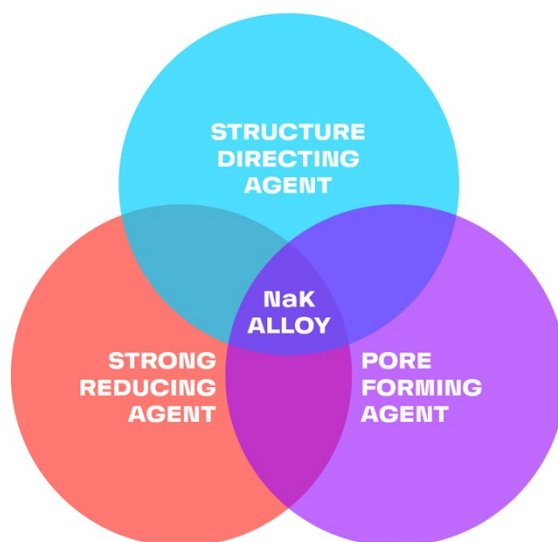


SUPPORTING INFORMATION

NaK alloy as a versatile reagent for template-free synthesis of porous metal- and metalloid-based nanostructures

Sergei S. Leonchuk, Aleksandra S. Falchevskaya, Polina A. Morozova, Nikolai V. Gromov, Vladimir V. Vinogradov*



RESEARCH TECHNIQUES

Scanning electron microscopy

Scanning electron microscopy (SEM) images of the synthesised samples were obtained using a Tescan Vega 3 electron microscope with secondary electron detector at an accelerating voltage of 5 kV. Samples were prepared for the analysis by way of putting 2 μ L of the material suspension in isopropanol on a carbon tape-covered aluminium table and then vacuum drying at room temperature for 24 h.

Energy-dispersive X-ray spectroscopy

Energy-dispersive X-ray spectroscopy (EDS or EDX) was conducted using an Oxford Instruments X-act EDS detector (as a part of Tescan Vega 3 SEM equipment) at an accelerating voltage of 20 kV. Qualitative and semi-quantitative element compositions of the materials were analysed using AZtec One software. EDS element mapping was performed at 1024p resolution and an exposure time of 1000 ms per pixel.

X-ray powder diffraction analysis

X-ray powder diffraction (XRD) data were measured using a Bruker D2 PHASER X-ray diffractometer with Cu K α radiation ($\lambda = 0.154184$ nm) at a voltage of 30 kV. Diffractograms were obtained at 2θ of 10-80°. Angle increment is 0.01825°; time per step is 0.250 s. Samples were prepared for analysis by grinding in an agate mortar. The sample cuvette was rotated at 3 rpm during measurement to reduce powder texture effect on the signal collecting. Qualitative and quantitative phase compositions and crystallite sizes (Scherrer evaluation, FWHM, $K = 0.89$) of the samples were determined using DIFFRAC.EVA software with PDF2 2023 crystallographic database.

Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy was carried out on an FT-IR Spectrometer Thermo Scientific Nicolet iS5 with ID7 Diamond ATR. The interpretation of the spectra was performed using literature.

BET specific surface area analysis

Brunauer-Emmett-Teller (BET) specific surface area analysis was conducted using nitrogen sorption-desorption measurement on a Quantachrome NOVA 1200e surface area and pore size analyzer with NOVAWin software. Sorption-desorption isotherms were obtained at 77 K (liquid nitrogen). Samples were prepared for analysis via vacuum degassing performed at 200 °C for 24 h before analysis.

Pore-size distribution analysis

Pore sizes and volumes were calculated from the data obtained by nitrogen sorption-desorption measurement on the Quantachrome NOVA 1200e surface area and pore size analyzer with NOVAwin software. The Barrett-Joyner-Halenda (BJH) method was used for mesopore size and volume calculations.

Batteries fabrication and testing

Electrochemical tests were performed in coin-type 2032 half-cells. Anodic slurries were obtained by mixing anode materials with Super P carbon (Timcal) and polyvinylidene fluoride PVDF (CAS 24937-79-9, purity 99,5%, HSV900, Gelon Lib) in a ratio of 80:10:10, respectively, and N-methyl-2-pyrrolidinone NMP (CAS 872-50-4, purity >99%, Acros Organics) was used as a solvent. The resulting slurries were spread on aluminium foil (Gelon Lib, 15 μ m) using a Zehntner ZAA 2300 automatic film applicator. The electrodes were calendered and dried in vacuum at 100 °C overnight. The resulting loadings were 0.13 – 0.4 mg·cm⁻².

For sodium cells, the electrolyte consisted of a 1 M mixture of sodium hexafluorophosphate salt, NaPF₆ (CAS 21324-39-0, purity 98%, Sigma-Aldrich) dissolved in a mixture of ethylene carbonate, EC (CAS 96-49-1, purity 99%, anhydrous, Sigma-Aldrich) and propylene carbonate, PC (CAS 108-32-7, purity 99%, anhydrous, Sigma-Aldrich) in a volume ratio of 1:1 with 2% wt. fluoroethylene carbonate, FEC (CAS 114435-02-8, purity 99%, anhydrous,

Sigma-Aldrich). For potassium cells, the electrolyte consisted of a 0.5 M mixture of potassium hexafluorophosphate salt, KPF₆ (CAS 17084-13-8, purity 99%, Acros organics) dissolved in a mixture of ethylene carbonate, EC and diethyl carbonate, DEC (CAS 105-58-8, purity >99%, Sigma-Aldrich) in a volume ratio of 1:1.

Cells were assembled in an MBraun MB-200B glove box under an inert argon atmosphere (H₂O < 0.1 ppm, O₂ < 0.1 ppm). All electrochemical measurements were performed using Neware battery testers at room temperature.

Testing results. The capacities of both the Sn- and Sb-based materials undergo fading within the first 10 cycles at C/20 rate: starting with average 353 mAh·g⁻¹ and 221 mAh·g⁻¹ in Na- and K-half-cells, it drops to 168 mAh·g⁻¹ and 70 mAh·g⁻¹ to the end of the step at C/20, respectively (Figure 3A). The cycling stability of the material at C/10 is quite good (91% after 50 cycles) but remains only 24 mAh·g⁻¹ in Na // Sn and 50 mAh·g⁻¹ in K // Sn. Differential capacity plots of the first cycles show irreversible processes at anode discharge apparently forming electrochemically inactive AxSny (A - alkali metal Na or K) phases leading to capacity fades in Na- and K-cells.

Similar fading is observed in Sb-based materials: average discharge capacity drops from 332 mAh·g⁻¹ to 20 mAh·g⁻¹ during 10 cycles at C/20 in Na // Sb cells, and from 274 mAh·g⁻¹ to 7.5 mAh·g⁻¹ in K // Sb cells, respectively. The residual capacities are less than 10 mAh·g⁻¹ at C/10 (Figure 3B), and asymmetrical charge-discharge behaviour observed in differential capacity plots signals materials degradation in both Na- and K-cells.

EXPERIMENTAL PART

Materials

Sodium metal (CAS 7440-23-5; purity > 99 %; "Component-Reaktiv"; Russia); potassium metal (CAS 7440-09-7; purity > 99 %; "Component-Reaktiv"; Russia); carbon tetrachloride CCl₄ (CAS 56-23-5; purity > 99.99 %; "EKOS-1"; Russia); silicon tetrachloride SiCl₄ (CAS 10026-04-7; purity 99.9 %; "Sigma Aldrich"; Germany); germanium tetrachloride GeCl₄ (CAS 10038-98-9; purity 99.999 %; "ABCR Chemie"; Germany); tin tetrachloride SnCl₄ (CAS 7646-78-8; purity 99 %; "Sigma Aldrich"; Germany); antimony pentachloride SbCl₅ (CAS 7647-18-9; purity 99 %; "Sigma Aldrich", Germany); antimony trichloride SbCl₃ (CAS 10025-91-9; purity 99 %; "Himpribor-SPb", Russia); iron trichloride FeCl₃ (CAS 7705-08-0; purity 99 %; "Sigma Aldrich"; Germany); ruthenium trichloride RuCl₃ (CAS 14898-67-0; purity 99.9 %; "ABCR Chemie"; Germany); tantalum pentachloride TaCl₅ (CAS 7721-01-9; purity 99.9 %; "LANHIT", Russia); niobium pentachloride NbCl₅ (CAS 10026-12-7; purity 99.9 %; "LANHIT", Russia); titanium tetrachloride TiCl₄ (CAS 7550-45-0; purity 99.9 %; "Promhimperm", Russia); n-hexane C₆H₁₄ (CAS 110-54-3; purity > 99 %; "EKOS-1"; Russia); m-xylene C₈H₁₀ (CAS 108-38-3; "Acros Organics"; USA); 1,2-dimethoxyethane (DME, monoglyme) C₄H₁₀O₂ (CAS 110-71-4; purity 99 %; "Sigma Aldrich", Germany); diethylene glycol dimethyl ether (DGM, diglyme) C₆H₁₄O₃ (CAS 111-96-6; purity 99 %; "Chemical Line", Russia); isopropyl alcohol (IPA, propanol-2) C₃H₈O (CAS 67-63-0; purity > 99 %; "EKOS-1"; Russia); mineral oil (paraffine oil,

vaseline oil) 0.850 g·cm⁻³ (CAS 8012-95-1; “Lenreactiv”; Russia). The NaK-78 eutectic liquid alloy was prepared by fusing sodium and potassium metals weighted in a proper proportion with 2 significant digits (fused at 100 °C under the mineral oil, then washed with xylene solution of IPA in an argon-filled glove box).

Table S1 – Physical properties of NaK-78 and solvents used in the work*

Liquid (at 20 °C)	NaK-78	n-hexane	m-xylene	monoglyme (1,2-DME)	diglyme (DGM)
Density, g·cm ⁻³	0.867	0.659	0.860	0.865	0.943
Viscosity, mPa*s	0.940	0.313	0.620	0.434	0.981
Surface tension, mN*m ⁻¹	110	18.22	28.90	24.70	27
Dielectric constant	–	1.88	2.374	7.20	7.30

* Sources:

1. CRC Handbook of Chemistry and Physics, ed. W. M. Haynes, CRC Press, 92nd edn, 2011.
2. <https://doi.org/10.1039/C3RA47191H>
3. <https://doi.org/10.1007/s10765-008-0503-0>
4. <https://doi.org/10.1021/acs.jced.9b00525>
5. <https://doi.org/10.1016/j.fluid.2010.03.040>
6. <https://doi.org/10.1039/D2TA06882F>

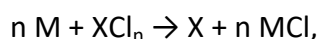
Fabrication of NaK emulsions

8 mL of solvent was placed in a 15 mL plastic (HDPE) tube. The required amount of the prepared NaK-78 eutectic alloy (up to 0.1 mL) was added to the tube with a Thermo Scientific Black pipette. Air in the tube was replaced with argon, the tube was intensely shaken manually (to produce sub-mm alloy drops), then closed with a cap and put in the centre of an Elmasonic S 30H ultrasonic bath filled with water. Metal drops were sonicated at a frequency of 37 kHz (double half-wave sound) and a power of 280 W (80 W effective US power) for 5 min. The resulting NaK-78 emulsions with concentrations of 2, 5, and 10 mg/mL were immediately used in synthesis. Unless otherwise stated, emulsification and all subsequent synthetic procedures were performed at room temperature (25 °C). NaK-78, its emulsions, and synthetic mixtures were handled in a fire-resistant fumehood (without using a glovebox).

General synthetic route

Estimated NaK-78 molar mass taken for the synthesis calculations: $M(\text{NaK-78}) = 33.8 \text{ g/mol}$ (for 78 wt. % K and 22 wt. % Na).

Synthetic reaction can be presented in the following way:



where M is K or Na in the NaK-78 alloy, X is the metalloid or metal synthesised in the work, and n is the valency of the metalloid.

NaK-78 is used in excess of 20 % to the stoichiometric chemical amount. This approach allows to achieve a higher degree of conversion as well as to prevent nanosized product oxidation (by the oxygen traces in the reaction media).

The concentrations of the metalloid precursors and NaK-78 emulsions were varied in three ways (Table S2) to investigate the effect of reagent concentration on the composition and structure of the synthesised metalloid materials. The volume of the final synthetic solution is constant for all concentration regimes: $V(\text{final solution}) = 10.0 \text{ mL} = \text{const.}$ The volume of the precursor solution was also constant for all concentration regimes: $V(\text{precursor solution}) = 2.0 \text{ mL} = \text{const.}$ The same is for NaK-78 emulsion: $V(\text{NaK-78 emulsion}) = 8.0 \text{ mL} = \text{const.}$ The volume change during emulsion and solution preparation is not taken into account because this change is not significant (less than 5 %).

Table S2 – Concentration regimes used in the work

Regime	Precursor concentration, $\text{mmol}\cdot\text{L}^{-1}$	NaK-78 emulsion concentration, $\text{mg}\cdot\text{mL}^{-1}$
1	10	2
2	25	5
3	50	10

The proposed method consisted of the following steps:

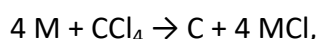
- 1) 8.0 mL of solvent was added to a 15 mL plastic tube,
- 2) the required amount of NaK-78 was placed in the tube,
- 3) the tube was filled with argon, sealed, and intensely shaken by hand to produce sub-mm drops of NaK-78,
- 4) the tube was placed in the middle of an ultrasonic bath and sonicated for 5 min to produce an emulsion,
- 5) another tube was used to prepare a metalloid precursor solution by adding required amount of metalloid chloride to 2 mL of solvent,
- 6) the prepared metalloid precursor solution was immediately added to the freshly prepared NaK-78 emulsion,
- 7) the resulting system was filled with argon again, hermetically sealed, manually shaken, and placed on the tube rotator (shaker) for 20 h,

- 8) after 20 h, the residual NaK-78 in the resulting product (suspension or precipitate) was etched by adding isopropyl alcohol (IPA) dropwise,
- 9) when hydrogen formation stopped, the solution with the product was poured into a 50 mL centrifuge plastic tube and IPA was added to obtain 20 mL solution,
- 10) the resulting system was centrifuged at 10000 rpm for 10 min and the precipitate (unprocessed product) was placed in a vacuum desiccator with silica gel for 24 h,
- 11) the sample (dried unprocessed product) was annealed at 500 °C (except for 45 min in a tube furnace in argon gas flow,
- 12) the resulting powder (annealed product) was washed with deionized water (40 mL) and centrifuged (10000 rpm; 10 min) thrice,
- 13) the resulting sample (final product) was dried in a vacuum desiccator with silica gel for 24 h.
- 14) the resulting unprocessed products were dried and characterised using scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), and X-ray powder diffraction (XRD); the crude products were then washed with deionised (DI) water to remove NaCl and KCl by-products, and the final products were dried and analysed using SEM, EDX, and nitrogen sorption-desorption analysis followed by BET and BJH calculations.

Before steps (10) and (13), small amounts of the sample were taken for SEM and EDS characterization of the obtained materials. XRD characterization was carried out mainly with the samples before step (12).

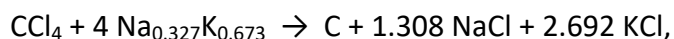
Synthesis of carbon-based materials in DME, hexane, and xylene

Scheme of the synthetic reaction is as follows:



where M is Na or K in the NaK-78 alloy.

The reaction for stoichiometric calculations (considering NaK-78 as $Na_{0.327}K_{0.673}$) can also be represented in a following way:



All the calculations required for the synthesis are presented in Table S3.

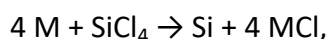
Table S3 – Stoichiometric calculations for the synthesis of carbon-based materials

Concentration of CCl_4 in the final solution, $mmol \cdot L^{-1}$	10	25	50
Chemical amount of CCl_4 , mol	0.00010	0.00025	0.00050
Mass of CCl_4 , g	0.0154	0.0385	0.0769
Volume of CCl_4 , μL	9.60	24.1	48.2
Chemical amount of NaK-78	0.00040	0.0010	0.0020

(stoichiometric), mol			
Chemical amount of NaK-78 (with an excess of 20 %), mol	0.00048	0.0012	0.0024
Mass of NaK-78 (in excess), g	0.0162	0.0406	0.0811
Volume of NaK-78 (in excess), μL	18.7	46.8	93.6
Concentration of NaK-78 emulsion, $\text{mg}\cdot\text{mL}^{-1}$	2.0	5.1	10

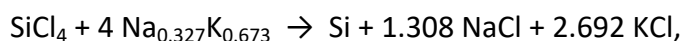
Synthesis of silicon-based materials in DME, hexane, and xylene

Scheme of the synthetic reaction is as follows:



where M is Na or K in the NaK-78 alloy.

The reaction for stoichiometric calculations (considering NaK-78 as $\text{Na}_{0.327}\text{K}_{0.673}$) can also be represented in a following way:



where the final product can bind with the NaK-78 alloy forming various compounds of Na_xSi_y and K_xSi_y compositions.

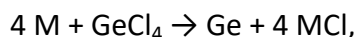
All the calculations required for the synthesis are presented in Table S4.

Table S4 – Stoichiometric calculations for the synthesis of silicon-based materials

Concentration of SiCl_4 in the final solution, $\text{mmol}\cdot\text{L}^{-1}$	10	25	50
Chemical amount of SiCl_4 , mol	0.00010	0.00025	0.00050
Mass of SiCl_4 , g	0.0170	0.0425	0.0850
Volume of SiCl_4 , μL	11.5	28.7	57.4
Chemical amount of NaK-78 (stoichiometric), mol	0.00040	0.0010	0.0020
Chemical amount of NaK-78 (with an excess of 20 %), mol	0.00048	0.0012	0.0024
Mass of NaK-78 (in excess), g	0.0162	0.0406	0.0811
Volume of NaK-78 (in excess), μL	18.7	46.8	93.6
Concentration of NaK-78 emulsion, $\text{mg}\cdot\text{mL}^{-1}$	2.0	5.1	10

Synthesis of germanium-based materials in DME, hexane, and xylene

Scheme of the synthetic reaction is as follows:



where M is Na or K in the NaK-78 alloy.

The reaction for stoichiometric calculations (considering NaK-78 as $\text{Na}_{0.327}\text{K}_{0.673}$) can also be represented in a following way:



where the final product can bind with the NaK-78 alloy forming various compounds of Na_xGe_y and K_xGe_y compositions.

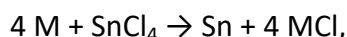
All the calculations required for the synthesis are presented in Table S5.

Table S5 – Stoichiometric calculations for the synthesis of germanium-based materials

Concentration of GeCl_4 in the final solution, $\text{mmol}\cdot\text{L}^{-1}$	10	25	50
Chemical amount of GeCl_4 , mol	0.00010	0.00025	0.00050
Mass of GeCl_4 , g	0.0214	0.0536	0.107
Volume of GeCl_4 , μL	11.4	28.5	57.1
Chemical amount of NaK-78 (stoichiometric), mol	0.00040	0.0010	0.0020
Chemical amount of NaK-78 (with an excess of 20 %), mol	0.00048	0.0012	0.0024
Mass of NaK-78 (in excess), g	0.0162	0.0406	0.0811
Volume of NaK-78 (in excess), μL	18.7	46.8	93.6
Concentration of NaK-78 emulsion, $\text{mg}\cdot\text{mL}^{-1}$	2.0	5.1	10

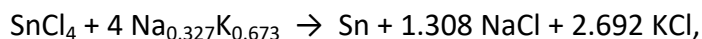
Synthesis of tin-based materials in DME, hexane, and xylene

Scheme of the synthetic reaction is as follows:



where M is Na or K in the NaK-78 alloy.

The reaction for stoichiometric calculations (considering NaK-78 as $\text{Na}_{0.327}\text{K}_{0.673}$) can also be represented in a following way:



where the final product can bind with the NaK-78 alloy forming various compounds of Na_xSn_y and K_xSn_y compositions.

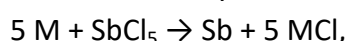
All the calculations required for the synthesis are presented in Table S6.

Table S6 – Stoichiometric calculations for the synthesis of tin-based materials

Concentration of SnCl ₄ in the final solution, mmol·L ⁻¹	10	25	50
Chemical amount of SnCl ₄ , mol	0.00010	0.00025	0.00050
Mass of SnCl ₄ , g	0.0261	0.0651	0.130
Volume of SnCl ₄ , μL	11.7	29.3	58.5
Chemical amount of NaK-78 (stoichiometric), mol	0.00040	0.0010	0.0020
Chemical amount of NaK-78 (with an excess of 20 %), mol	0.00048	0.0012	0.0024
Mass of NaK-78 (in excess), g	0.0162	0.0406	0.0811
Volume of NaK-78 (in excess), μL	18.7	46.8	93.6
Concentration of NaK-78 emulsion, mg·mL ⁻¹	2.0	5.1	10

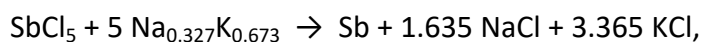
Synthesis of antimony-based materials in DME, hexane, and xylene

Scheme of the synthetic reaction is as follows:



where M is Na or K in the NaK-78 alloy.

The reaction for stoichiometric calculations (considering NaK-78 as Na_{0.327}K_{0.673}) can also be represented in a following way:



where the final product can bind with the NaK-78 alloy forming various compounds of Na_xSb_y and K_xSb_y compositions.

All the calculations required for the synthesis are presented in Table S7.

Table S7 – Stoichiometric calculations for the synthesis of antimony-based materials

Concentration of SbCl ₅ in the final solution, mmol·L ⁻¹	10	25	50
Chemical amount of SbCl ₅ , mol	0.00010	0.00025	0.00050
Mass of SbCl ₅ , g	0.0299	0.0748	0.150

Volume of SbCl ₅ , μL	12.8	32.0	64.0
Chemical amount of NaK-78 (stoichiometric), mol	0.00050	0.0013	0.0025
Chemical amount of NaK-78 (with an excess of 20 %), mol	0.00060	0.0015	0.0030
Mass of NaK-78 (in excess), g	0.0203	0.0507	0.1014
Volume of NaK-78 (in excess), μL	23.4	58.5	117
Concentration of NaK-78 emulsion, $\text{mg}\cdot\text{mL}^{-1}$	2.5	6.3	12.7

Characterisation of the samples synthesised in DME, hexane, and xylene

Table S8 – Semi-quantitative elemental compositions of synthesised metalloids-based materials (at $50 \text{ mmol}\cdot\text{L}^{-1}$ concentration regime)

Sample	Elemental composition, %	Element ratio
Carbon-based (DME, final product)	C – 78.17; O – 11.49; Na – 4.71; Cl – 3.87; K – 1.75	C : O = 6.8 : 1
Silicon-based (DME, final product)	O – 52.53; Cl – 13.64; Si – 12.16; Na – 11.30; K – 10.36	Si : O = 1 : 4.3
Germanium-based (DME, final product)	O – 75.99; Ge – 21.89; K – 1.33; Cl – 0.73; Na – 0.05	Ge : O = 1 : 3.5
Tin-based (hexane, unprocessed product)	Cl – 26.85; K – 23.32; Sn – 22.98; O – 18.86; Na – 8.09	Sn : O = 1.2 : 1

Tin-based (xylene, unprocessed product)	Cl – 31.13; K – 25.84; Sn – 22.77; O – 15.08; Na – 5.17	Sn : O = 1.5 : 1
Tin-based (DME, unprocessed product)	Cl – 31.42; K – 29.99; Sn – 22.20; O – 12.40; Na – 3.98	Sn : O = 1.8 : 1
Antimony-based (hexane, unprocessed product)	Cl – 24.96; K – 26.92; O – 26.60; Sb – 17.35; Na – 4.17	Sb : O = 1 : 1.5
Antimony-based (xylene, unprocessed product)	Cl – 28.81; K – 26.44; Sb – 21.53; O – 20.08; Na – 3.14	Sb : O = 1.1 : 1
Antimony-based (DME, unprocessed product)	Cl – 33.75; K – 28.85; Sb – 19.54; O – 14.76; Na – 3.10	Sb : O = 1.3 : 1

Table S9 – Yields and phase compositions of carbon-based materials

Solvent	Concentration of a precursor, mmol·L ⁻¹	Yield (raw product), %	Yield (final product), %	Phase composition (unprocessed product), %	Crystallite size (KCl), nm
hexane	10	12.3	0	KCl – 100	–
	25	74.1	0		–
	50	67.4	0		44.81
xylene	10	8.8	0	KCl – 100	–
	25	62.5	0		–

	50	85.4	0		35.04
DME	10	88.9	0	KCl – 92.0 NaCl – 8.0	–
	25	104.9	13.5		–
	50	106.5	18.6		34.27

Table S10 – Yields and phase compositions of silicon-based materials

Solvent	Concentration of a precursor, mmol·L ⁻¹	Yield (raw product), %	Yield (final product), %	Phase composition (unprocessed product), %	Crystallite size (KCl), nm
hexane	10	6.9	0	KCl – 95.7 NaCl – 4.3	–
	25	67.2	0		52.28
	50	80.9	0		54.24
xylene	10	6.4	0	–	–
	25	8.9	0		–
	50	28.0	0		–
DME	10	73.8	0	KCl – 85.7 NaCl – 14.3	–
	25	94.6	14.8		54.65
	50	90.2	20.1		58.94

Table S11 – Yields and phase compositions of germanium-based materials

Solvent	Concentration of a precursor, mmol·L ⁻¹	Yield (raw product), %	Yield (final product), %	Phase composition (unprocessed product), %	Crystallite size (KCl), nm
hexane	10	70.9	0	KCl – 89.5 NaCl – 10.5	–
	25	82.3	2.9		–

	50	71.7	4.8		49.88
xylene	10	129.1	0	KCl – 90.7	–
	25	109.3	3.8	NaCl – 9.3	–
	50	92.3	6.1		50.59
DME	10	125.7	2.0	–	–
	25	118.1	15.1	KCl – 84.8 NaCl – 15.2	49.83
	50	98.0	26.9	KCl – 87.6 NaCl – 12.4	49.98

Table S12 – Yields and phase compositions of tin-based materials

Solvent	Concentration of a precursor, mmol·L ⁻¹	Yield (raw product), %	Yield (final product), %	Phase composition (unprocessed product), %	Crystallite size (KCl), nm
hexane	10	25.0	8.8	KCl – 87.0 NaCl – 13.0	54.73
	25	40.7	15.4	KCl – 88.7 Sn – 11.3	49.41
	50	46.4	19.8	KCl – 93.6 NaCl – 5.0 Sn – 1.3	50.85
xylene	10	97.7	23.2	KCl – 77.4 NaCl – 22.6	45.35

	25	89.1	28.9	KCl – 85.4 NaCl – 9.6 Sn – 5.1	56.52
	50	87.4	30.1	KCl – 80.2 NaCl – 13.4 Sn – 6.4	54.78
DME	10	78.5	35.4	KCl – 85.7 NaCl – 14.3	59.50
	25	55.4	25.9	KCl – 75.2 NaCl – 21.4 Sn – 1.4	43.64
	50	48.6	38.2	KCl – 86.4 Sn – 13.6	45.92

Table S13 – Yields and phase compositions of antimony-based materials

Solvent	Concentration of a precursor, mmol·L ⁻¹	Yield (raw product), %	Yield (final product), %	Phase composition (unprocessed product), %	Crystallite size (KCl), nm
hexane	10	94.5	17.3	–	–
	25	70.0	29.8	KCl – 96.1 NaCl – 3.9	64.16
	50	80.2	38.3	KCl – 88.2 NaCl – 11.8	61.73

xylene	10	98.3	11.6	–	–
	25	73.1	20.0	KCl – 100	61.86
	50	90.7	20.8	KCl – 96.2 NaCl – 3.8	69.45
DME	10	128.2	28.4	–	–
	25	84.9	20.0	KCl – 96.8 NaCl – 3.2	61.20
	50	91.2	27.2	KCl – 87.5 NaCl – 12.5	61.59

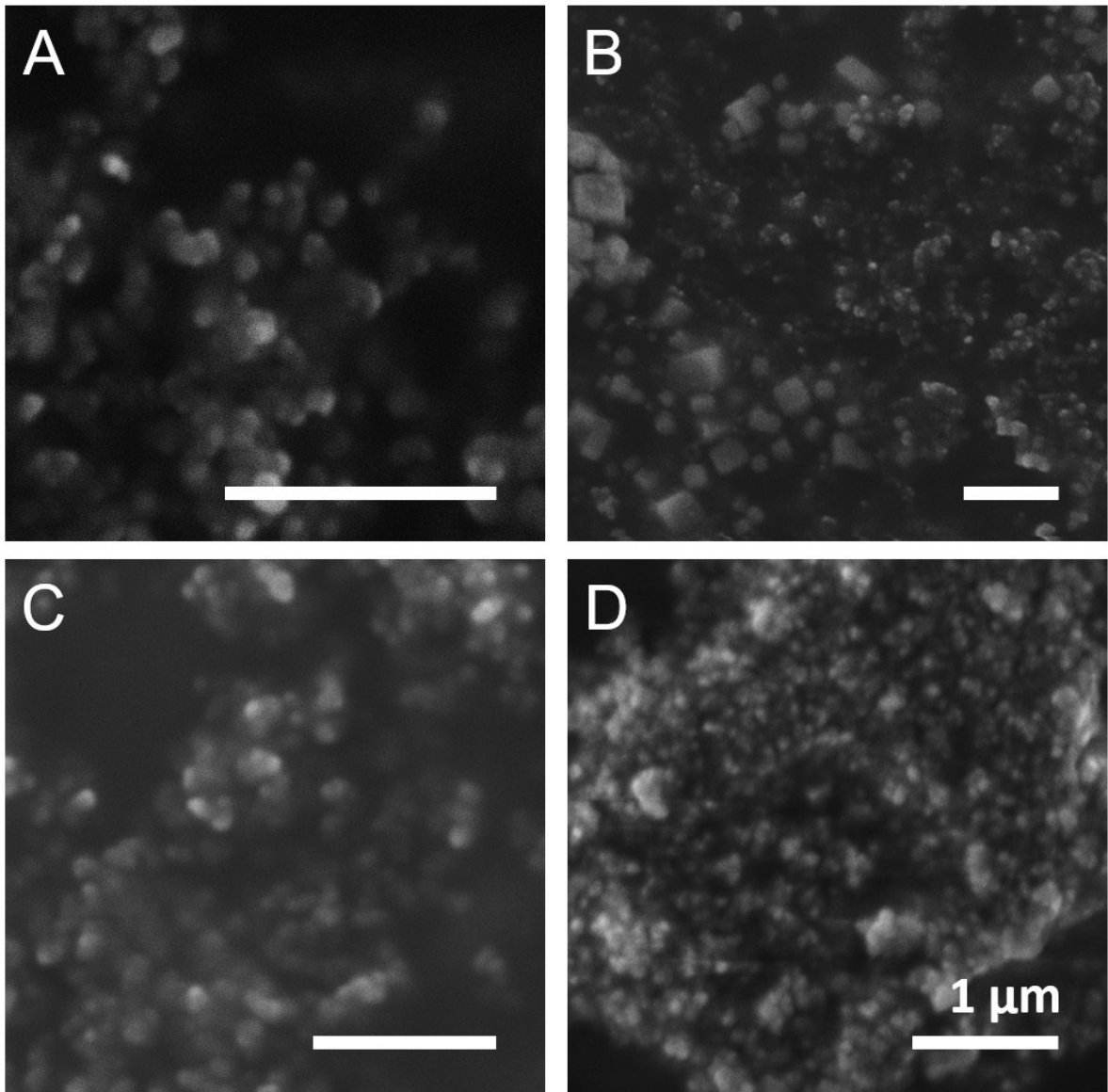


Figure S1 – SEM micrographs of nanoparticles obtained in the work. (A) Si-based final product; (B) Ge-based unprocessed product; (C) Ti-based final product; (D) Ta-based unprocessed product.

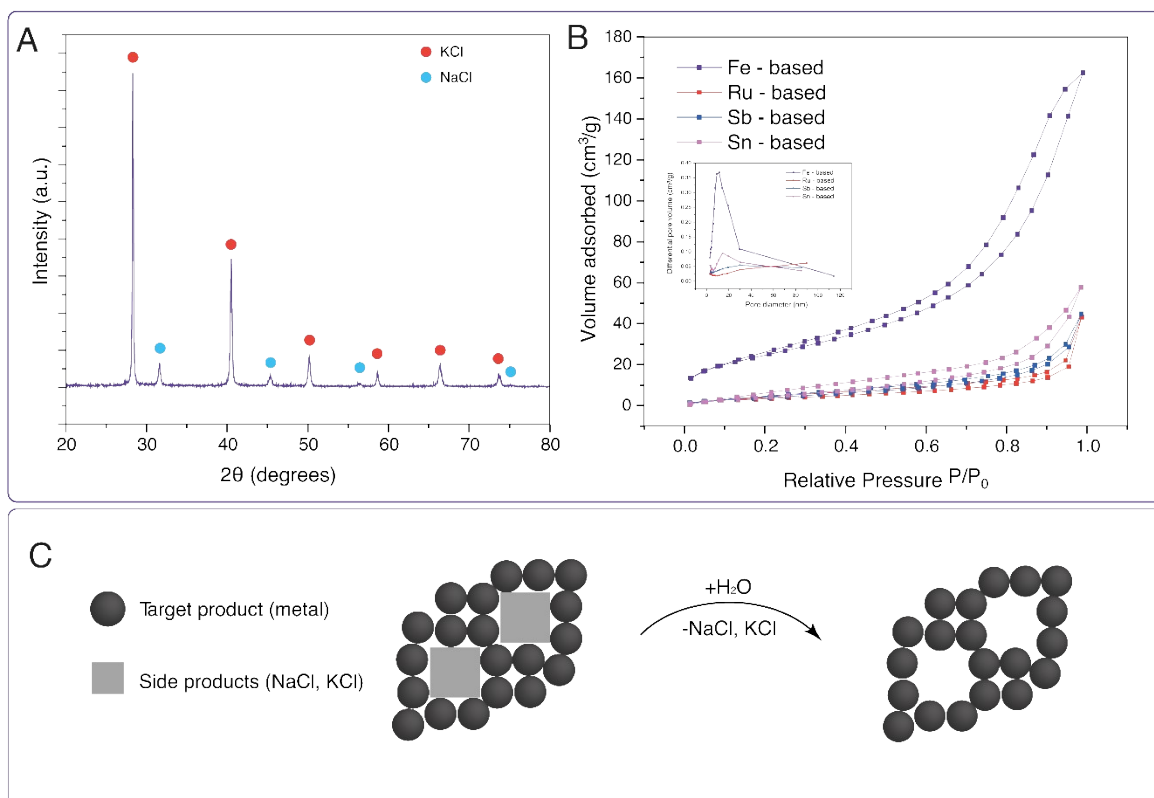


Figure S2 – (A) Typical XRD pattern obtained for most unprocessed materials. (B) Nitrogen sorption-desorption curves obtained for the final Sn-, Sb-, Ru-, Fe-based materials synthesised in diglyme. (C) The assumed mechanism of pore formation.

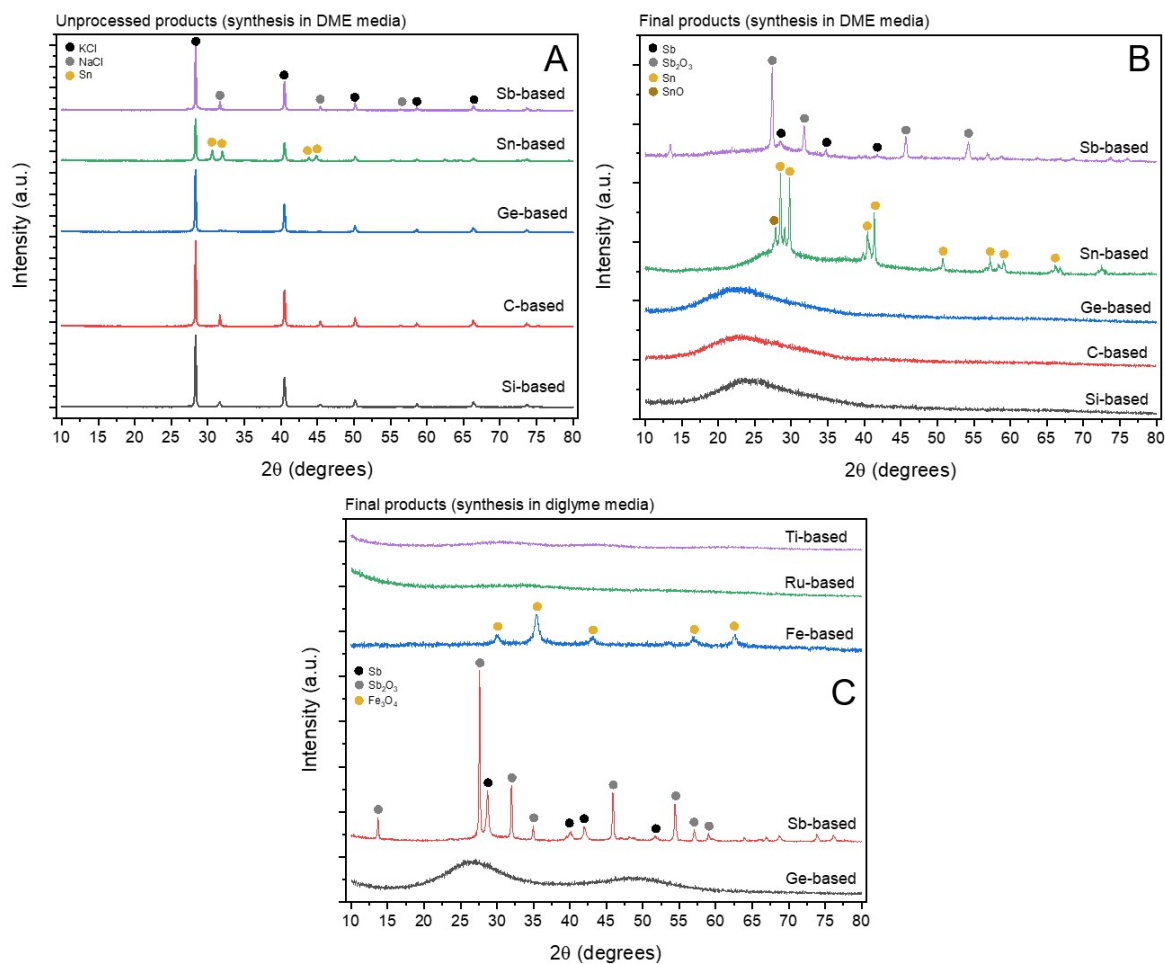


Figure S3 – Diffractograms obtained for (A) unprocessed products synthesised in DME media, (B) final products synthesised in DME media, and (C) final products synthesised in diglyme media.

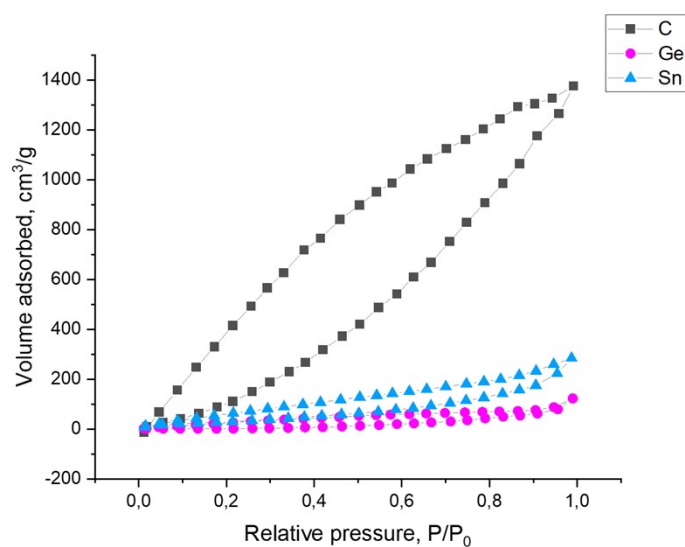
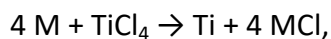
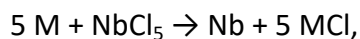
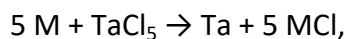
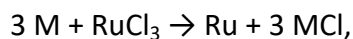
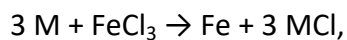
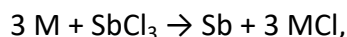
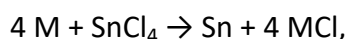


Figure S4 – Nitrogen sorption-desorption curves obtained for the unprocessed C-, Ge-, and Sn-based materials synthesised in DME

Synthesis of Sn-, Sb-, Fe-, Ru-, Ta-, Nb-, and Ti-based materials in diglyme (DGM)

Schemes of the synthetic reactions are as follows:



where M is Na or K in the NaK-78 alloy.

The reaction for stoichiometric calculations (considering NaK-78 as $\text{Na}_{0.327}\text{K}_{0.673}$) can also be represented using $\text{Na}_{0.327}\text{K}_{0.673}$ alloy formula.

All the calculations required for the synthesis are presented in Table S14.

Table S14 – Stoichiometric calculations for the synthesis performed in diglyme (DGM).

Precursor used for the synthesis	SnCl_4	SbCl_3	FeCl_3	RuCl_3	TaCl_5	NbCl_5	TiCl_4
Concentration of precursor in the final solution, $\text{mmol}\cdot\text{L}^{-1}$	100	100	100	100	100	100	100
Chemical amount of precursor, mmol	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Mass of precursor, g	0.78	0.68	0.49	0.62	1.1	0.81	0.57
Volume of precursor, μL	35	–	–	–	–	–	33
Chemical amount of NaK-78 (stoichiometric), mol	0.012	0.0090	0.0090	0.0090	0.015	0.015	0.012
Chemical amount of NaK-78 (with an excess of 20 %), mol	0.014	0.011	0.011	0.011	0.018	0.018	0.014
Mass of NaK-78 (in	0.49	0.37	0.37	0.37	0.61	0.61	0.49

excess), g							
Volume of NaK-78 (in excess), mL	0.56	0.43	0.43	0.43	0.70	0.70	0.56
Concentration of NaK-78 emulsion, mg·mL ⁻¹	20	15	15	15	24	24	20

The proposed method consisted of the following steps:

- 1) 25.0 mL of solvent was added to a 50 mL plastic tube,
- 2) the required amount of NaK-78 was placed in the tube,
- 3) the tube was filled with argon, sealed, and intensely shaken by hand to produce sub-mm drops of NaK-78,
- 4) the tube was placed in the middle of an ultrasonic bath and sonicated for 5 min to produce an emulsion,
- 5) another tube was used to prepare a metalloid precursor solution by adding the required amount of metalloid chloride to 5 mL of solvent,
- 6) the prepared metalloid precursor solution was immediately added to the freshly prepared NaK-78 emulsion,
- 7) the resulting system was filled with argon again, hermetically sealed, sonicated for 5 min, manually shaken, sonicated for 5 min again, and placed on the tube rotator (shaker) for 2 h,
- 8) after 2 h, residual NaK-78 in the resulting product (suspension or precipitate) was etched by adding isopropyl alcohol (IPA) dropwise,
- 9) when hydrogen formation stopped, IPA was added to obtain a 50 mL solution,
- 10) the resulting system was centrifuged at 10000 rpm for 10 min and the precipitate (unprocessed product) was placed in a vacuum desiccator with silica gel for 24 h,
- 11) the obtained powder (dried crude product) was washed with deionized water (40 mL) and centrifuged (10000 rpm; 10 min) thrice,
- 12) the resulting sample (final product) was dried in a vacuum desiccator with silica gel for 24 h.
- 13) the resulting unprocessed products were dried and characterised using scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), and X-ray powder diffraction (XRD); the crude products were then washed with deionised (DI) water to remove NaCl and KCl by-products, and the final products were dried and analysed using SEM, EDX, and nitrogen sorption-desorption analysis followed by BET and BJH calculations.

Before steps (10) and (12), small amounts of the sample were taken for SEM and EDS characterization of the obtained materials. XRD characterization was carried out mainly with the samples after the step (12).

Table S15 – N₂ adsorption-desorption data.

Solvent used for the synthesis	Sample (final product)	Surface area [m ² /g] ^{a)}	Pore volume [cm ³ /g] ^{b)}	Pore diameter [nm] ^{b)}
Monoglyme (DME)	C-based	2156	1.6	3.5
	Ge-based	112	0.16	3.9
	Sn-based	129	0.39	3.2
Diglyme (DGM)	Fe-based	92	0.25	7.9
	Ru-based	13	0.064	3.9
	Sb-based	16	0.068	3.5
	Sn-based	22	0.088	3.2

^{a)} Specific surface area data calculated using multi-point BET method; ^{b)} Pore size estimated from the desorption isotherm by the BJH model

Mechanism of pore formation

The mechanism of pore formation is considered by Dai et al. [14] Solid phases formed in the reaction are represented by the nano-structured mixture of an amorphous metal or metalloid and crystalline NaCl and KCl. When salts are dissolved during water washing, micro- and mesopores are left instead of them (Figure S3C).

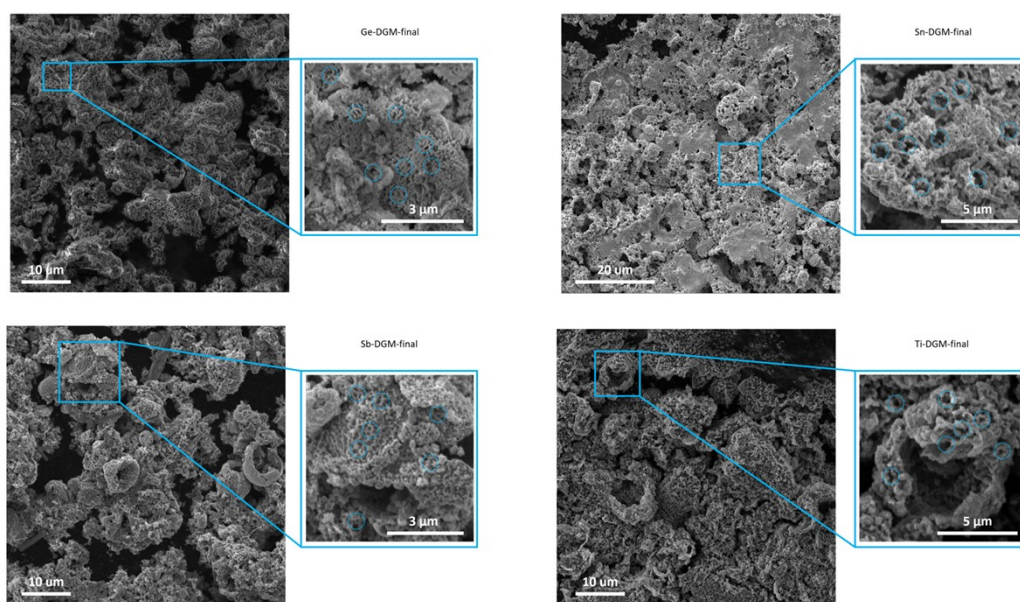


Figure S5 – Macroporous structure of final products synthesized in diglyme media (SEM)

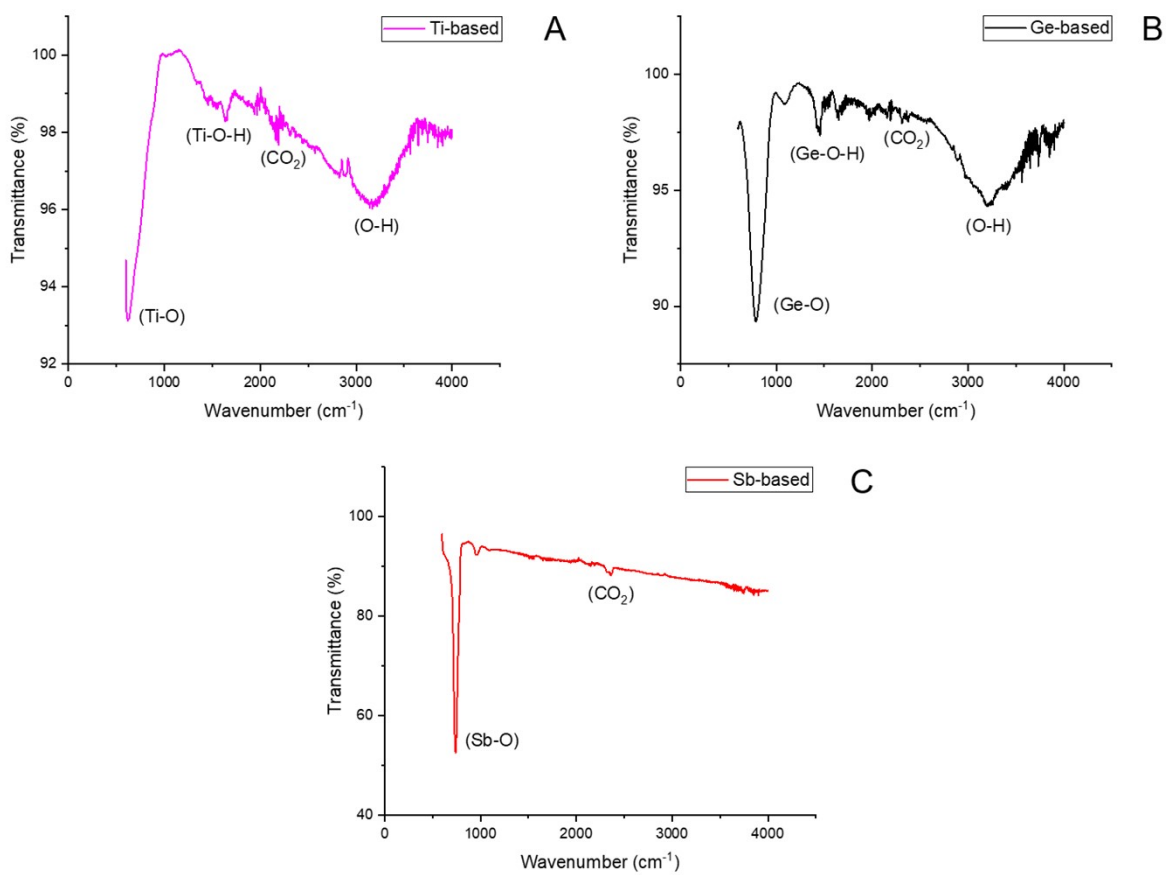


Figure S6 – Fourier-transform infrared spectra of final products synthesised in diglyme media: (A) Ti-based; (B) Ge-based; (C) Sb-based. Interpreted using the following sources: <https://doi.org/10.1039/C0CE00170H>, [http://dx.doi.org/10.21272/jnep.9\(4\).04005](http://dx.doi.org/10.21272/jnep.9(4).04005), <https://doi.org/10.1016/j.ceramint.2019.01.100>.

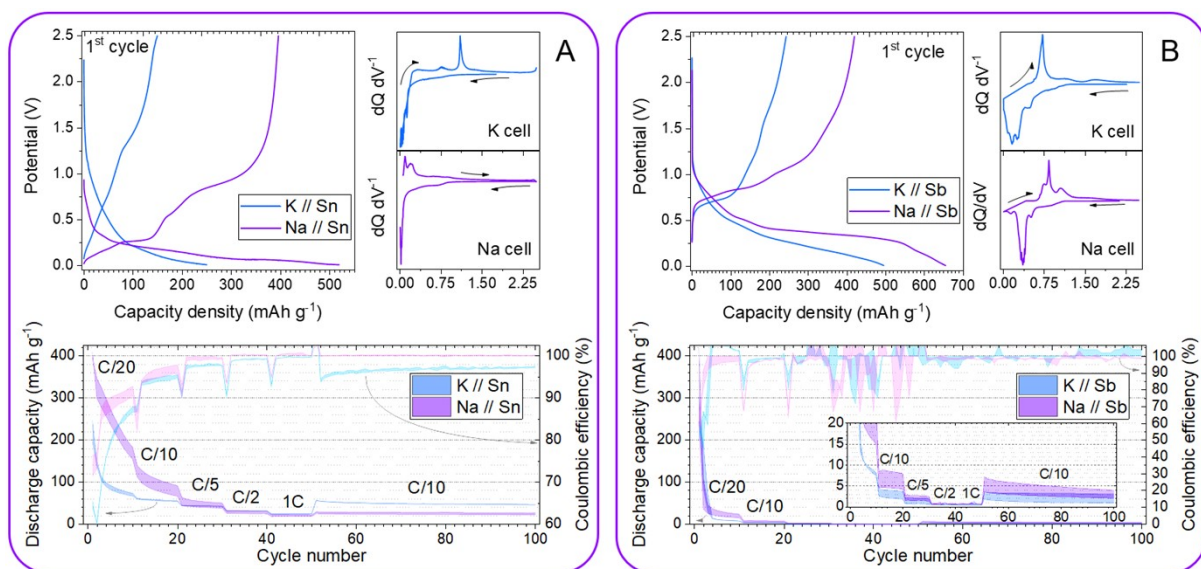


Figure S7 (zoomed copy of Figure 3) – Anode materials testing. (A) Galvanostatic profiles of 1st cycles, their differential capacity plots, and cycling life (with deviations) of Na // Sn and K // Sn half-cells at C/20, C/10, C/5, C/2, 1C rates. (B) Galvanostatic profiles of 1st cycles, differential capacity plots, and cycling life (with deviations) of Na // Sb and K // Sb half-cells at C/20, C/10, C/5, C/2, 1C rates. The insert in the cycling stability curve is its zoomed in version.

Table S16 – Semi-quantitative elemental compositions and element ratios of the unprocessed and final products presented in Figure 2

Sample	Elemental composition, %	Element ratio
A1 Sb-based (DME, unprocessed)	Cl – 31.74; O – 28.41; K – 27.92; Na – 6.76; Sb – 5.16	Sb : O = 1 : 5.5
A2 C-based (DME, unprocessed)	Cl – 44.41; O – 23.05; K – 19.92; Na – 7.95; C – 4.67	C : O = 1 : 4.9
A3 Si-based (DME, unprocessed)	Cl – 34.48; O – 29.48; K – 21.22; Na – 11.09; Si – 3.73	Si : O = 1 : 7.9
A4 Sn-based (DME, unprocessed)	Cl – 31.42; K – 29.99; Sn – 22.20; O – 12.40; Na – 3.98	Sn : O = 1.8 : 1
A5 Ge-based (DME, unprocessed)	Cl – 33.72; O – 30.93; K – 18.55; Na – 10.42; Ge – 6.38	Ge : O = 1 : 4.8
B1 Sb-based (DGM, final product)	O – 44.75; Sb – 36.04; Cl – 8.48; K – 8.35; Na – 2.38	Sb : O = 1 : 1.2
B2 Fe-based (DGM, final product)	O – 67.79; Fe – 32.21	Fe : O = 1 : 2.1
B3 Ge-based (DGM, final product)	O – 65.75; Ge – 33.01; K – 1.24	Ge : O = 1 : 2
B4 Sn-based (DGM, final product)	Sn – 100.00	–
B5 Ti-based (DGM, final product)	O – 48.36; Ti – 47.79; K – 2.42; Na – 1.42	Ti : O = 1 : 1