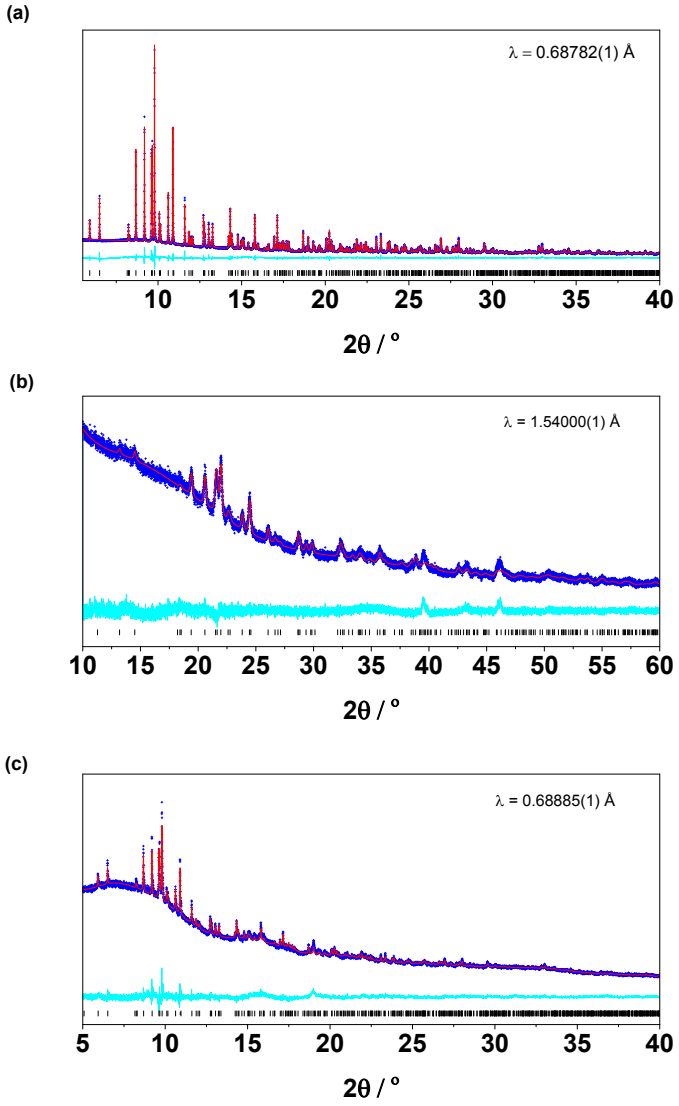

Figure S2 (a) 12.5% discharged Rietveld-refined $Sc_2W_3O_{12}$ model with XRD data, wR=4.280%. (b) 25% discharged Rietveld-refined model with XRD data, wR=4.034%. (c) 50% discharged Rietveld-refined model with XRD data, wR=2.622%. In (b-d) the data are represented as blue, the calculated model as red line and the difference between the data and model as the cyan curve below, the black points are $Sc_2W_3O_{12}$ peak markers.

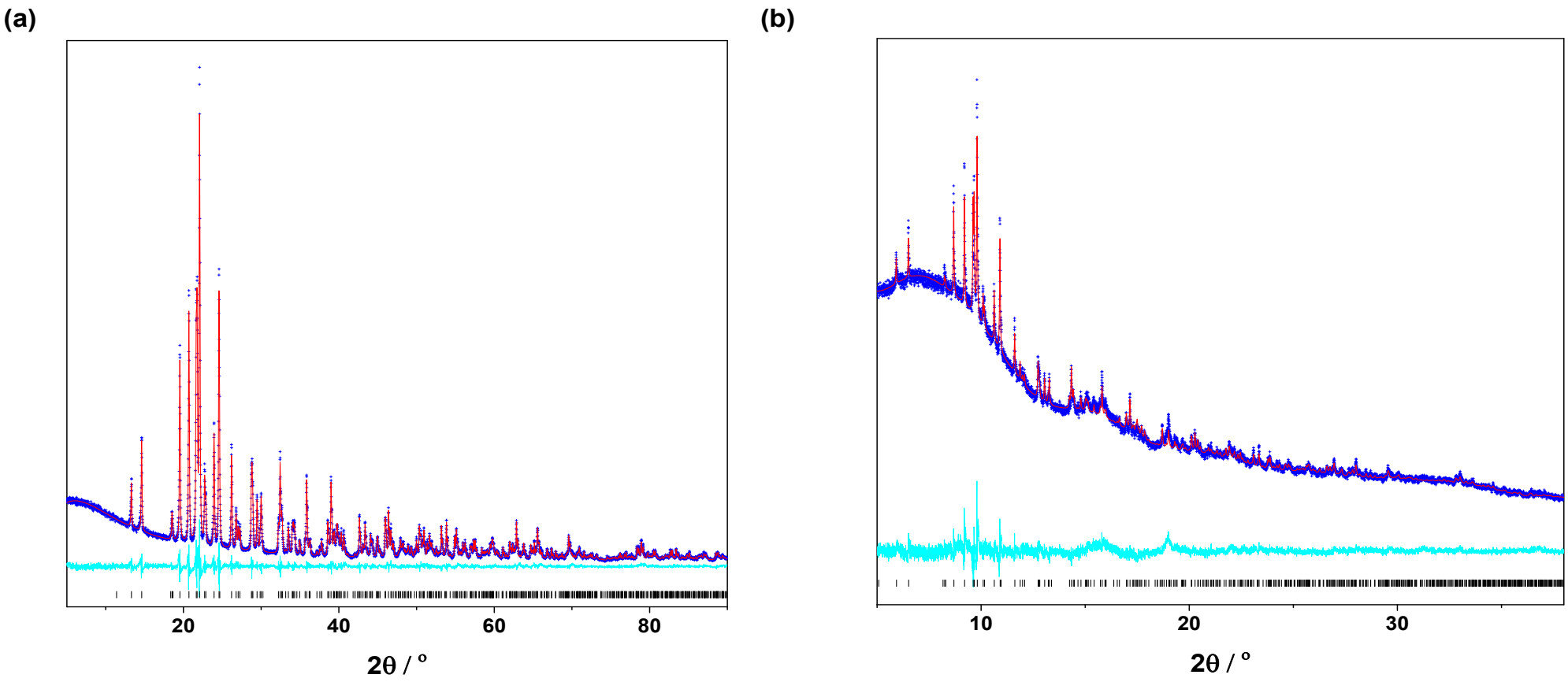

Figure S3 (a) Rietveld-refined fit of the $Sc_2W_3O_{12}$ model with XRD data wR=6.107%. (b) Rietveld-refined fit of the 50% Li discharged $Sc_2W_3O_{12}$ electrode using the $Sc_2W_3O_{12}$ model with XRD data, wR=2.65%. Note, these two results are from different XRD data collected at 2 different wavelengths, the parent $Sc_2W_3O_{12}$ collected at 1.54 Å and for 50% Li discharged $Sc_2W_3O_{12}$ electrode collected at 0.68885(1) Å. In (a-b), the data are represented as dark blue, the calculated model as red line and the difference between the data and model as the cyan curve below, the black points are $Sc_2W_3O_{12}$ peak markers.

Table S1 Pertinent structural and refinement details of the parent $Sc_2W_3O_{12}$ and 50% Li discharged $Sc_2W_3O_{12}$ based on Figure S2.

	a	***b***	***c***
$Sc_2W_3O_{12}$	**9.6735(2)**	**13.3218(3)**	**9.5812(2)**
50% discharged $Sc_2W_3O_{12}$	**9.6747(5)**	**13.3171(7)**	**9.5804(5)**

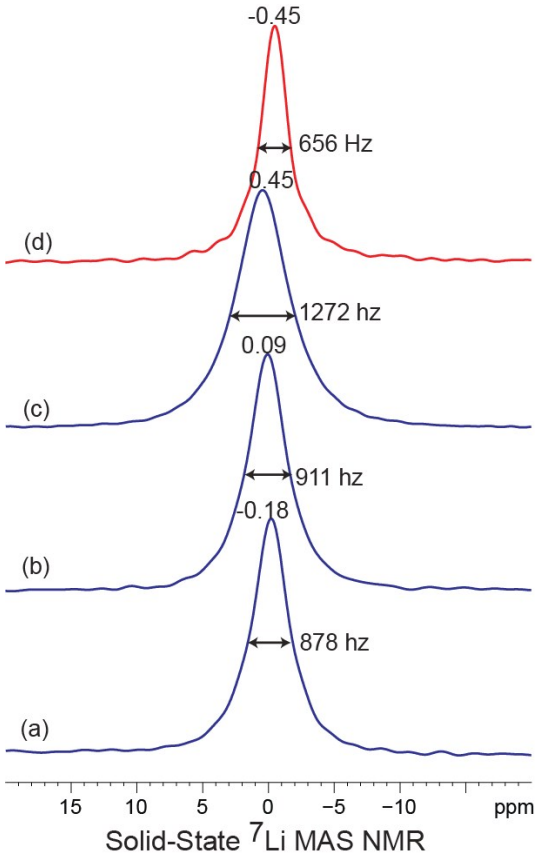

Figure S4 Solid-state ^{7}Li MAS NMR of $Sc_2W_3O_{12}$ electrodes discharged to (a) 12.5 %, (b) 25 % and (c) 50% of the full Li discharge capacity and (d) is the 25 % discharged $Sc_2W_3O_{12}$ heat treated to 700 °C. The chemical shifts of the peak maxima in ppm and the peak full width at half maximum (FWHM) in Hz are indicated.

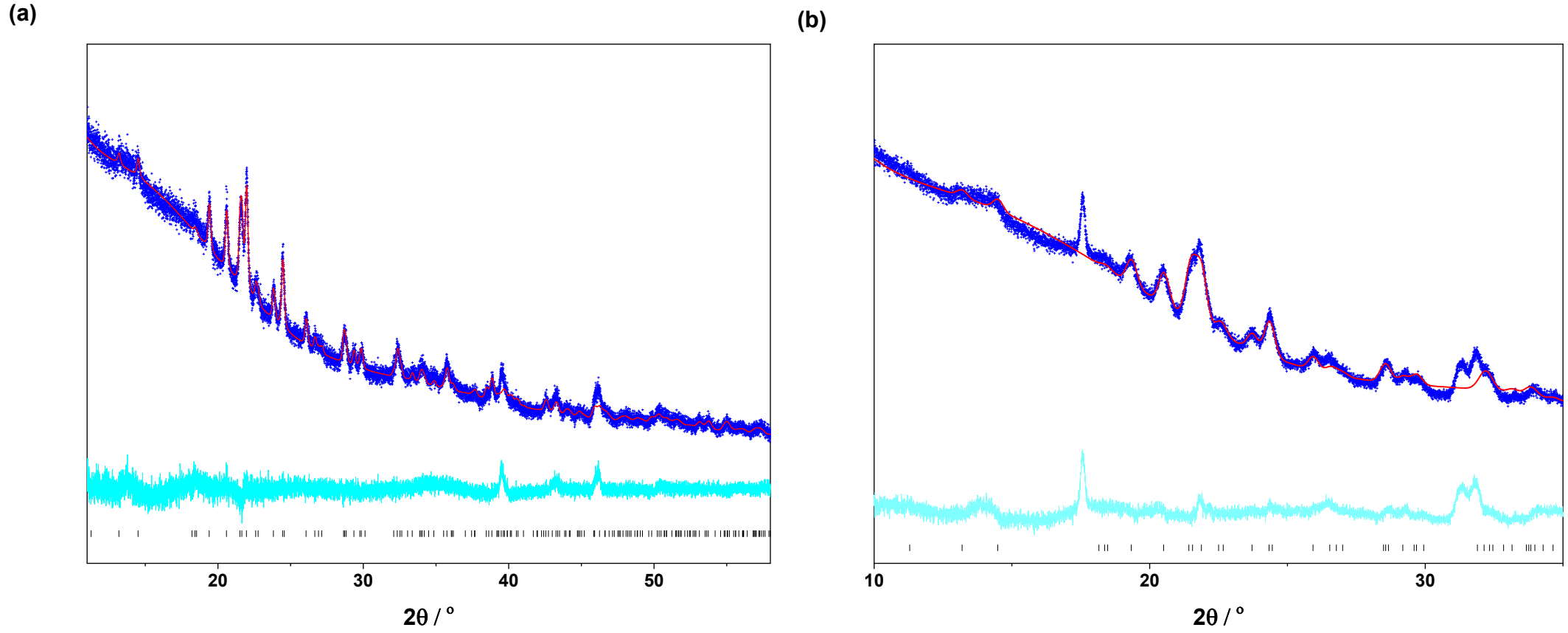

Figure S5 (a) Rietveld refined fit of the structural model with XRD data for electrodes extracted from EC/DMC based electrolyte at 25% discharged (wR=4.034%). (b) Rietveld refined fit of the structural model with XRD data for electrodes extracted from PC based electrolyte at 25% discharged (wR=3.933%). In (a-b), the data are represented as blue, the calculated model as red line and the difference between the data and model as the cyan curve below, the black points are $Sc_2W_3O_{12}$ peak markers. Additional reflections are observed, particularly in the PC based electrodes whch are currently unidentified. These phases could be related to electrolyte decomposition products or crystalline components in the SEI layer.

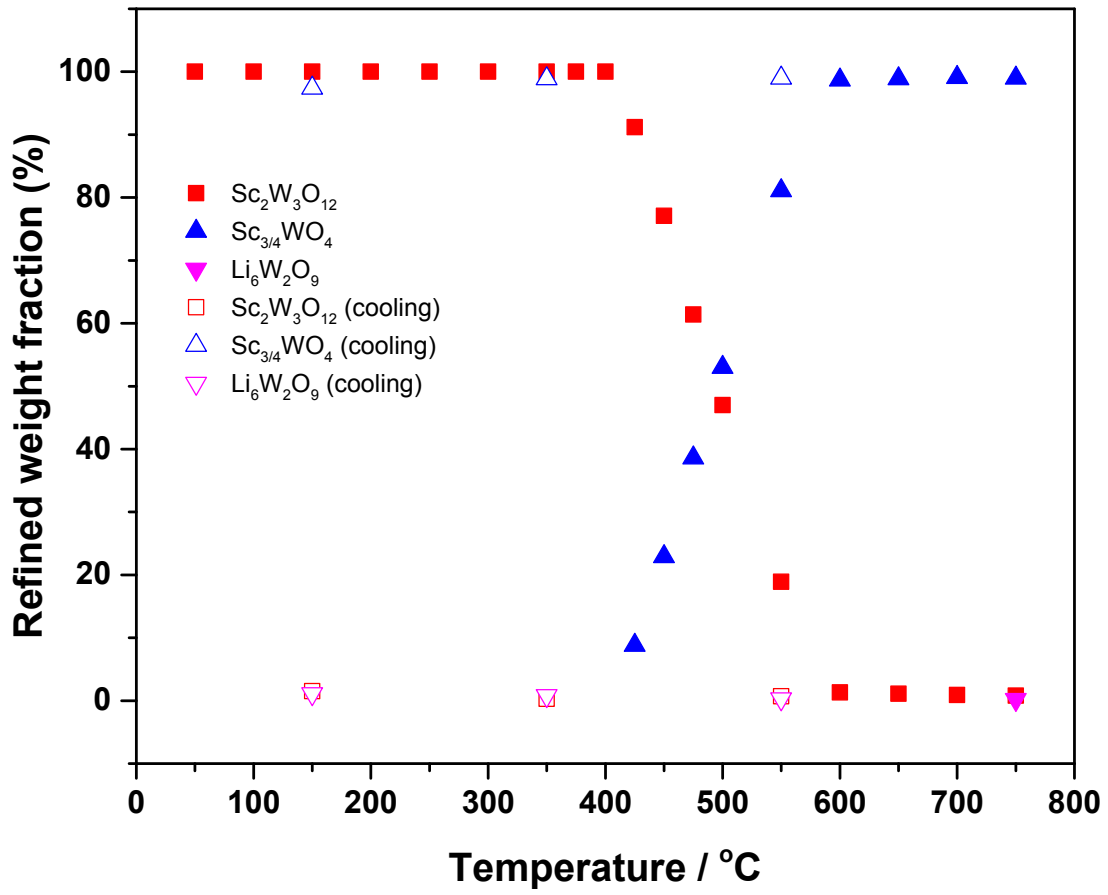

Figure S6 Refined weight fraction of phases during heating and cooling process for the thermal treatment of the 12.5% Li discharged $Sc_2W_3O_{12}$ electrode

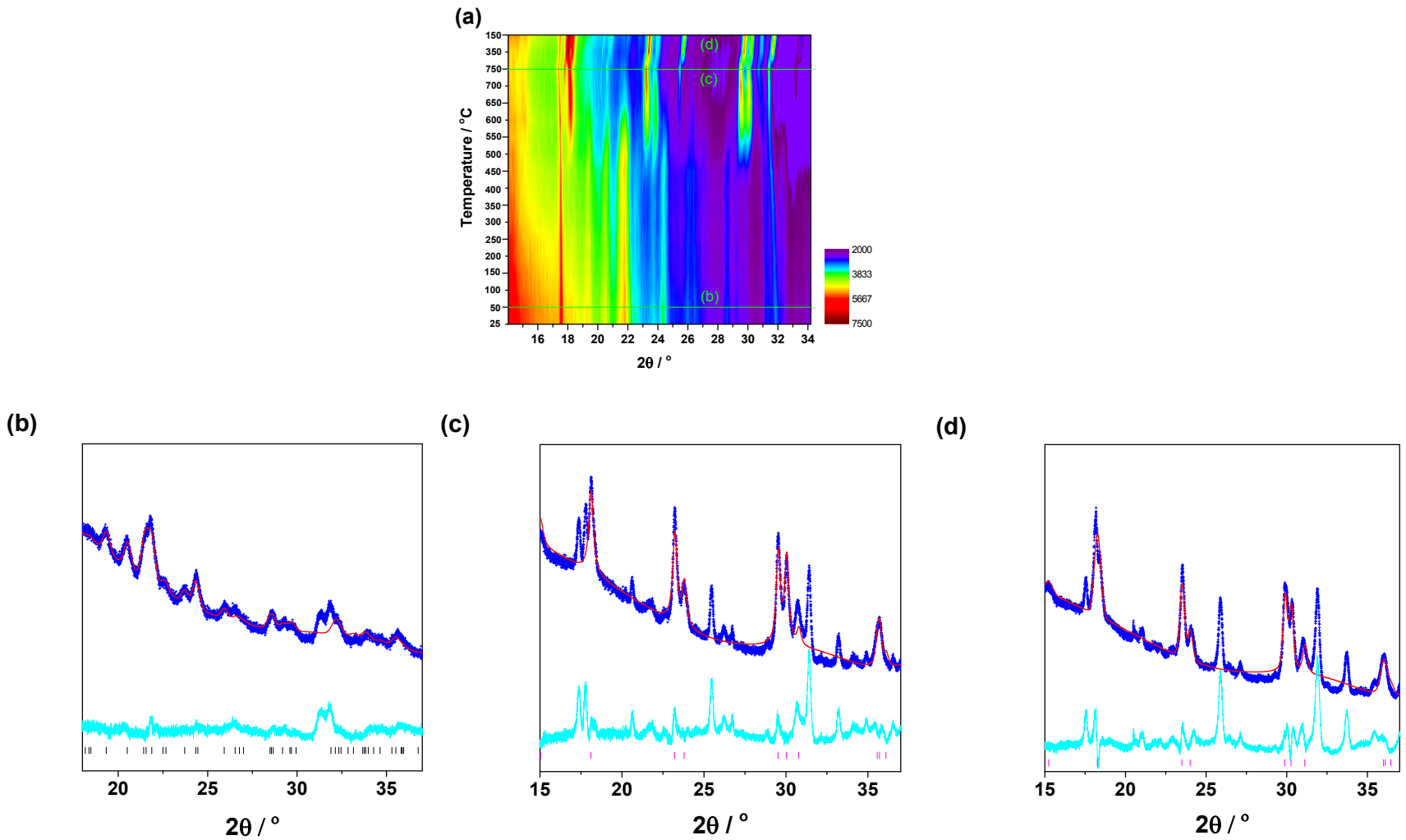

Figure S7 (a) Thermal evolution of 25% discharged $Sc_2W_3O_{12}$ electrode using PC based electrolyte. Rietveld refined fit of $Sc_2W_3O_{12}$ and $Sc_{0.67}WO_4$ structural models with XRD data at (b) 50°C, wR=3.93%, (c) 750°C, wR=7.75% and (d) 150°C after cooling, wR=9.46%. %. In (b-d) the data are represented as blue, the calculated model as red and the difference between the data and model as the cyan curve below, black points are $Sc_2W_3O_{12}$ peak markers, magenta points are $Sc_{0.67}WO_4$ peak markers. Additional reflections are observed, particularly in the PC based electrodes whch are currently unidentified. These phases could be related to electrolyte decomposition products, crystalline components in the SEI layer or the formation of a different selection of products due to thermal treatment.

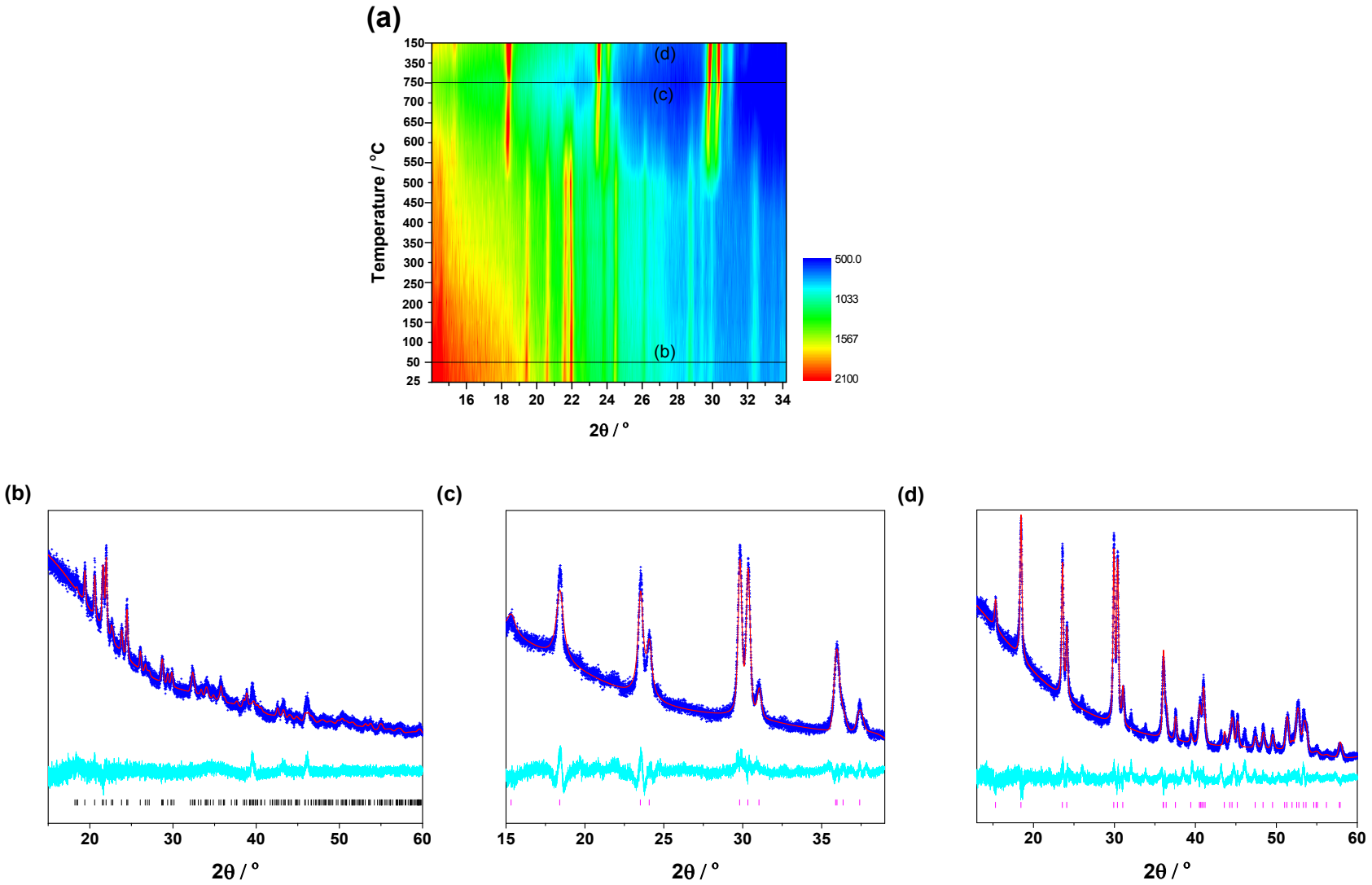

Figure S8 Thermal evolution of 25% discharged $Sc_2W_3O_{12}$ electrode using EC/DMC based electrolyte. Rietveld refined fit of $Sc_2W_3O_{12}$ and $Sc_{0.67}WO_4$ structural models with XRD data at (b) 50°C, wR=4.03%, (c) 750°C, wR=5.13% and (d) 150°C after cooling, wR=5.84%. In (b-d) the data are represented as blue, the calculated model as red and the difference between the data and model as the cyan curve below, black points are $Sc_2W_3O_{12}$ peak markers, magenta points are $Sc_{0.67}WO_4$ peak markers.

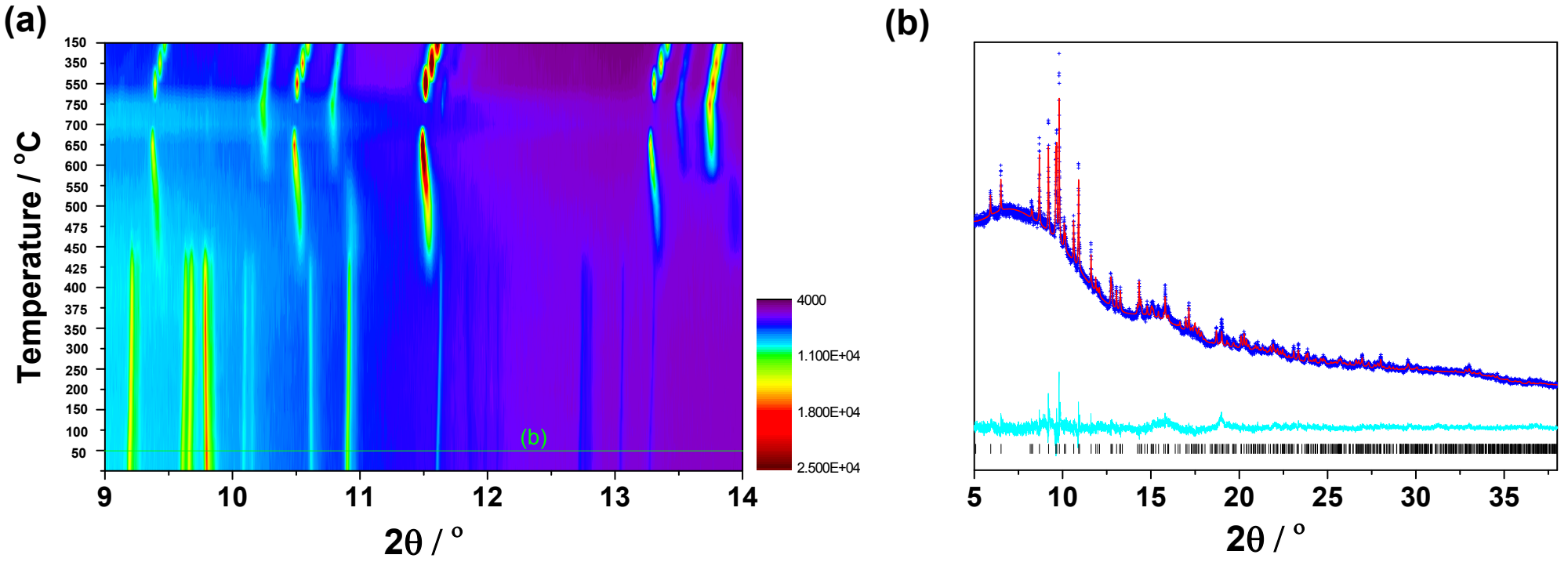

Figure S9 (a) Thermal evolution of 50% discharged $Sc_2W_3O_{12}$ electrode in PC based electrolyte and (b) Rietveld refined fit of the $Sc_2W_3O_{12}$ model with XRD data at 50°C, wR=2.62%. Note: for 50% discharged $Sc_2W_3O_{12}$ electrode, after 450 °C the formation of an unidentified phase is noted. In b, the data are represented as blue, the calculated model as red and the difference between the data and model as the cyan curve below, black are $Sc_2W_3O_{12}$ peak markers. Phase identification details are presented below.

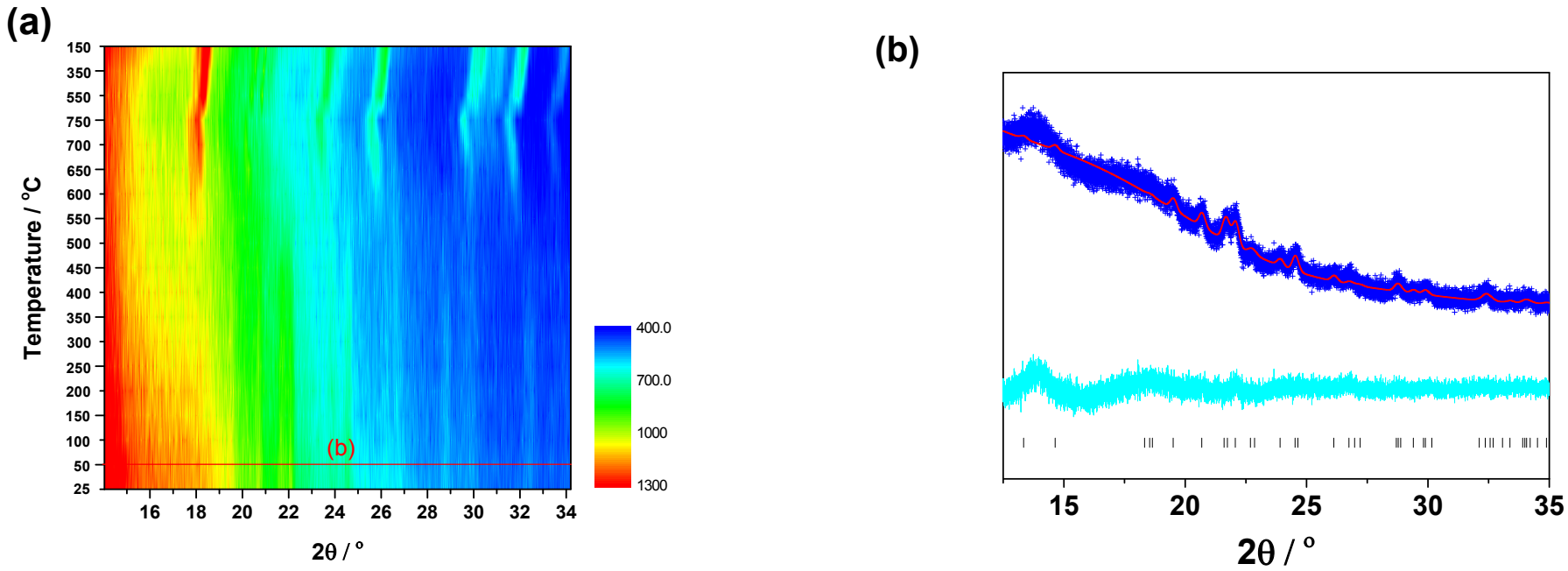

Figure S10 Thermal evolution of 25% discharged $Sc_2W_3O_{12}$ electrode in PC-electrolyte without binder. (b) Rietveld refined fit of the $Sc_2W_3O_{12}$ model with XRD data at 50°C, wR=4.081%. In b, the data are represented as blue, the calculated model as red and the difference between the data and model as the cyan curve below, black are $Sc_2W_3O_{12}$ peak markers. Please note these data were collected on the laboratory XRD.

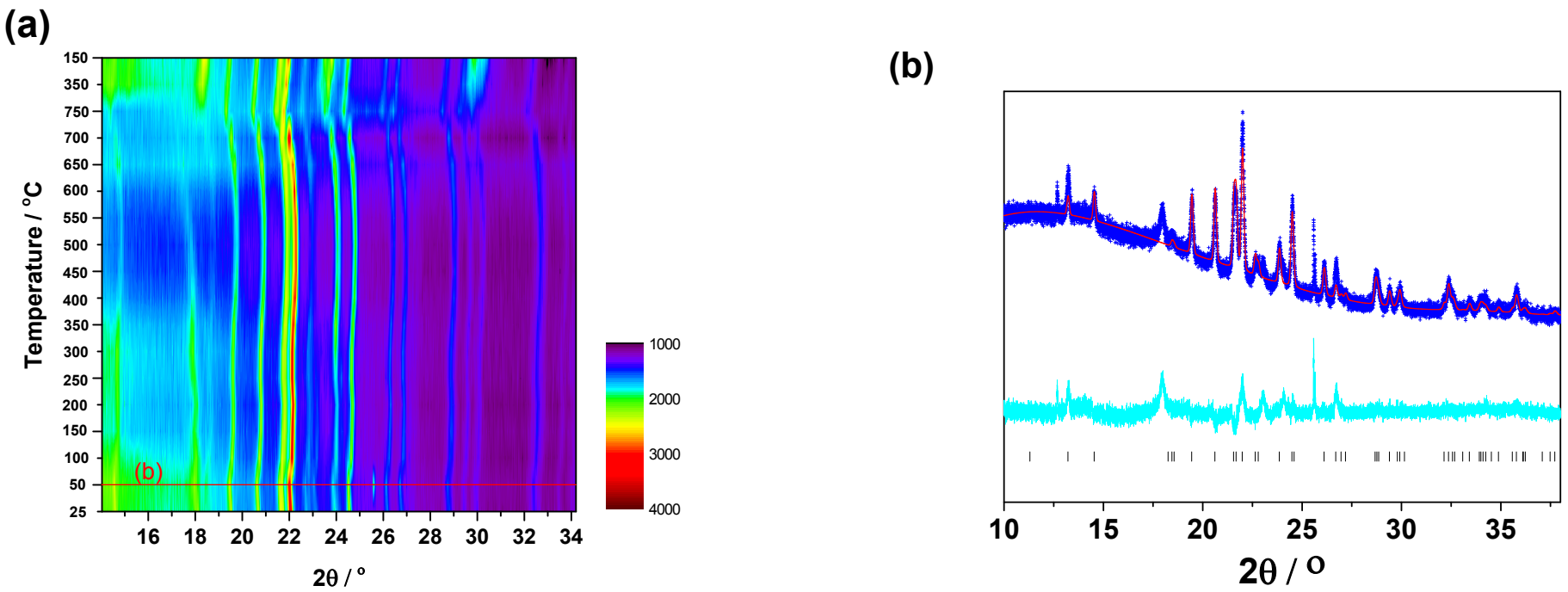

Figure S11 Thermal evolution of 25% discharged $Sc_2W_3O_{12}$ electrode in PC electrolyte with Teflon binder. (b) Rietveld refined fit of the $Sc_2W_3O_{12}$ model with XRD data at 50°C, wR=5.071%. In b, the data are represented as blue, the calculated model as red and the difference between the data and model as the cyan curve below, black are $Sc_2W_3O_{12}$ peak markers. Note the presence of some new reflections in the PC whch are currently unidentified. These phases could be related to electrolyte decomposition products, crystalline components in the SEI layer or the formation of a different selection of products due to thermal treatment.

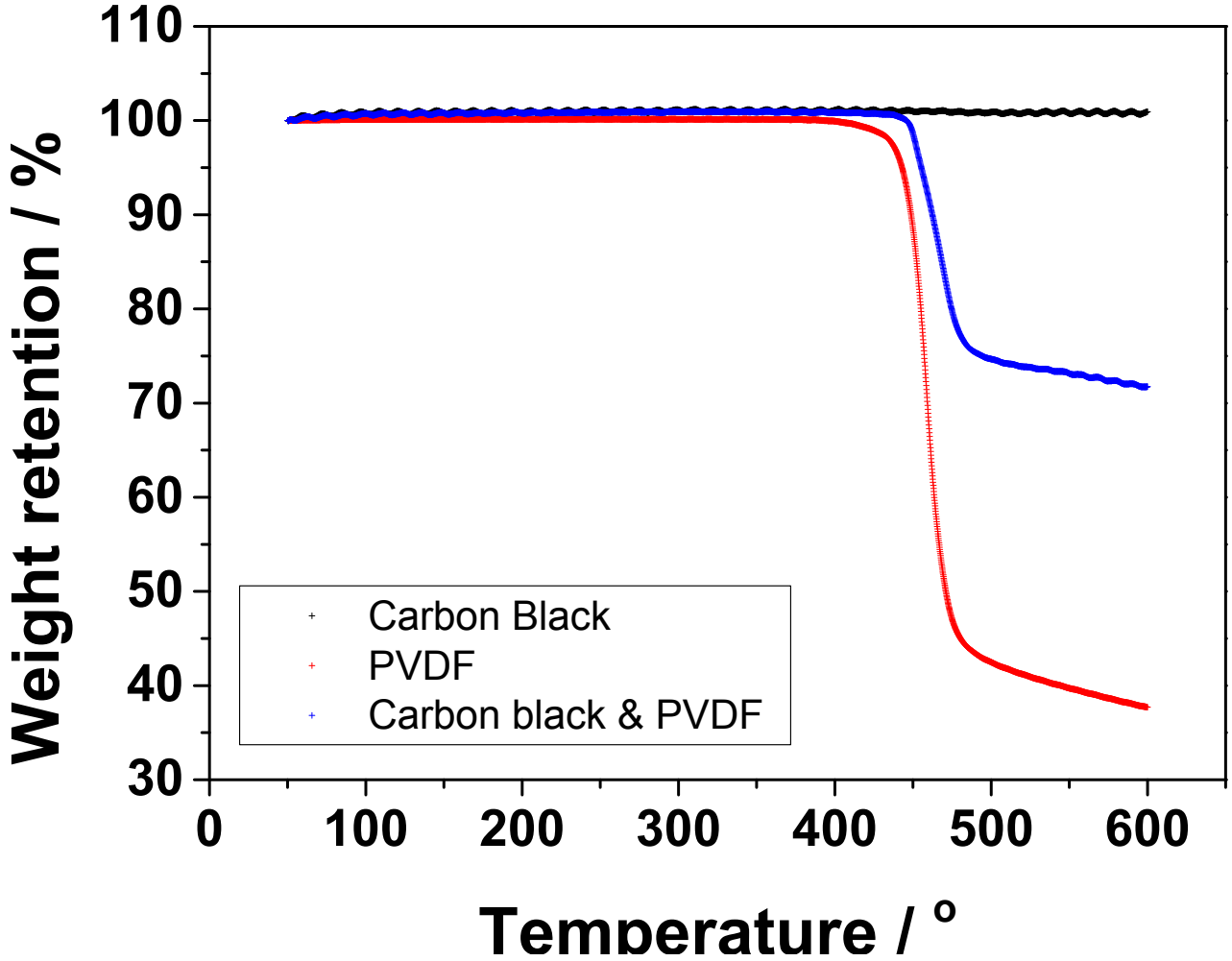

Figure S12 TGA data of carbon black and PVDF.

Phase identification for the 50% discharged $Sc_2W_3O_{12}$ electrode

From the 2D data shown in Figure S7, there are at least two new phases at ~550 °C and 750 °C, which could not be indexed to any known structures in the ICSD and ICCD databases. Preliminary phase identification was attempted:

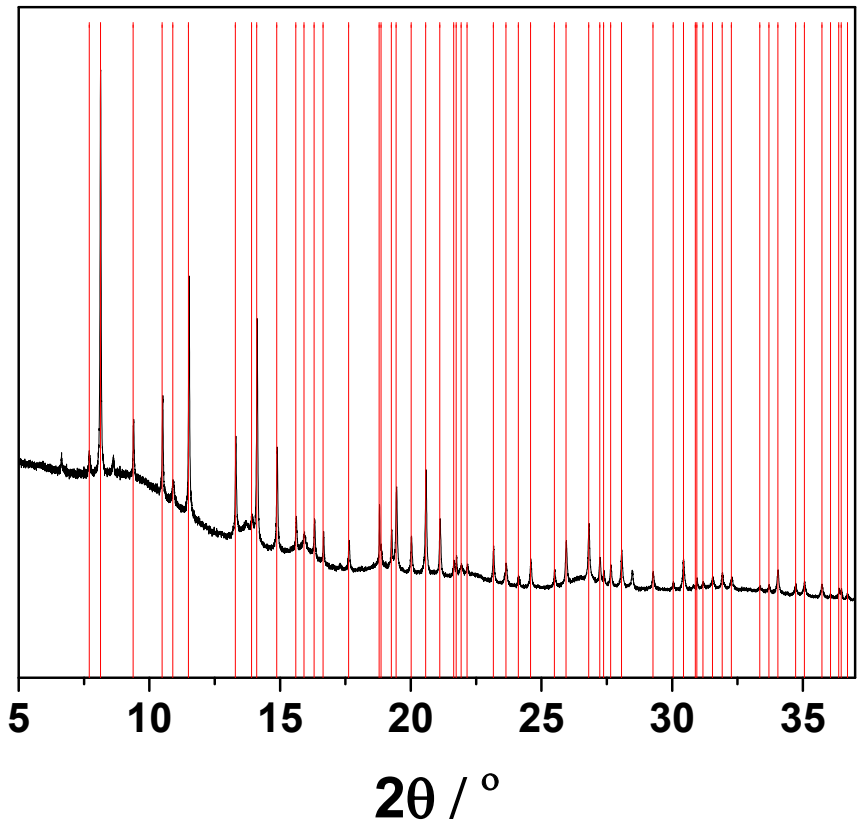

Figure S13 50% Li discharged $Sc_2W_3O_{12}$ electrode at 550°C XRD pattern and extraction of peak positions.

Using the raw data of 50% Li discharged $Sc_2W_3O_{12}$ heated to 550 °C and 700°C, peak identification was undertaken and the positions input into EXPO 2014. Indexing was attempted using N-TEROR09 and DICVOL programs[3]. The best hits are listed in table S2 and S3.

Table S2 Possible phases at 550°C

Nr.	Program	Sym.	a (Å)	b (Å)	c (Å)	alpha (°)	beta (°)	gamma (o)	Vol.(Å^3)	M20	shift (°)
1	N-TEROR09	Triclinic	9.2488	7.9989	6.9748	113.57	103.66	102.7	430.02	8	-0.008
2	N-TEROR09	Triclinic	13.7396	5.9703	10.1604	90	93.67	90	831.75	6	0
3	N-TEROR09	Triclinic	13.7224	5.9603	10.1553	90	93.59	90	828.97	5	-0.008
4	N-TEROR09	Triclinic	11.9326	8.4342	10.9251	90	94.99	90	1095.35	5	0.008
5	DICVOL	Monoclinic	11.5383	16.8293	8.8445	90	106.69	90	1645.1	8.9	0.008
6	DICVOL	Monoclinic	14.6557	10.3149	12.3865	90	96.39	90	1860.88	6.2	0.011

As indicated by the M20 figure-of-merit, the best estimate of the unit cell of phase at 550°C is a monoclinic cell with a = 14.6557, b = 10.3149 and c = 12.3865 Å. Space group determination was also attempted for this unit cell and the best estimate for space group is $\boldsymbol{P2_1}$.

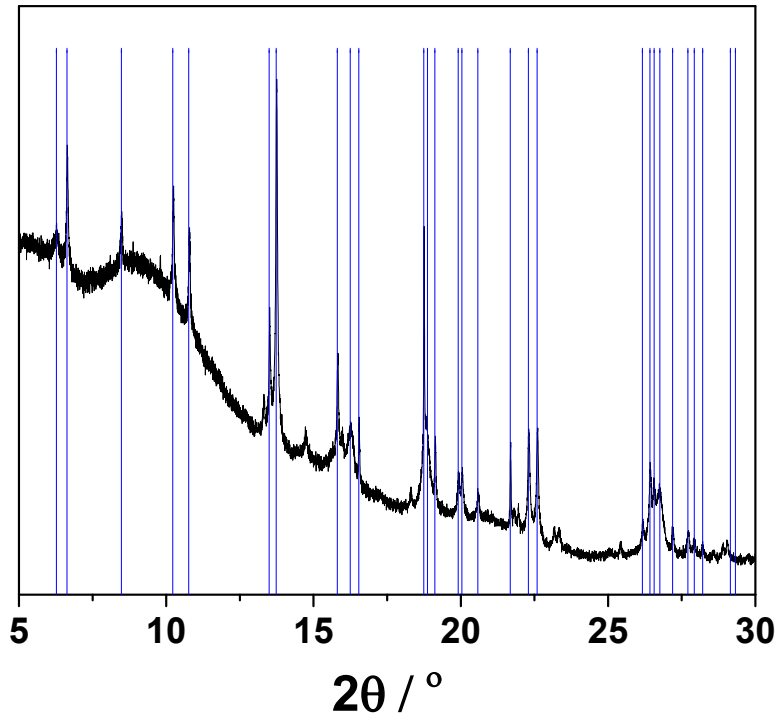

Figure S14 50% Li discharged $Sc_2W_3O_{12}$ electrode at 700°C with extracted peak positions indicated.

Table S3 Possible phases at 700°C

Nr.	Program	Sym.	a (Å)	b (Å)	c (Å)	alpha (°)	beta (°)	gamma (o)	Vol.(Å³)	M20	shift (°)
1	N-TEROR09	Triclinic	6.8822	6.5717	6.1696	94.49	102.29	108.11	256	9	0.015
2	N-TEROR09	Triclinic	8.4676	9.3029	7.7063	90	91.9	90	606.72	8	-0.03
3	N-TEROR09	Triclinic	9.3075	7.7159	8.3277	90	91.32	90	597.91	6	-0.015
4	N-TEROR09	Triclinic	10.3123	9.0192	8.4411	97.44	113.03	78.39	706.61	9	0.038
5	DICVOL	Monoclinic	15.3138	5.9442	12.5884	90	114.75	90	1040.6	8.5	0.018

There are two possible estimates of the unit cell of the phase at 700 °C, the first one is a triclinic cell with *a* = 6.8822, *b* =6.5717 and *c* = 6.1696 Å, the second one is also a triclinic cell with *a* = 10.3123, *b* =9.0192 and *c* = 8.4411. The best estimate group space is $\boldsymbol{P\bar{1}}$.