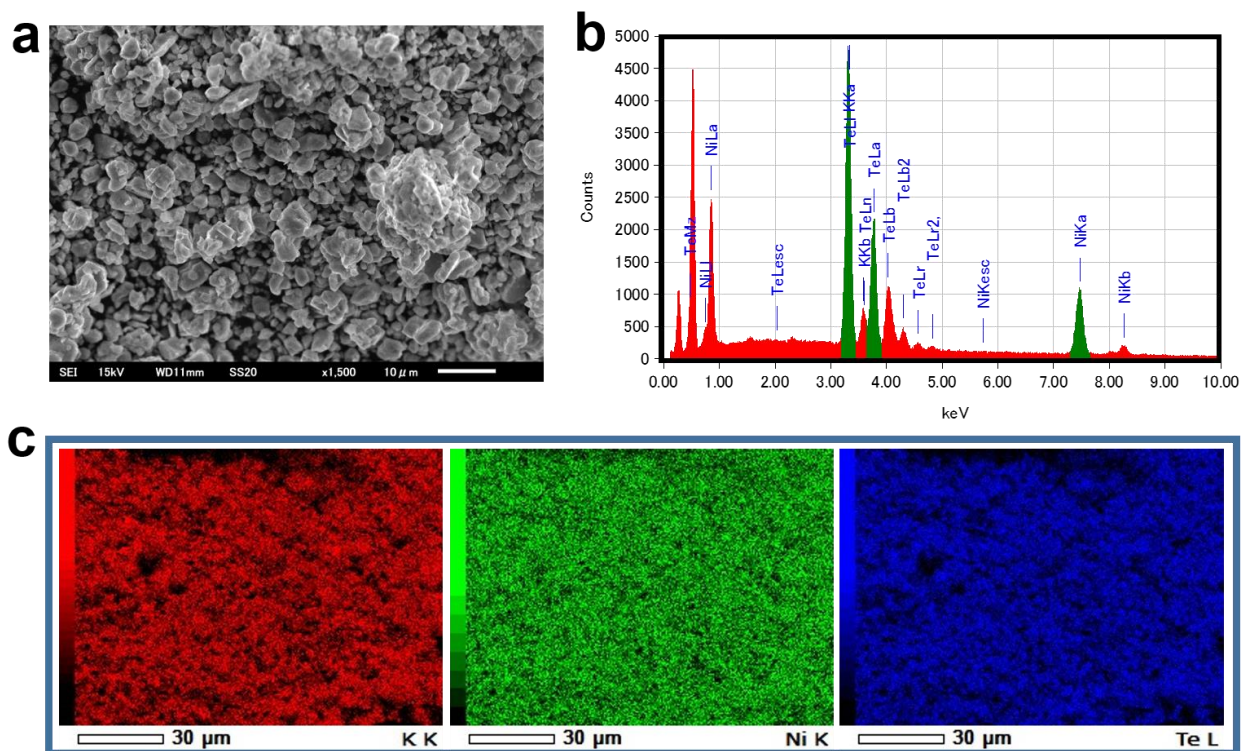


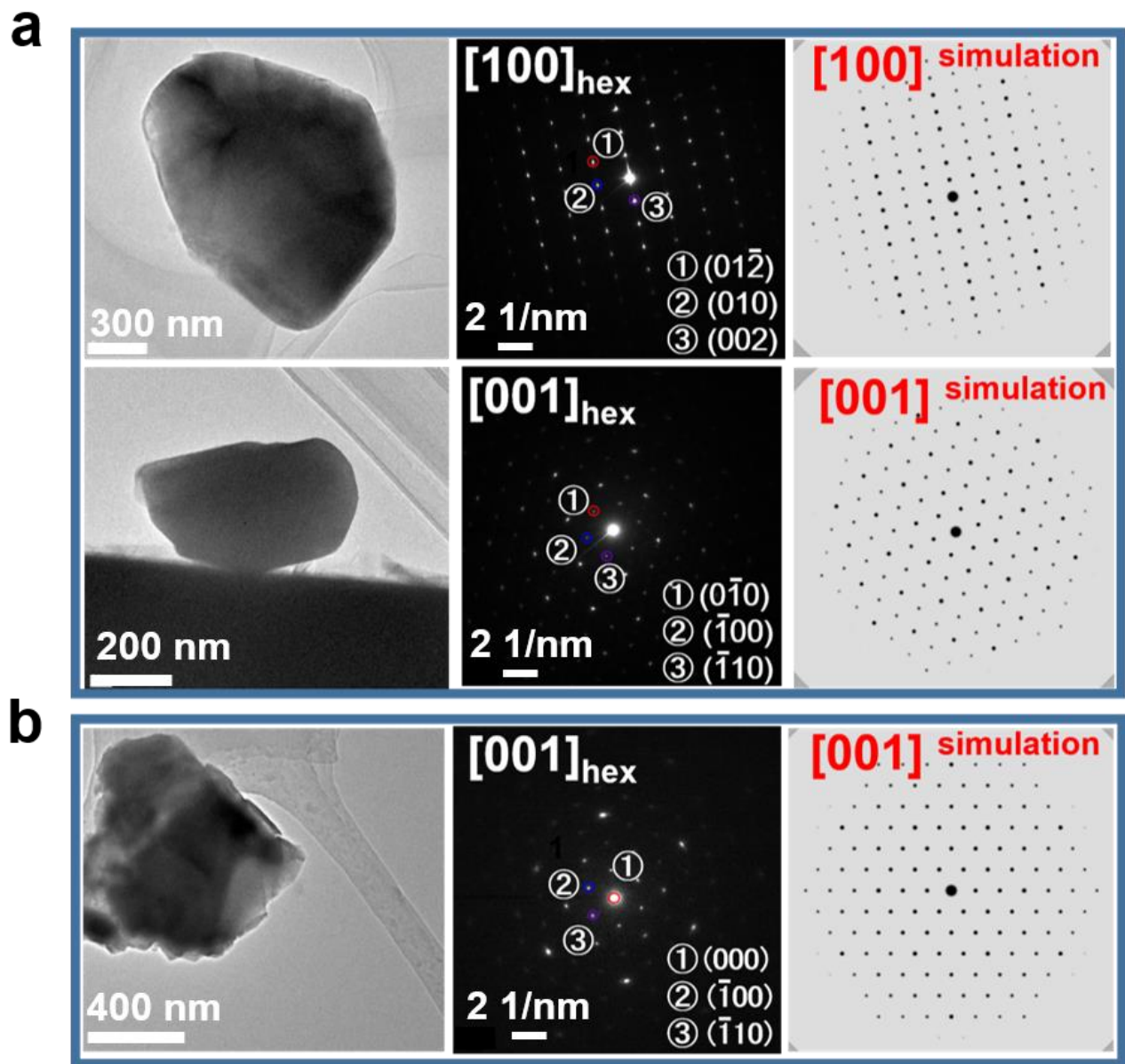
Supplementary Information

**Rechargeable Potassium-Ion Batteries with Honeycomb-Layered
Tellurates Inducing New High Voltage Cathodes and Fast
Potassium-Ion Conductors**

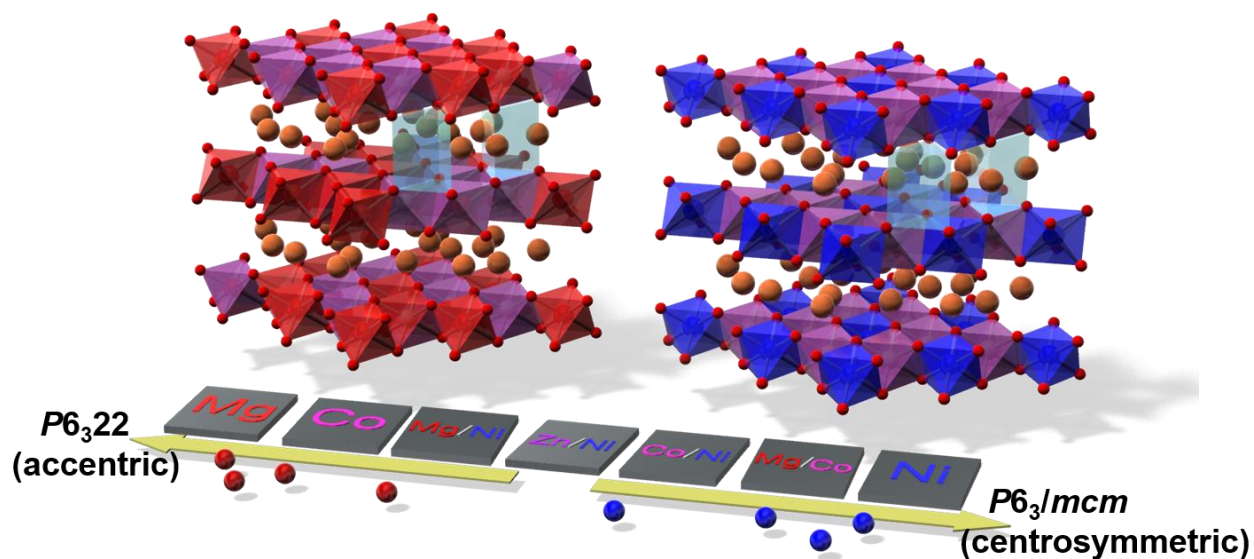
T. Masese *et al.*



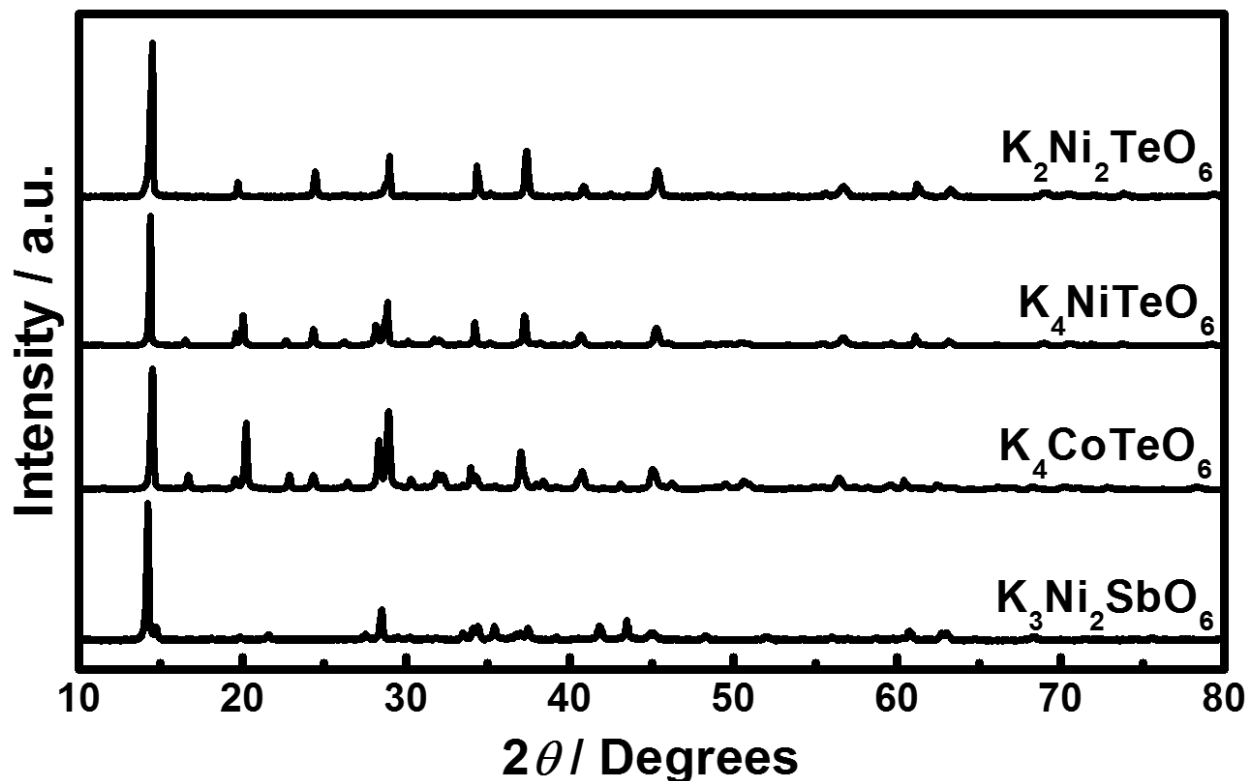
Supplementary Figure 1. **a.** SEM picture of the $K_2Ni_2TeO_6$ powders and **b.** the SEM-EDX spectrum of the powders, while **c.** shows the elemental mapping of $K_2Ni_2TeO_6$. The general flake-like grain morphology that is usually seen in some lamellar K_xMO_2 ($M = Co, Mn$) compounds is also evident here.



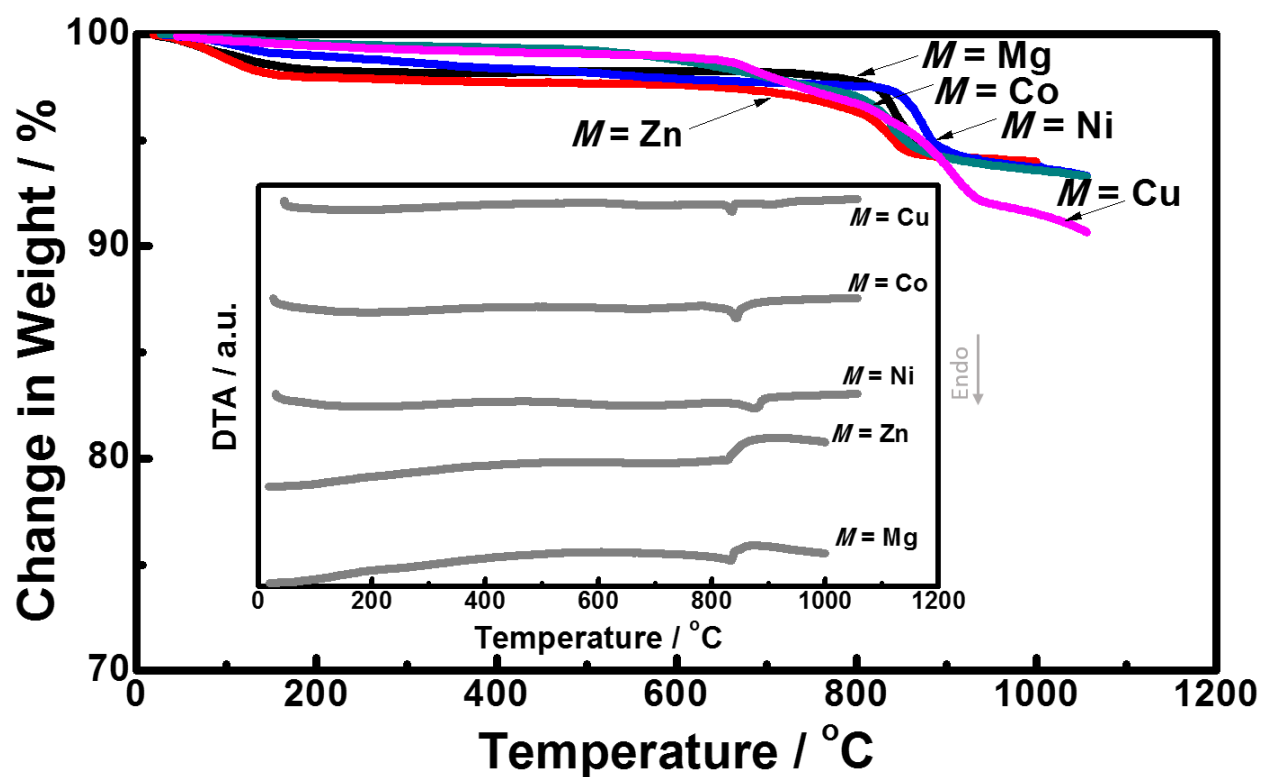
Supplementary Figure 2. a. Electron diffraction patterns recorded on $\text{K}_2\text{Ni}_2\text{TeO}_6$ indexed in a hexagonal lattice along $[100]$ and $[001]$ directions, and **b.** $\text{K}_2\text{Mg}_2\text{TeO}_6$ along $[001]$ zone axis.



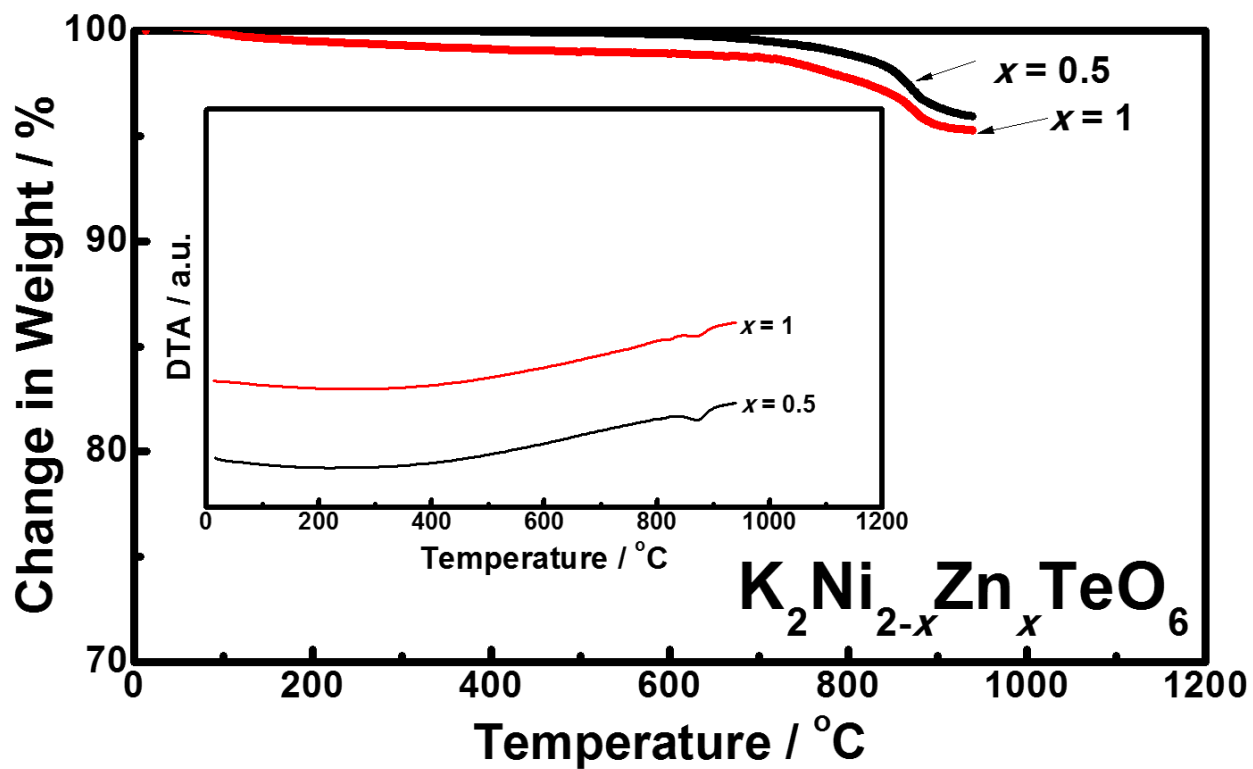
Supplementary Figure 3. Crystal structure transition of potassium orthotellurate family described by the formula $K_2M_2TeO_6$ and $K_2M_{1-x}M'_xTeO_6$, (in which M and M' are Co, Ni, Zn or Mg). A comparison between the structure of $K_2M_2TeO_6$ ($M = Ni, Mg, Co$) and solid-solution derivatives evinces the stacking difference with distinct atom sequences along the hexagonal c -axis. For $K_2Ni_2TeO_6$ end-phase member crystallising in $P6_3/mcm$ space group, both Te and Ni atoms of one slab are located exactly above Te and Ni atoms of the last slab, whereas Te and Mg atoms are alternatively located along the hexagonal c -axis for $P6_322$ space group as adopted by $K_2Mg_2TeO_6$ end-phase member



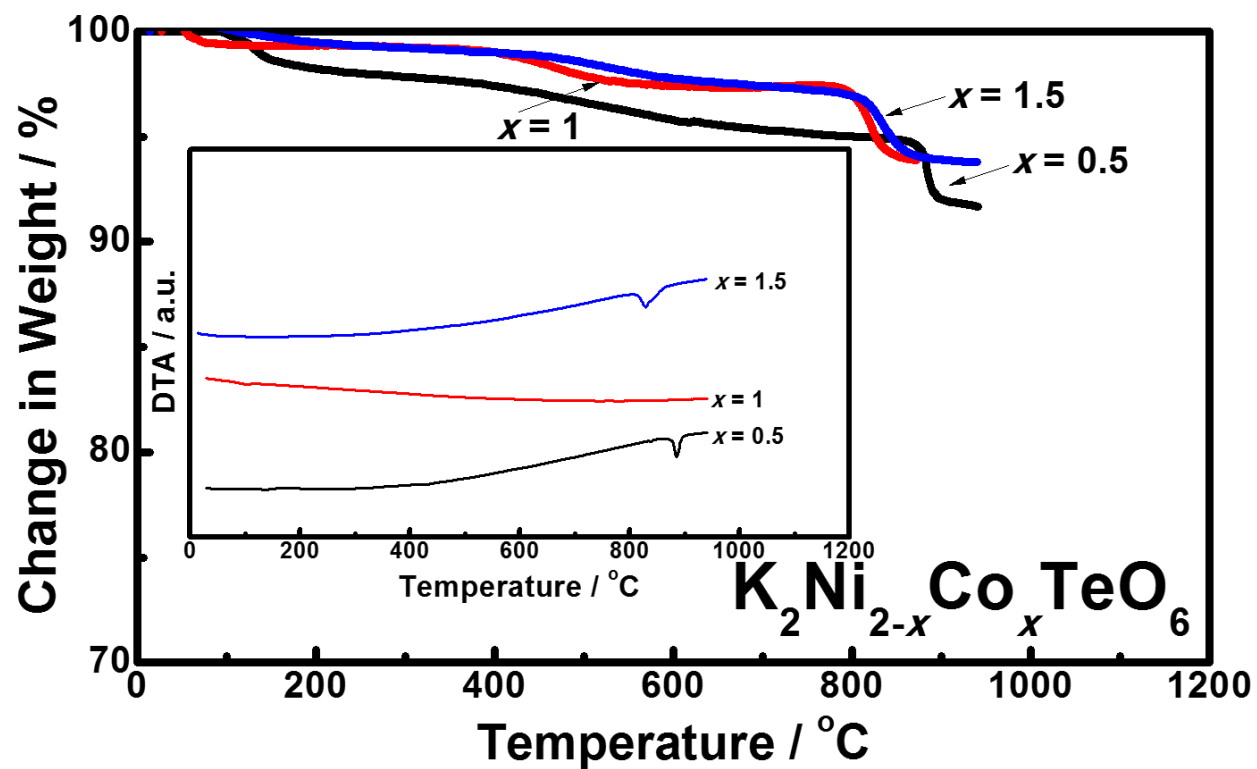
Supplementary Figure 4. Conventional XRD patterns of other derivatives of $\text{K}_2\text{Ni}_2\text{TeO}_6$ (namely, K_4MTeO_6 ($M = \text{Ni}, \text{Co}$) and $\text{K}_3\text{Ni}_2\text{SbO}_6$ (with impurities)) prepared via a conventional solid state ceramics route at 800 °C, as described in the **METHODS** section. K_4MTeO_6 are isostructural with $\text{Na}_4\text{NiTeO}_6$ honeycomb layered phases. K_4NiTeO_6 crystallises in a monoclinic structure with lattice parameters $a = 7.26 \text{ \AA}$, $b = 10.08 \text{ \AA}$, $c = 8.65 \text{ \AA}$, $\beta = 114.14^\circ$ ($V = 574.6 \text{ \AA}^3$). Detailed structural analyses of K_4MTeO_6 ($M = \text{Ni}, \text{Co}, \text{Mg}, \text{Zn}$) and phase-pure $\text{K}_3\text{Ni}_2\text{SbO}_6$ are beyond the scope of the current study. Synchrotron XRD studies complemented with TEM analyses are subject of future work. Nonetheless, the present results show that the layered $\text{K}_2\text{Ni}_2\text{TeO}_6$ materials can be extended to encompass a plethora of new stoichiometries, presumably adopting the honeycomb layering scheme seen in the orthotellurate compounds.



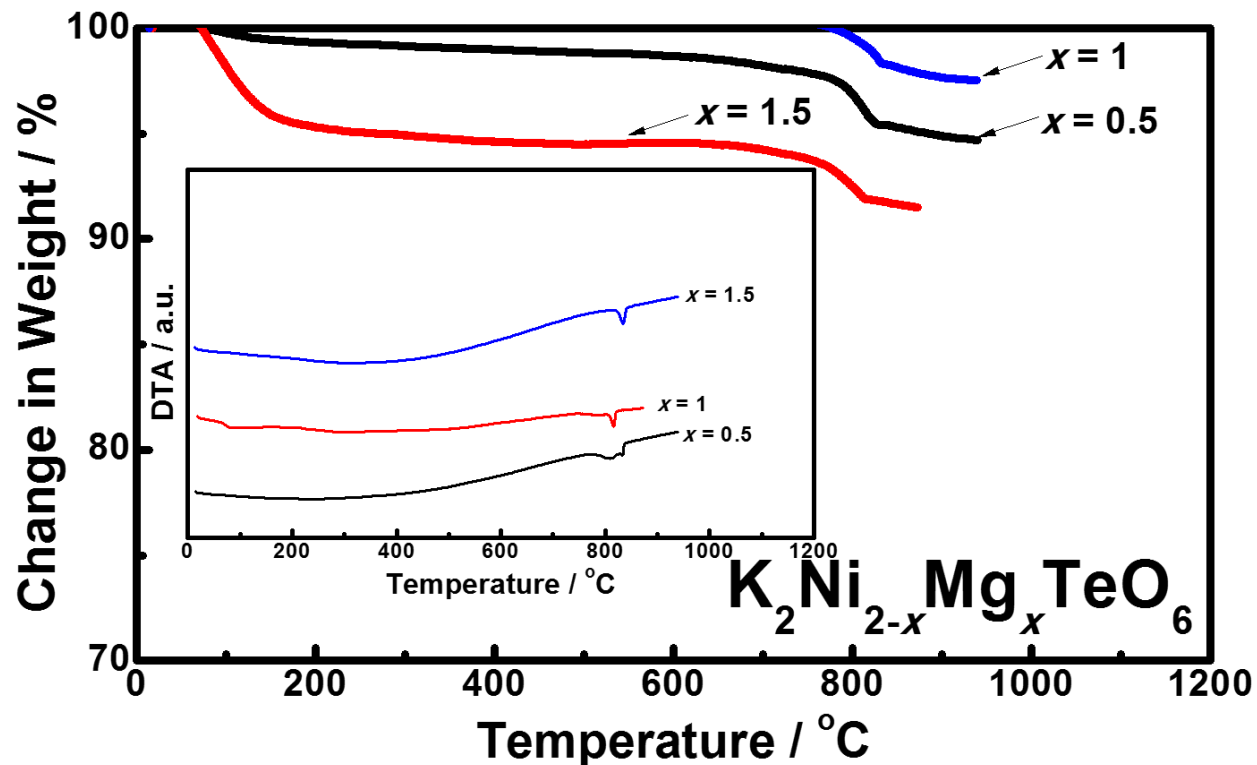
Supplementary Figure 5. Thermogravimetry (TG) and differential thermal analysis (DTA) curves (inset) of $K_2M_2TeO_6$ ($M = Ni, Co, Mg, Cu$ and Zn) ranging from 25 to 1000 °C. The onset of an endothermic peak at the DTA curve (around 800~900 °C) indicates the melting point temperature of $K_2M_2TeO_6$. The weight loss observed at around 100 °C arises from water absorbed during the loading of the powders in Pt ampoules prior to measurements.



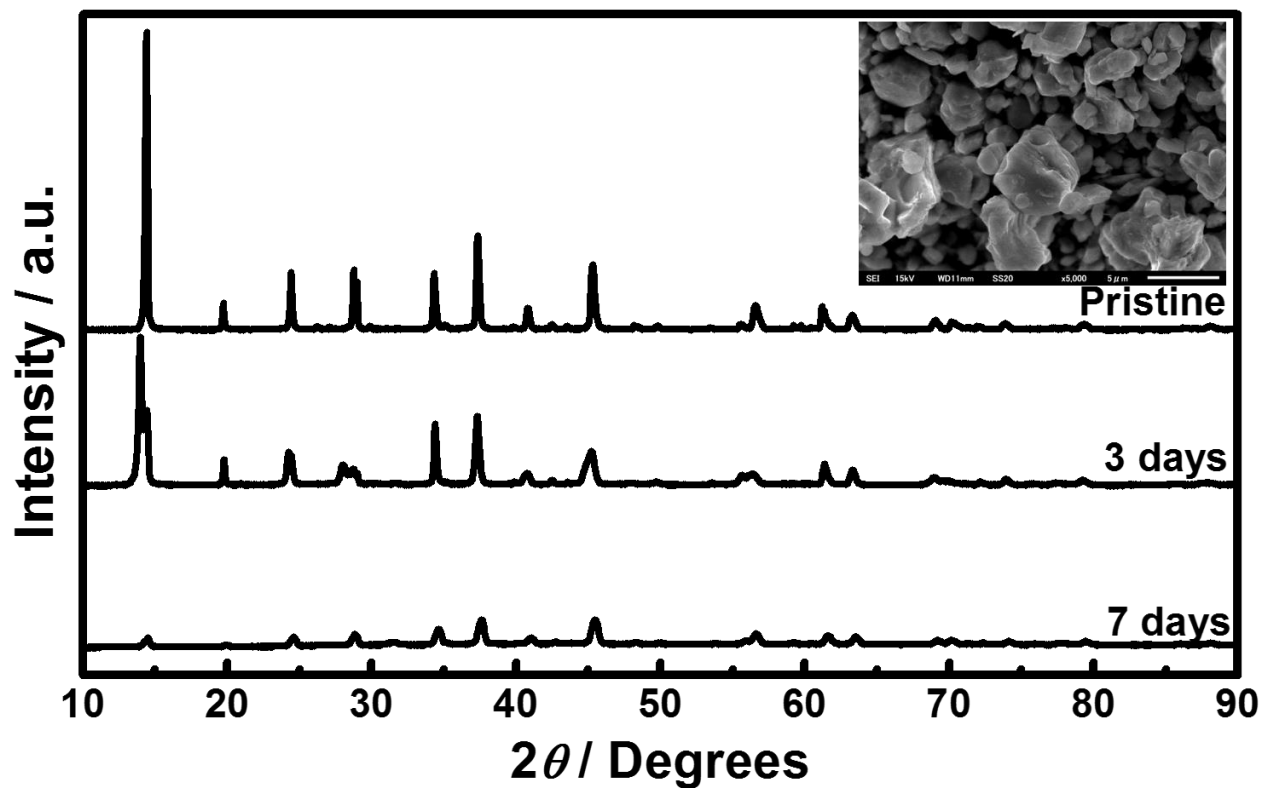
Supplementary Figure 6. Thermogravimetry (TG) and differential thermal analysis (DTA) curves (inset) of $\text{K}_2\text{Ni}_{2-x}\text{Zn}_x\text{TeO}_6$ ($x = 0.5$ and 1) ranging from 25 to 950 $^{\circ}\text{C}$.



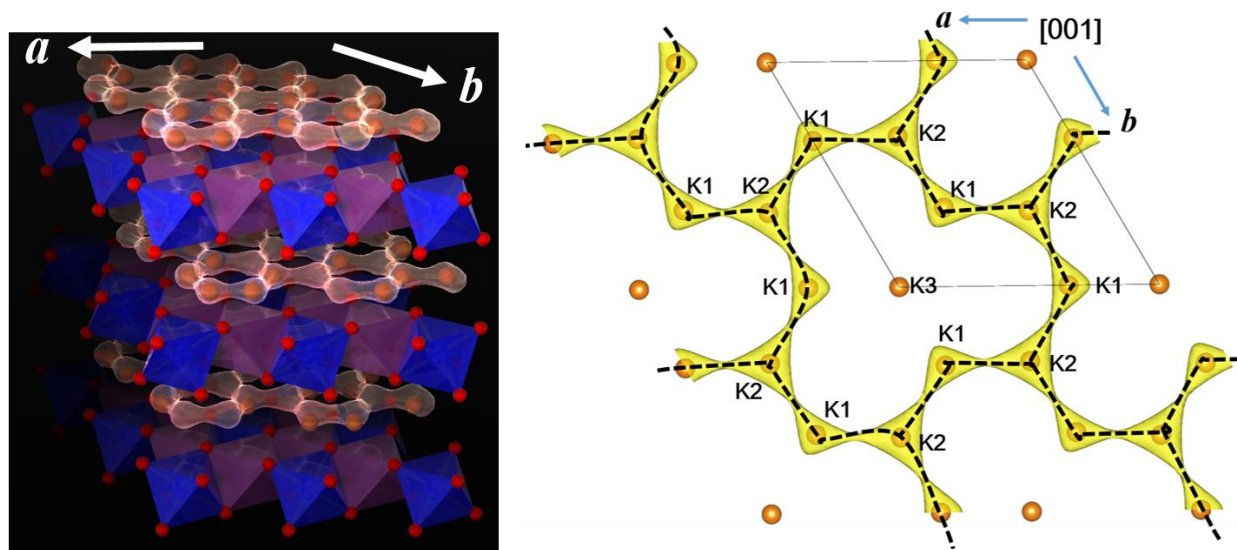
Supplementary Figure 7. Thermogravimetry (TG) and differential thermal analysis (DTA) curves (inset) of $\text{K}_2\text{Ni}_{2-x}\text{Co}_x\text{TeO}_6$ ($x = 0.5, 1.0$ and 1.5) ranging from 25 to 950 $^{\circ}\text{C}$.



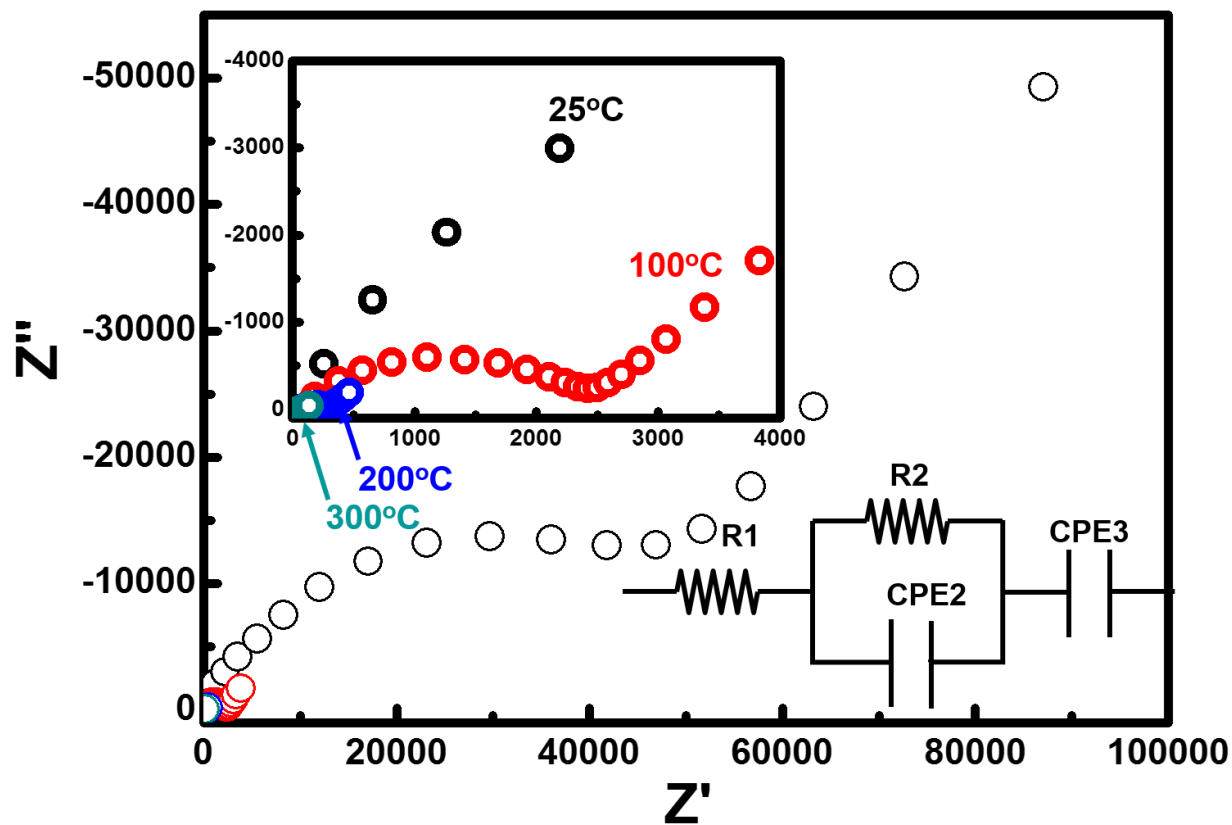
Supplementary Figure 8. Thermogravimetry (TG) and differential thermal analysis (DTA) curves (inset) of $\text{K}_2\text{Ni}_{2-x}\text{Mg}_x\text{TeO}_6$ ($x = 0.5, 1.0$ and 1.5) ranging from 25 to 950 $^{\circ}\text{C}$.



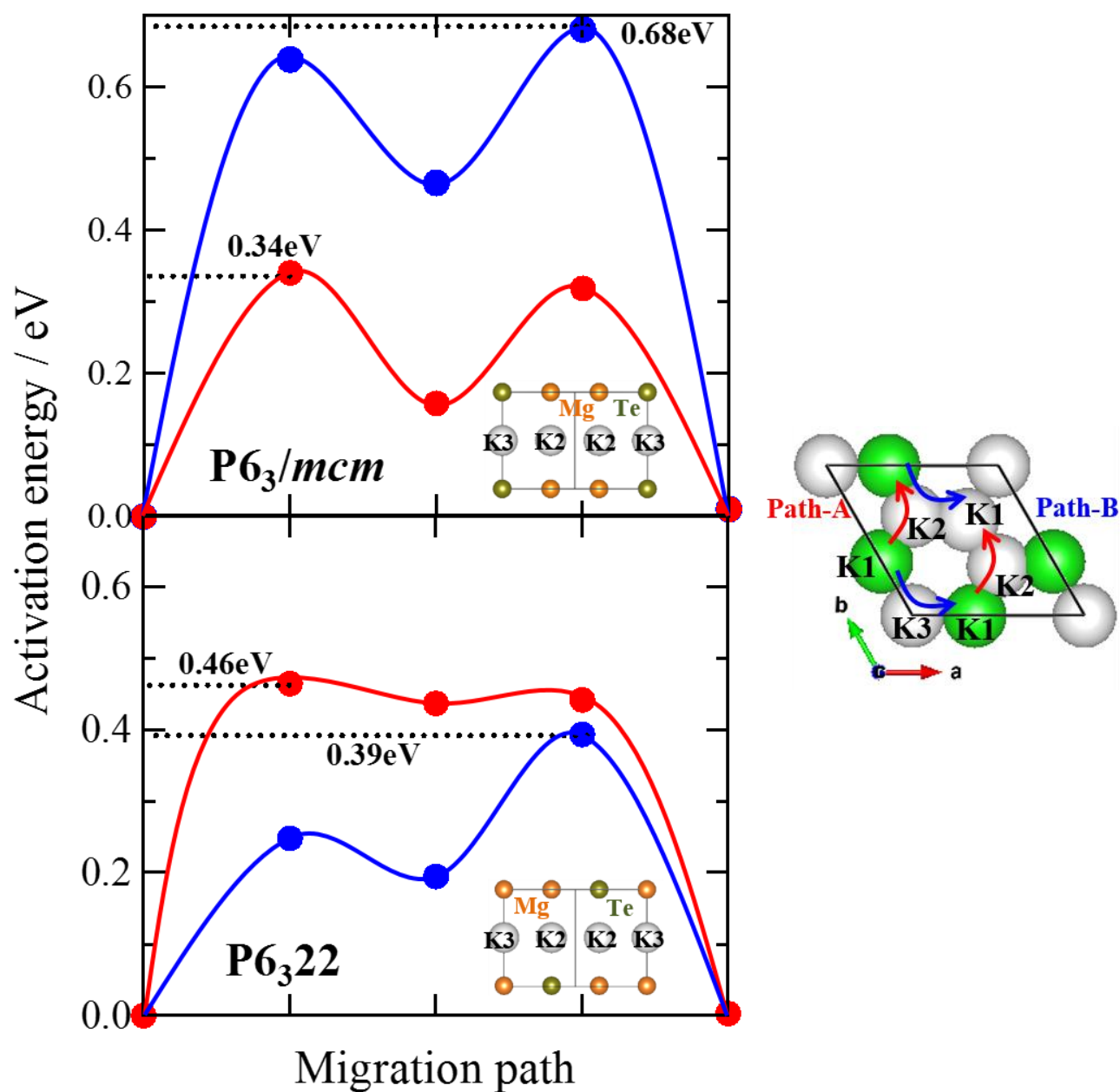
Supplementary Figure 9. Conventional XRD patterns of pristine $K_2Ni_2TeO_6$, revealing a diminution in the intensity of diffraction peaks upon moist air exposure with a relative humidity in the range of 70 ~ 75 %. $K_2Ni_2TeO_6$ needs to be handled in dry inert atmosphere owing to the propensity to amorphise (or undergo phase change) upon exposure to moist air.



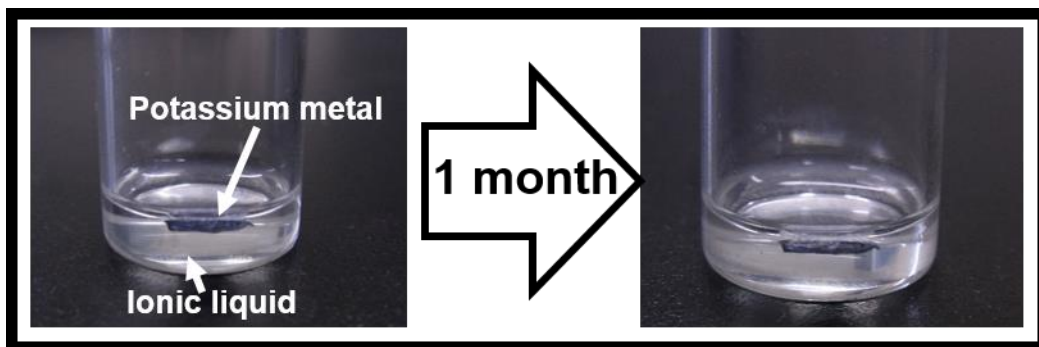
Supplementary Figure 10. **a.** Schematic presentation of $K_2Ni_2TeO_6$ viewed along $[110]$ direction. NiO_6 tetrahedra (purple), TeO_6 octahedra (blue), and K atoms (brown) are illustrated. **b.** 2D bond valency energy landscape (BVEL) map of $K_2Ni_2TeO_6$ (yellow) with isosurfaces of 0.35 eV for K depicting a circular K -ion diffusion pattern (akin to a rotary Wankel-type motor engine).



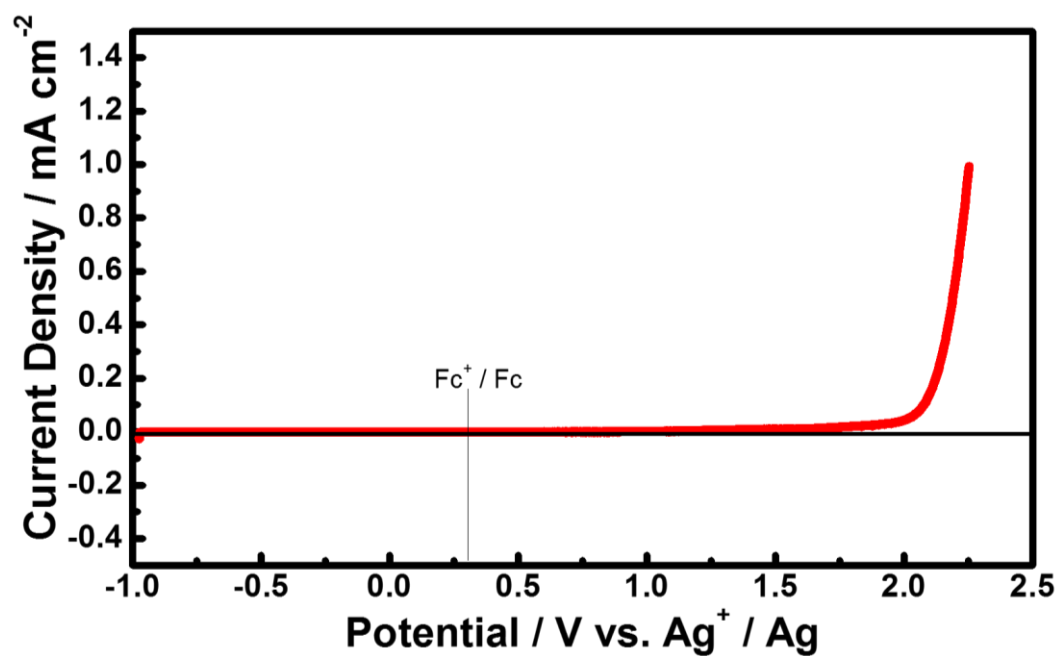
Supplementary Figure 11. Complex a.c. impedance spectra (Nyquist plots) obtained for K₂Mg₂TeO₆ at various temperatures (namely, 25, 100, 200 and 300 °C). A semicircle can be observed at high frequencies, which can be attributed to the solid electrolyte potassium ion conduction. The spectra were fitted by an equivalent circuit (shown in inset figure) composed of an initial resistor R1 (for the device and current collectors' resistances) in series with one resistor R2 (for solid electrolyte resistance) in parallel with a constant phase element CPE2 (for the non-ideal capacitance between particles) and in series with another CPE3 (for the impedance of both the top and bottom electrode-electrolyte junctions). The ionic conductivity (σ) was then calculated using the equation $\sigma = l / RS$ in which l is the thickness of the solid electrolyte pellet, while S denotes the pellet surface area and R is the resistance obtained from the fitted R2 value. A drastic diminution of the semicircle diameter is noticeable upon heating, in accord with the enhancement of the ionic conductivity with temperature.



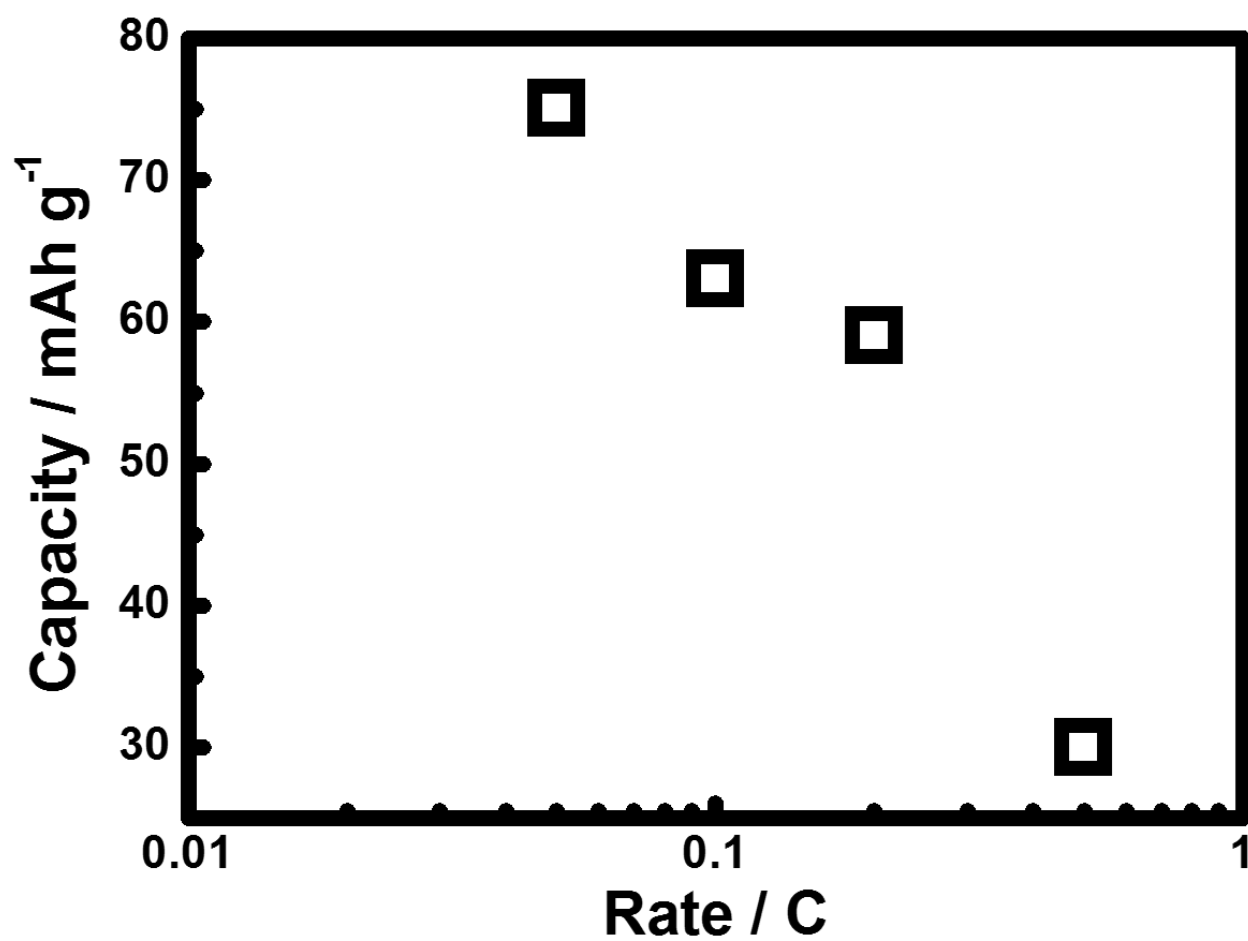
Supplementary Figure 12. Calculated K^+ migration activation energies along the pathways A and B in $K_2Mg_2TeO_6$. The green and white balls represent, respectively, occupied and vacant K^+ sites in the initial model before migration. Cooperative diffusion pathways formed by correlated two K^+ ions at K1 sites via K2+K2 sites (Path-A; red) or via K2+K3 sites (Path-B; blue) are schematically drawn. Schematic structures at $\frac{1}{2} c$ size on the [110] planes including Mg and Te ions are inserted.



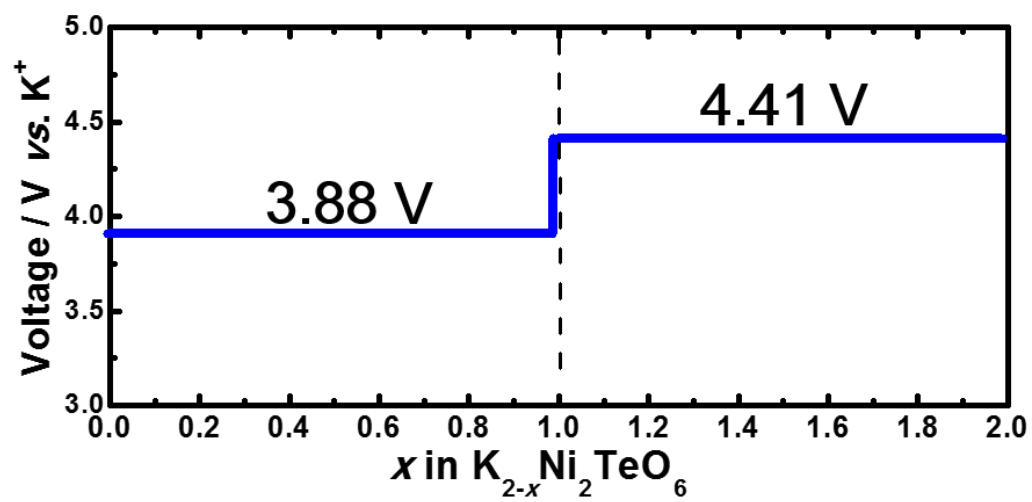
Supplementary Figure 13. Stability of (0.5 M KTFSI in Pyr₁₃TFSI) ionic liquid against potassium (K) metal after one month. The colour does not change, indicating no decomposition of electrolyte in the presence of potassium. This further confirms the stable electrochemical performance observed.



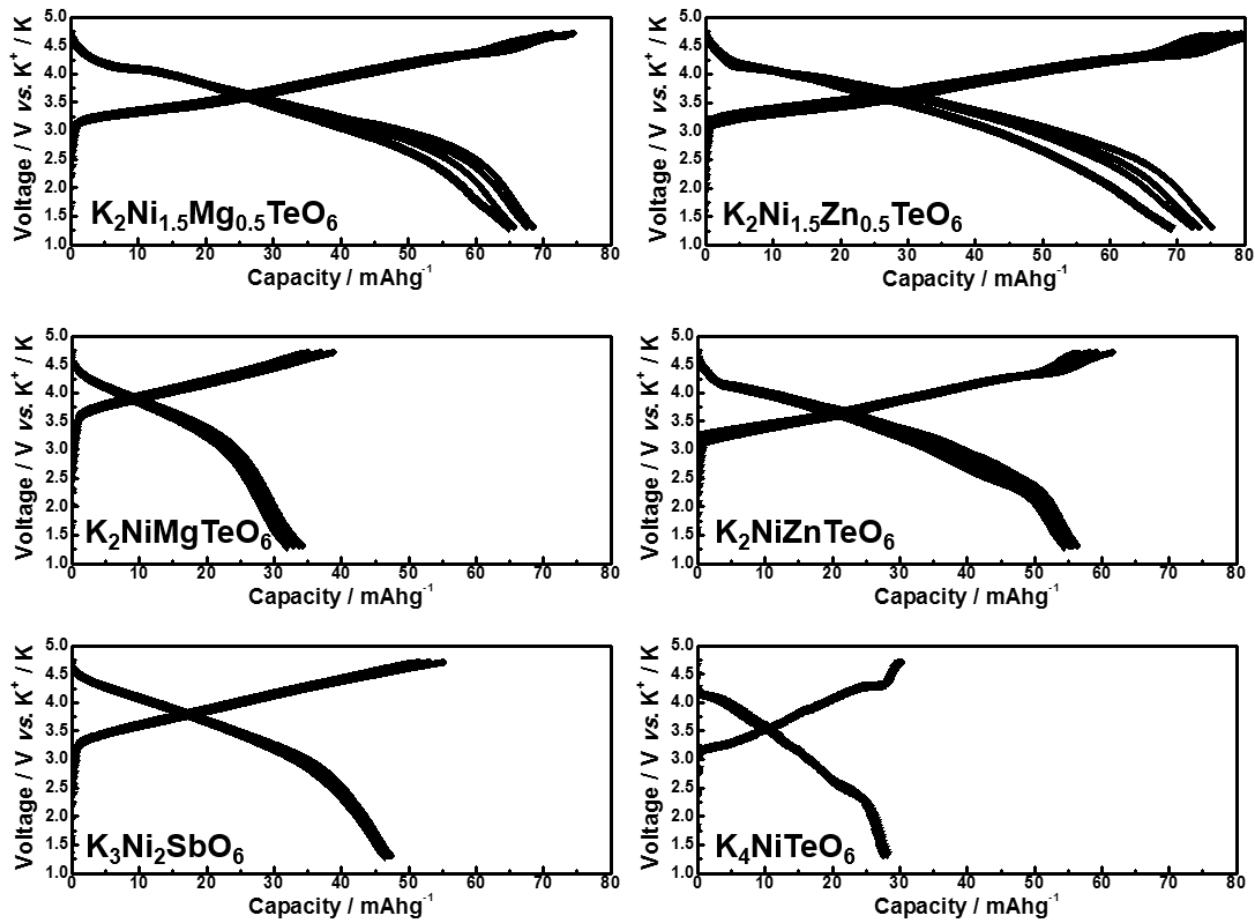
Supplementary Figure 14. Linear sweep voltammogram of Pt electrode in Pyr₁₃TFSI ionic liquid containing 0.5 M KTFSI using three-electrode cells. Pt was used as the counter electrode. Reference electrode was silver wire immersed in Pyr₁₃TFSI containing 0.1 M AgCF₃SO₃. Potential sweep rate was set at 1.0 mV s⁻¹, and measurements were conducted at 25 °C. Ionic conductivity of the 0.5 M KTFSI in Pyr₁₃TFSI ionic liquid was 1.8 mS cm⁻¹ at 25 °C.



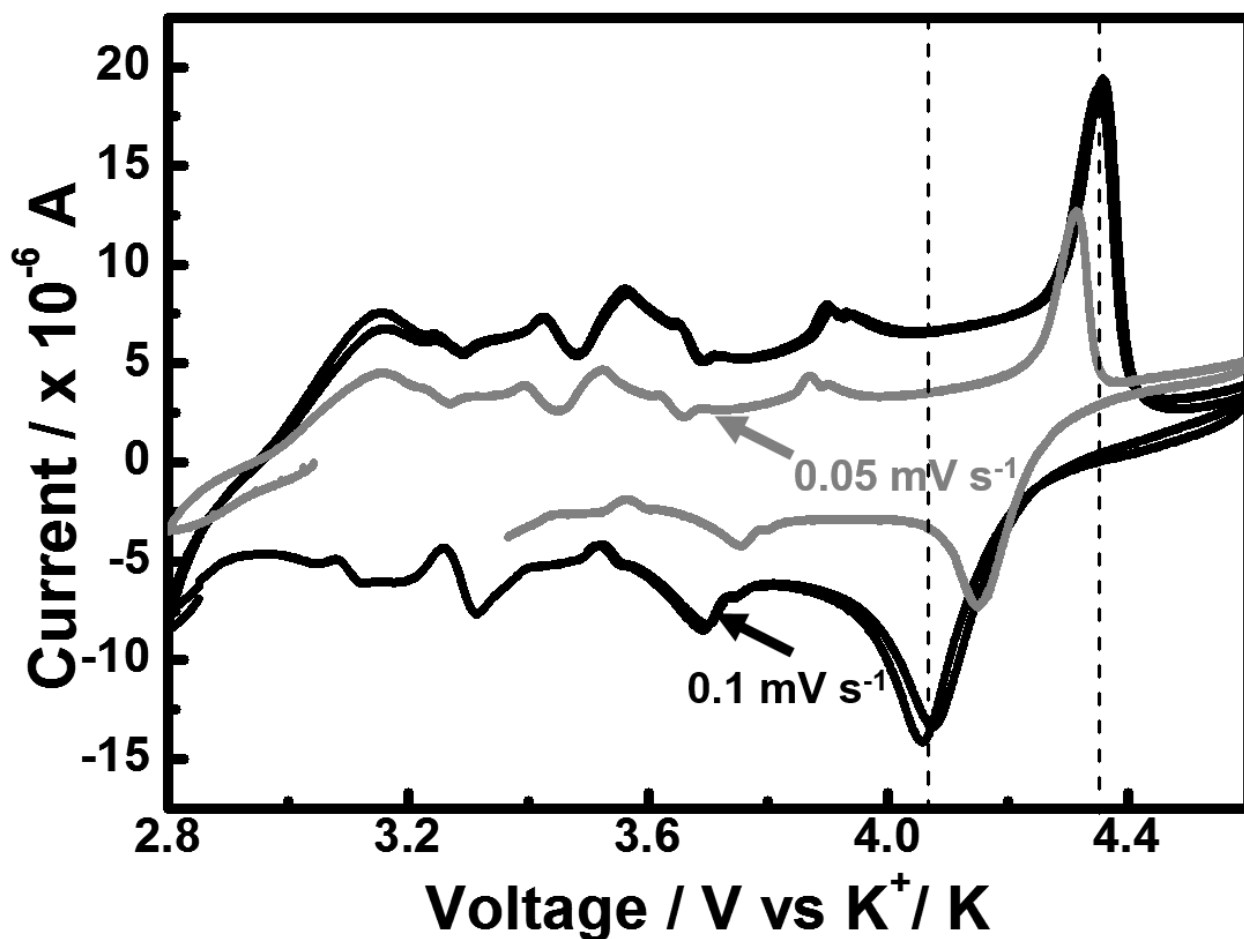
Supplementary Figure 15. Rate performance of $\text{K}_2\text{Ni}_2\text{TeO}_6$ in K half-cells using 0.5 M KTFSI in Pyr₁₃TFSI ionic liquid. Galvanostatic measurements were conducted at various rates at room temperature.



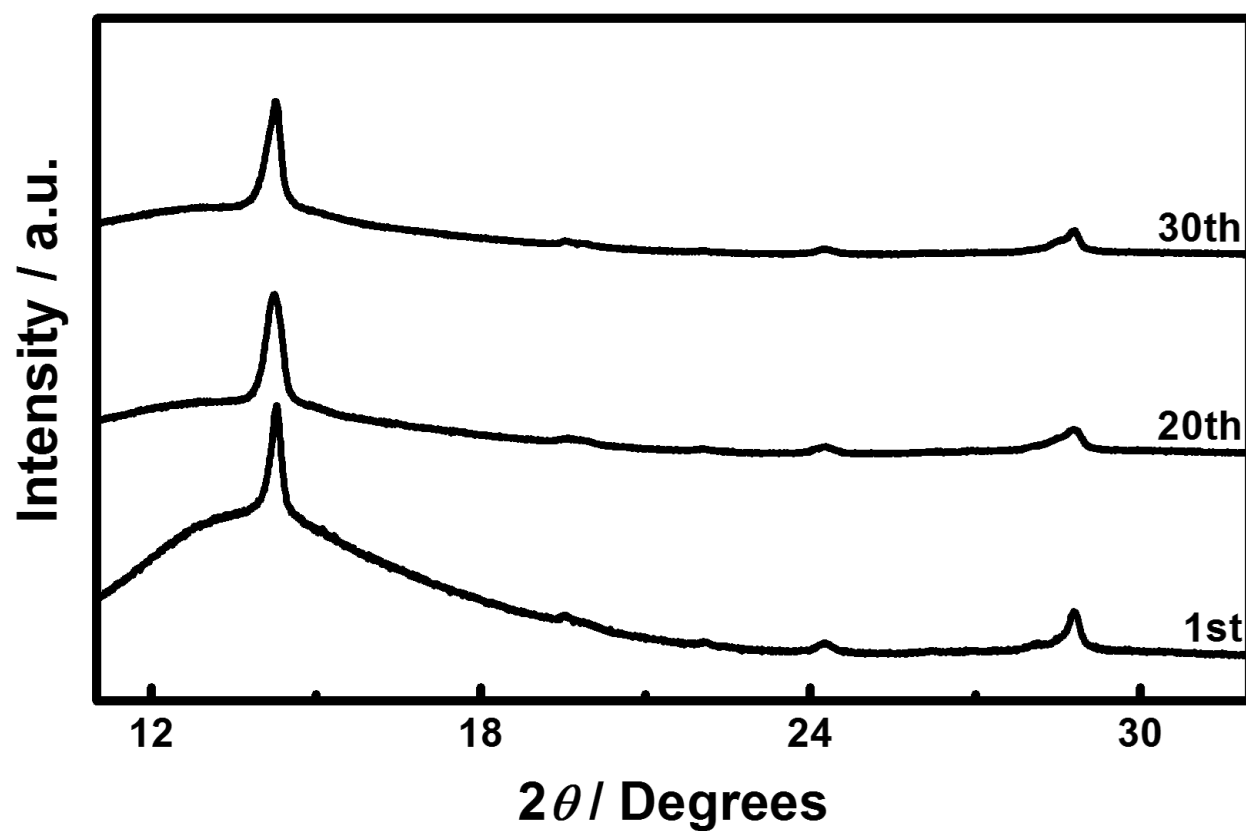
Supplementary Figure 16. Calculated voltages of $K_2Ni_2TeO_6$ upon K-ion extraction.



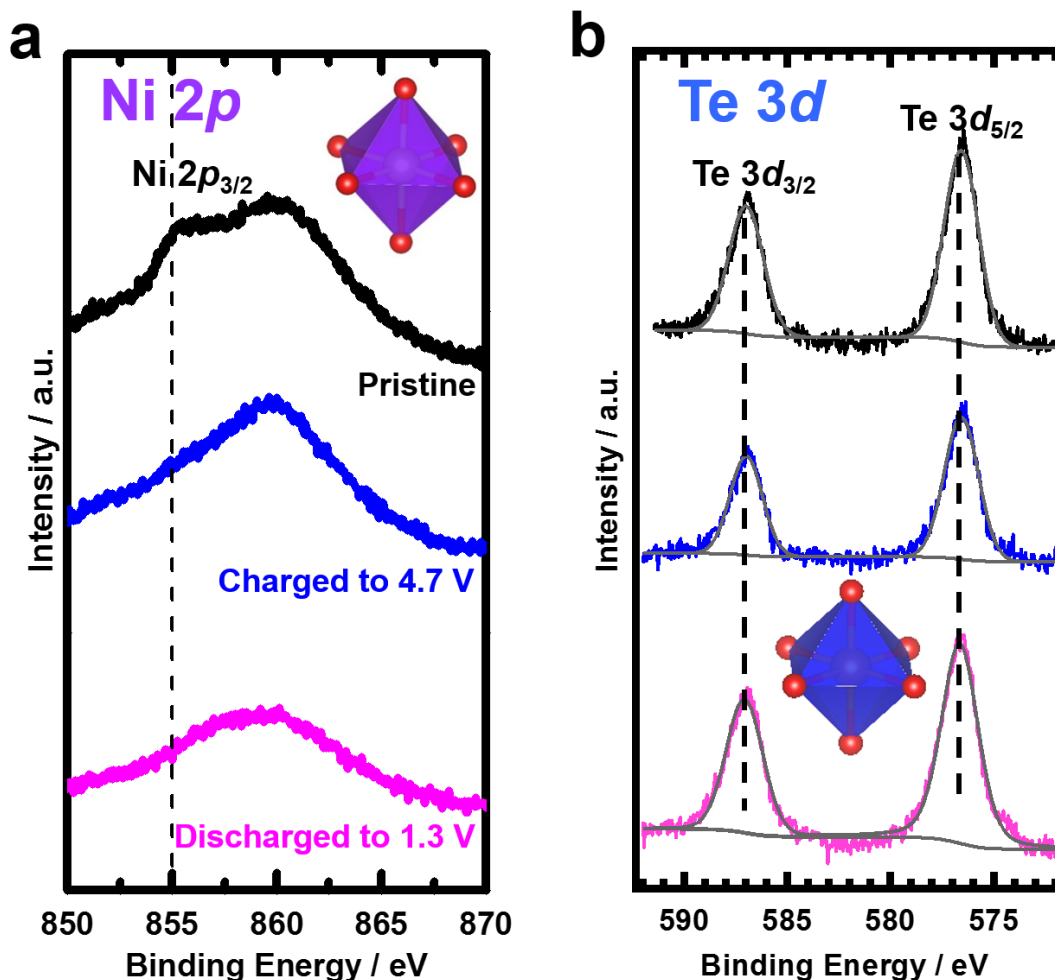
Supplementary Figure 17. Voltage-capacity profiles (20 cycles) for $K_2Ni_2TeO_6$ solid solutions in K half-cells using 0.5 M KTFSI in Pyr₁₃TFSI ionic liquid. Galvanostatic measurements were conducted at C/20 rate at room temperature. For the sake of readability, the 1st, 5th, 10th and 20th voltage profiles have been shown for $K_2Ni_{1.5}Mg_{0.5}TeO_6$ and $K_2Ni_{1.5}Mg_{0.5}TeO_6$.



Supplementary Figure 18. Cyclic voltammograms of $\text{K}_2\text{Ni}_2\text{TeO}_6$ taken at a scanning rate of 0.05 mV s^{-1} (grey curve) and 0.1 mV s^{-1} (black curve) revealing redox voltages above 4 V versus (vs.) K^+ / K . Cyclic voltammograms of $\text{K}_2\text{Ni}_2\text{TeO}_6$ taken at a scanning rate of 0.1 mV s^{-1} revealing redox voltages above 4 V vs. K^+ / K . Minor peaks emanating from a multitude of $\text{K}^+ /$ vacancy ordering as has been noted in P2-type structures during K-ion (de)insertion are also evident.



Supplementary Figure 19. X-ray diffraction *ex situ* patterns of $\text{K}_2\text{Ni}_2\text{TeO}_6$ taken upon initial, 20th and 30th cycling. No discernible change in the XRD powder pattern was found for samples that had been cycled for more than 20 and 30 cycles, which is consistent with a sustained reversibility of the P2-type $\text{K}_2\text{Ni}_2\text{TeO}_6$ upon repeated K^+ extraction / insertion.



Supplementary Figure 20. **a.** Ni $2p_{3/2}$ and **b.** Te $3d$ XPS spectra of $\text{K}_2\text{Ni}_2\text{TeO}_6$ taken after charging to 4.7 V and discharging to 1.3 V. The broad peak (hump) appearing at around 860 eV shows the $\text{F}(\text{KL}_1\text{L}_{23})$ Auger peak. The binding energy of the Ni $2p_{3/2}$ peak shifts to a higher value of 857 eV, which corresponds to Ni^{3+} after charging to 4.6 V. After discharging, the Ni $2p_{3/2}$ peak recovers to the shape of pristine phase, confirming mainly the reversibility of the process in agreement with the electrochemical data. Turning to Te $3d$ core spectra, the Te $3d_{5/2}$ peak at 576.3 eV is characteristic of Te^{6+} referenced to K_2TeO_3 (Te $3d_{5/2}$ respectively at 576.3 and 575.7 eV). It remains invariant for the entire charge–discharge process indicating that Te, as a spectator ion, does not participate in the redox process.

Supplementary Table 1. Results of Inductively Coupled Plasma (ICP) measurements of $K_2M_2TeO_6$ ($M = Ni, Co, Mg$).

Compound	K	M	Te
	(molar ratio)	(molar ratio)	(molar ratio)
$K_2Ni_2TeO_6$	1.91	2.01	1
$K_2Co_2TeO_6$	1.70	1.86	1
$K_2Mg_2TeO_6$	1.89	1.95	1

Supplementary Table 2. Atomic coordinates (x , y , z), occupancies (g), and isotropic atomic displacement parameters (U_{iso}) obtained by Rietveld refinement of synchrotron X-ray diffraction data for as-prepared $\text{K}_2\text{Ni}_2\text{TeO}_6$ indexed in the space group $P6_3/mcm$ (hexagonal) with lattice constants $a = b = 5.2606(1)$ Å, $c = 12.4669(3)$ Å, and $V = 298.79(1)$ Å³ ($R_{\text{Bragg}} = 4.29$ %, $\chi^2 = 1.77$). The crystal structure of $\text{K}_2\text{Ni}_2\text{TeO}_6$ was solved using the crystal structure of isotypic $\text{Na}_2\text{Ni}_2\text{TeO}_6$ as a starting structural model. The K1, K2 and K3 sites, respectively, have multiplicities of three, two, and one at each interlayer per unit cell. Further details of the crystal structure investigation(s) may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository (accession) numbers CSD-434032, -434033, and -434061.

Atom	Wyckoff	x	y	z	g	U_{iso}
Te1	$2b$	0	0	0	1	0.0035(8)
Ni1	$4d$	$2/3$	$1/3$	0	1	0.0013(4)
O1	$12k$	0.6723(6)	0.6723(6)	0.5924(3)	1	0.0010(2)
K1	$6g$	0.3495(7)	0	$1/4$	0.4984(43)	0.0213(7)
K2	$4c$	$1/3$	$2/3$	$1/4$	0.2061(35)	0.0025(5)
K3	$2a$	0	0	$1/4$	0.0452(21)	0.0709(13)

* g and U_{iso} denote the occupancy and isotropic thermal factor, respectively.

Supplementary Table 3. Comparison of the lattice parameters of the potassium orthotellurate family described by the formula $K_2M_2TeO_6$ and $K_2M_{1-x}M'_xTeO_6$, (in which M and M' are Co, Ni, Zn, Mg, Mn or Cu). Subject to the requirement of charge balance, practically any combination of such solid solutions can be realised. Lattice parameters for solid solution derivatives were determined through Le Bail fitting procedure. Detailed structural analyses of $K_2Zn_2TeO_6$, $K_2Mn_2TeO_6$ and $K_2Cu_2TeO_6$ parent phases will be reported elsewhere.

Compound	Lattice	Symmetry	a_{hex} (=b) (Å)	c_{hex} (Å)	V (Å ³)	ρ (g cm ⁻³)
$K_2Co_2TeO_6$	Hexagonal	$P6_322$	5.2426(7)	12.4162(14)	295.54(4)	4.6983
$K_2Mg_2TeO_6$	Hexagonal	$P6_322$	5.2863(5)	12.5388(20)	303.45(6)	4.5758
$K_2Ni_2TeO_6$	Hexagonal	$P6_3/mcm$	5.2606(1)	12.4669(3)	298.79(1)	4.6473
$K_2Co_{1.5}Ni_{0.5}TeO_6$	Hexagonal	$P6_3/mcm$	5.2415(2)	12.5196(9)	297.88(2)	4.6777
$K_2CoNiTeO_6$	Hexagonal	$P6_3/mcm$	5.1952(11)	12.5692(6)	293.79(1)	4.7413
$K_2Co_{0.5}Ni_{1.5}TeO_6$	Hexagonal	$P6_3/mcm$	5.2075(1)	12.5252(5)	294.15(1)	4.7342
$K_2NiZnTeO_6$	Hexagonal	$P6_3/mcm$	5.2691(4)	12.5072(15)	300.71(5)	4.7036
$K_2Ni_{1.5}Zn_{0.5}TeO_6$	Hexagonal	$P6_3/mcm$	5.2651(3)	12.4905(13)	299.87(4)	4.6797
$K_2Co_{0.5}Mg_{1.5}TeO_6$	Hexagonal	$P6_3/mcm$	5.2556(12)	12.6568(53)	302.76(1)	4.0337
$K_2Co_{1.5}Mg_{0.5}TeO_6$	Hexagonal	$P6_3/mcm$	5.2558(2)	12.5386(12)	299.96(3)	4.4548
$K_2NiMgTeO_6$	Hexagonal	$P6_322$	5.5034(11)	12.0903(18)	317.13(7)	4.0311
$K_2Ni_{1.5}Mg_{0.5}TeO_6$	Hexagonal	$P6_3/mcm$	5.4665(10)	12.1301(12)	313.91(6)	4.2544
$K_2Ni_{0.5}Mg_{1.5}TeO_6$	Hexagonal	$P6_322$	5.1161(11)	12.4817(27)	282.93(10)	4.3164
$K_2Ni_{1.5}Cu_{0.5}TeO_6$	Hexagonal	$P6_3/mcm$	5.2042(5)	12.0723(11)	283.16(39)	4.9450
$K_2NiCuTeO_6$	Hexagonal	$P6_3/mcm$	5.1833(5)	11.8619(9)	276.01(3)	5.1022
$K_2MgCoTeO_6$	Hexagonal	$P6_3/mcm$	5.1807(6)	12.1783(15)	283.08(4)	4.5173
$K_2Ni_{1.5}Mn_{0.5}TeO_6$	Hexagonal	$P6_3/mcm$	5.1399(7)	12.0485(14)	275.65(4)	5.0295
$K_2NiMnTeO_6$	Hexagonal	$P6_3/mcm$	5.1319(7)	12.0715(15)	275.32(4)	5.0128

Supplementary Table 4. Atomic coordinates (x , y , z), occupancies (g), and isotropic atomic displacement parameters (U_{iso}) obtained by Rietveld refinement of conventional X-ray diffraction data for as-prepared $\text{K}_2\text{Mg}_2\text{TeO}_6$ indexed in the space group $P6_322$ (hexagonal) with lattice constants $a = b = 5.2863(5)$ Å, $c = 12.5388(2)$ Å, and $V = 303.45(6)$ Å³ ($R_{\text{Bragg}} = 5.92$ %, $\chi^2 = 2.38$).

Atom	Wyckoff	x	y	z	g	U_{iso}
Mg1	$2b$	0	0	1/4	1	0.0082(10)
Mg2	$2d$	2/3	1/3	1/4	1	0.0082(10)
Te1	$2c$	1/3	2/3	1/4	1	0.0093(5)
O1	$12i$	0.6432(6)	-0.0252(4)	0.3452(1)	1	0.0154(42)
K1	$12i$	0.2408(37)	0.6534(29)	-0.0267(38)	0.0815(73)	0.0083(31)
K2	$2a$	0	0	0	0.1124(32)	0.0083(31)
K3	$12i$	0.7022(31)	0.0661(18)	-0.0064(22)	0.2341(58)	0.0083(31)

* g and U_{iso} denote the occupancy and isotropic thermal factor, respectively.

Supplementary Table 5. Atomic coordinates (x , y , z), occupancies (g), and isotropic atomic displacement parameters (U_{iso}) obtained by Rietveld refinement of conventional X-ray diffraction data for as-prepared $\text{K}_2\text{Co}_2\text{TeO}_6$ indexed in the space group $P6_322$ (hexagonal) with lattice constants $a = b = 5.2426(7)$ Å, $c = 12.4162(14)$ Å, and $V = 295.54(4)$ Å³ ($R_{\text{Bragg}} = 5.78$ %, $\chi^2 = 2.14$).

Atom	Wyckoff	x	y	z	g	U_{iso}
Co1	$2b$	0	0	1/4	1	0.0078(5)
Co2	$2d$	2/3	1/3	1/4	1	0.0078(5)
Te1	$2c$	1/3	2/3	1/4	1	0.0088(4)
O1	$12i$	0.6381(7)	-0.0248(6)	0.3391(5)	1	0.0152(6)
K1	$12i$	0.2371(4)	0.6489(4)	-0.0271(14)	0.0543(28)	0.0081(4)
K2	$2a$	0	0	0	0.1056(21)	0.0081(4)
K3	$12i$	0.7051(4)	0.0642(8)	-0.0057(3)	0.2265(64)	0.0083(4)

Supplementary Table 6. List of feasible potassium-based cathode materials grouped according to their dimensionality (1D, 2D and 3D) and diffusion barriers obtained by BVOL. Selected potassium-based compounds with low diffusion barriers have been shown for brevity.

Compound	Lattice	Symmetry	Diffusion Barrier (eV)	Dimensionality	Reference ICSD
K ₃ CoO ₂	Orthorhombic	<i>Pnma</i>	0.25	2D	73212
K _{0.3} MnO ₂	Orthorhombic	<i>Ccmm</i>	0.27	2D	156080
K ₂ FeSiO ₄	Cubic	<i>F-43m</i>	0.30	3D	434059*
KFeSiO ₄	Tetragonal	<i>I4mm</i>	0.32	1D	73423
K ₂ Ni ₂ TeO ₆	Hexagonal	<i>P6₃/mcm</i>	0.35	2D	434032*
K ₂ CoNiTeO ₆	Hexagonal	<i>P6₃/mcm</i>	0.35	2D	434033*
KFePO ₄ F	Orthorhombic	<i>Pna 2₁</i>	0.59	1D	39560
K ₂ NiO ₂	Tetragonal	<i>I4/mmm</i>	0.80	3D	201891
K ₂ CuP ₂ O ₇	Tetragonal	<i>P-42₁m</i>	0.91	2D	191282
K ₂ FeSiO ₄	Orthorhombic	<i>Pca 2₁</i>	0.92	1D	434055*
KFeSi ₂ O ₆	Tetragonal	<i>I4₁/a</i>	1.13	1D	66922
KMnPO ₄	Triclinic	<i>P-1</i>	1.17	1D	78840
K ₂ FeGeO ₄	Orthorhombic	<i>Pca 2₁</i>	1.24	1D	434060*
KVP ₂ O ₇	Monoclinic	<i>P 2₁/c</i>	1.25	1D	68625
K ₂ NiP ₂ O ₇	Monoclinic	<i>P 2₁</i>	1.25	2D	80978
KFeP ₂ O ₇	Monoclinic	<i>P 2₁/c</i>	1.27	1D	202814
K ₂ FeP ₂ O ₇	Tetragonal	<i>P-42₁m</i>	1.30	2D	191281
K ₂ CoV ₂ O ₇	Tetragonal	<i>P-42₁m</i>	1.45	2D	195619
KFePO ₄	Monoclinic	<i>P 2₁/n</i>	1.82	1D	415458
K ₂ MnP ₂ O ₇	Monoclinic	<i>P 2₁/n</i>	2.08	1D	74600
KFeSiO ₄	Hexagonal	<i>P 6₃22</i>	2.13	1D	280085
K ₂ CuP ₂ O ₇	Orthorhombic	<i>Pbnm</i>	2.16	1D	79916
KMnVO ₄	Monoclinic	<i>P 2₁/n</i>	2.19	1D	158975
KNiPO ₄	Orthorhombic	<i>Pna 2₁</i>	2.30	1D	81271
KFeGeO ₄	Hexagonal	<i>P 6₃</i>	2.59	2D	280084
KFeO ₂	Orthorhombic	<i>Pbca</i>	2.68	1D	94467
K ₂ FeB ₂ O ₇	Tetragonal	<i>P 321</i>	3.38	1D	247415

Crystal structure depot (CSD) number indicated in asterisks are for new crystal structures deposited in the ICSD repository database.

Supplementary Table 7. Calculated BVEL activation energies for some selected potassium-based solid electrolyte materials grouped according to calculated BVEL diffusion barriers and their BVEL migration map dimensionality (1D, 2D and 3D).

Compound	Lattice	Symmetry	Diffusion Barrier (eV)	Dimensionality	Reference ICSD
K ₂ CdO ₂	Orthorhombic	<i>Pbcn</i>	0.09	1D	25004
K ₂ ZnO ₂	Orthorhombic	<i>Ibam</i>	0.12	1D	34603
K ₄ SiO ₄	Monoclinic	<i>P 2₁/c</i>	0.26	1D	66073
K ₄ GeO ₄	Triclinic	<i>P- 1</i>	0.31	1D	37271
K _{0.72} In _{0.72} Sn _{0.28} O ₂	Hexagonal	<i>P- 6m 2</i>	0.32	2D	30062
K ₂ Mg ₂ TeO ₆	Hexagonal	<i>P 6₃22</i>	0.33	2D	434061*
KBiO ₃	Cubic	<i>Im- 3</i>	0.75	2D	73746
K ₂ MgSiO ₄	Orthorhombic	<i>Pca 2₁</i>	0.81	1D	83226
K ₃ Sc(MoO ₄) ₃	Orthorhombic	<i>Pbc 2₁</i>	0.91	1D	201281
KMgPO ₄	Monoclinic	<i>P 2₁/c</i>	1.04	1D	50926
K ₂ MgV ₂ O ₇	Tetragonal	<i>P 4₂/mmm</i>	1.05	2D	202823
K ₂ CaP ₂ O ₇	Monoclinic	<i>P 2₁/n</i>	1.69	1D	281572
K ₂ ZnGeO ₄	Orthorhombic	<i>Pca 2₁</i>	1.86	1D	85006
KAl(MoO ₄) ₂	Hexagonal	<i>P -3m 1</i>	1.94	1D	28018
K ₂ Mg ₂ (MoO ₄) ₃	Orthorhombic	<i>P 2₁2₁2₁</i>	2.02	1D	200931
K ₄ Mg(WO ₄) ₃	Triclinic	<i>P- 1</i>	2.03	1D	194187
K ₂ CaPO ₄ F	Orthorhombic	<i>Pcmn</i>	2.52	1D	ref [5]
K ₃ Na(SO ₄) ₂	Hexagonal	<i>P -3m 1</i>	5.57	2D	26018
K ₂ Mg ₂ (SO ₄) ₃	Cubic	<i>P 2₁3</i>	7.59	1D	100420
K ₂ Ca ₂ Si ₂ O ₇	Hexagonal	<i>P 6₃/m</i>	10.46	1D	180795

Crystal structure depot (CSD) accession number indicated in asterisks are for new crystal structures deposited in the ICSD repository database.

Supplementary Table 8. Ionic conductivity values reported for K-ion superionic conductors, showing performance comparison with $\text{K}_2\text{Mg}_2\text{TeO}_6$.

Compound	$\sigma_{573\text{ K}} / \text{mS cm}^{-1}$ (300 °C (573 K))	$\sigma_{300\text{ K}} / \text{mS cm}^{-1}$ (25±3 °C (298±3 K))	Bibliography
$\text{K}_2\text{Mg}_2\text{TeO}_6$	38	$\sim 10^{-2}$	This work
$\text{K}_{2-2x}\text{Mg}_{1-x}\text{Si}_{1+x}\text{O}_4$	36		[6]
$\text{K}_{0.59}\text{Mg}_{0.53}\text{Sb}_{0.47}\text{O}_2$	21		[7]
$\text{K}_2\text{O} \cdot 5.2\text{Fe}_2\text{O}_3 \cdot 0.8\text{ZnO}$	18		[8]
$\text{K}_{0.56}\text{Ni}_{0.52}\text{Sb}_{0.48}\text{O}_2$	16		[7]
KFeO_2	1		[9]
KBiO_3	10^{-2}		[10]
$\text{K}_{1+x}\text{Ga}_{11}\text{O}_{17+x/2}$ ($x=0\sim0.3$)	~ 1		[11]
$\text{K}_{0.405}\text{Bi}_{0.865}\text{AsO}_4$	1.607×10^{-4}		[12]
$\text{K}_5\text{Sb}_5\text{P}_2\text{O}_{20}$	3.162×10^{-3}		[13]
K_2SbPO_6	1×10^{-4}		[13]
$\text{K}_{2-2x}\text{Fe}_{2-x}\text{P}_x\text{O}_4$ ($x=0.05\sim0.10$)	7.1		[14]
$\text{K}_{1.9}\text{Al}_{1.95}\text{V}_{0.05}\text{O}_4$	1.38		[15]
$\text{K}_{1.9}\text{Fe}_{1.95}\text{V}_{0.05}\text{O}_4$	6.94		[15]
$\text{K}_{0.70}\text{Zn}_{0.35}\text{Sn}_{0.65}\text{O}_2$		7.5×10^{-3}	[16]
$\text{K}_{0.72}\text{Sc}_{0.72}\text{Hf}_{0.28}\text{O}_2$		4×10^{-5}	[17]
$\text{K}_{0.72}\text{In}_{0.72}\text{Zr}_{0.28}\text{O}_2$		1×10^{-4}	[17]
$\text{K}_{0.72}\text{In}_{0.72}\text{Hf}_{0.28}\text{O}_2$		3.5×10^{-4}	[17]
$\text{K}_{0.72}\text{In}_{0.72}\text{Sn}_{0.28}\text{O}_2$		5.6×10^{-4}	[17]
$\text{K}_{0.80}\text{Zn}_{0.40}\text{Sn}_{0.60}\text{O}_2$		1×10^{-3}	[11]
$\text{K}_4\text{Nb}_6\text{O}_{17}$		1×10^{-2}	[11]
$\text{K}_{1.8}(\text{Li}_{2.45}\text{Sb}_{5.55})\text{O}_{16}$		1	[18]
$\text{K}_{1.54}(\text{Mg}_{0.77}\text{Ti}_{7.23})\text{O}_{16}$		220	[19]
KTiOAsO_4		$10^{-3} \sim 10^{-6}$	[20]

Supplementary Table 9. Volumetric energy densities attained by reported cathode materials for rechargeable potassium ion battery in comparison with new tellurate compounds detailed in this work. The achieved volumetric energy density was obtained based on the product of the attained capacity and the average voltage of the respective cathode material. Also note that the attained volumetric capacity is the product of the density of the active cathode material and the capacity attained.

Compound	K-half cell configuration	Attained capacity	Average voltage	Attained capacity (energy density)
		mAhg ⁻¹	V vs. K ⁺ / K	mAh cm ⁻³ (mWh cm ⁻³)
P3-K _{0.5} MnO ₂ [33]	K _{0.5} MnO ₂ /0.7M KPF ₆ in EC/DEC (1:1 vol%)/K metal	100	2.5 ~2.7 (2.6)	454.7 (1182.2)
K _{0.3} MnO ₂ [34]	K _{0.3} MnO ₂ /1.5M KFSI in EC/DMC /K metal	136	2.7	482.8 (1303.5)
P2-K _{0.6} CoO ₂ [35]	K _{0.6} CoO ₂ /0.7M KPF ₆ in EC/DEC (1:1 vol%)/K metal	80	2.7	352.9 (952.8)
K _{2/3} Ni _{1/6} Co _{1/6} Mn _{2/3} O ₂ [36]	K _{2/3} Ni _{1/6} Co _{1/6} Mn _{2/3} O ₂ /0.8M KPF ₆ in EC/DEC (1:1 vol%)/K	76.5	3.1	284.1 (880.7)
P2-K _{0.41} CoO ₂ [37]	K _{0.41} CoO ₂ /1M KFSI in EC/DEC (1:1 vol%)/K metal	60	3	
Prussian blue (PB) [38]	K ₂ MnFe(CN) ₆ /saturated KClO ₄ in PC /K metal	142	3.6	255.6 (920.2)
Prussian white (PW) [39]	PW / 0.8M KPF ₆ in PC;4wt%FEC/K metal	110	3.2	201.3 (644.2)
PTCDA [40]	PTCDA/0.8M KPF ₆ in EC/DEC (1:1 vol%)/K metal	122	2.5	207.4 (518.5)
KVPO ₄ F [41]	KVPO ₄ F/1M KPF ₆ in EC/PC/K metal	92	4.02	286.6 (1152.1)
K ₃ V ₂ (PO ₄) ₃ [42]	K ₃ V ₂ (PO ₄) ₃ /0.8M KPF ₆ in EC/DEC (1:1 vol%)/K metal	54	3.7	
KVOPO ₄ [41]	KVOPO ₄ /1M KPF ₆ in EC/PC/K metal	84	3.95	262.6 (1037.2)
KVP ₂ O ₇ [43]	KVP ₂ O ₇ /0.5M KPF ₆ in EC/DEC/K metal	60	4.2	181.0 (760.2)
K ₂ CoNiTeO ₆	K ₂ CoNiTeO ₆ /0.5M KTFSI in Pyr ₁₃ TFSI/K metal	30	4.3	142.2 (611.6)
K ₂ Ni ₂ TeO ₆	K ₂ Ni ₂ TeO ₆ /0.5M KTFSI in Pyr ₁₃ TFSI/K metal	70	3.6	325.3 (1171.2)
K ₂ NiMgTeO ₆	K ₂ NiMgTeO ₆ /0.5M KTFSI in Pyr ₁₃ TFSI/K metal	34.7	3.98	139.9 (556.7)
K ₂ NiZnTeO ₆	K ₂ NiZnTeO ₆ /0.5M KTFSI in Pyr ₁₃ TFSI/K metal	56.8	3.75	267.2 (1001.9)
K ₂ Ni _{1.5} Mg _{0.5} TeO ₆	K ₂ Ni _{1.5} Mg _{0.5} TeO ₆ /0.5M KTFSI in Pyr ₁₃ TFSI/K metal	69	3.7	293.6 (1086.2)
K ₂ Ni _{1.5} Zn _{0.5} TeO ₆	K ₂ Ni _{1.5} Zn _{0.5} TeO ₆ /0.5M KTFSI in Pyr ₁₃ TFSI/K metal	75.4	3.7	352.9 (1305.5)
K ₂ Co _{0.5} Ni _{1.5} TeO ₆	K ₂ Co _{0.5} Ni _{1.5} TeO ₆ /0.5M KTFSI in Pyr ₁₃ TFSI/K metal	51.7	3.9	244.8 (954.6)
K ₂ Co _{1.5} Ni _{0.5} TeO ₆	K ₂ Co _{1.5} Ni _{0.5} TeO ₆ /0.5M KTFSI in Pyr ₁₃ TFSI/K metal	8	3.6	35.6 (128.3)
K ₂ Ni _{0.5} Mg _{1.5} TeO ₆	K ₂ Ni _{0.5} Mg _{1.5} TeO ₆ /0.5M KTFSI in Pyr ₁₃ TFSI/K metal	22.9	3.86	98.9 (381.5)
K ₂ Ni _{1.5} Cu _{0.5} TeO ₆	K ₂ Ni _{1.5} Cu _{0.5} TeO ₆ /0.5M KTFSI in Pyr ₁₃ TFSI/K metal	37	3.68	183.0 (673.3)
K ₂ Ni _{1.5} Mn _{0.5} TeO ₆	K ₂ Ni _{1.5} Mn _{0.5} TeO ₆ /0.5M KTFSI in Pyr ₁₃ TFSI/K metal	38.8	3.63	195.1 (708.4)
K ₂ NiCuTeO ₆	K ₂ NiCuTeO ₆ /0.5M KTFSI in Pyr ₁₃ TFSI/K metal	27	3.79	137.8 (522.1)
K ₂ NiMnTeO ₆	K ₂ NiMnTeO ₆ /0.5M KTFSI in Pyr ₁₃ TFSI/K metal	4.65	3.25	23.3 (75.8)
K ₄ NiTeO ₆	K ₄ NiTeO ₆ /0.5M KTFSI in Pyr ₁₃ TFSI/K metal	28.51	3.58	
K ₄ CoTeO ₆	K ₄ CoTeO ₆ /0.5M KTFSI in Pyr ₁₃ TFSI/K metal	4.5	3.2	
K ₃ Ni ₂ SbO ₆	K ₃ Ni ₂ SbO ₆ /0.5M KTFSI in Pyr ₁₃ TFSI/K metal	47.98	3.868	

*Co-based tellurates such as K₂Co₂TeO₆ and K₄CoTeO₆ were found to be electrochemically inactive.

Supplementary Table 10. Volumetric energy densities attained by other polyanion-based cathode materials for rechargeable potassium ion battery also evaluated in this work. Owing to the inherently low electronic conductivity of polyanion moieties, a higher carbon loading on the assembled composite electrode was used (namely, 70: 15:15 (active cathode material: carbon: binder)). Note also that the particle size was in the micrometric range, just as was observed in the tellurates, for all the polyanion compounds tested.

Compound	K-half cell configuration	Attained capacity	Average voltage	Attained capacity (energy density)
		mAhg ⁻¹	V vs. K ⁺ / K	mAh cm ⁻³ (mWh cm ⁻³)
KFePO ₄ F	KFePO ₄ F/0.5M KTFSI in Pyr ₁₃ TFSI/K metal	×	×	×
KFePO ₄	KFePO ₄ /0.5M KTFSI in Pyr ₁₃ TFSI/K metal	6.6	2.7	20.3 (54.8)
KMnPO ₄	KMnPO ₄ /0.5M KTFSI in Pyr ₁₃ TFSI/K metal	2.5	2.92	7.5 (21.8)
KCoPO ₄	KCoPO ₄ /0.5M KTFSI in Pyr ₁₃ TFSI/K metal	2.2	2.9	6.9 (20.1)
KNiPO ₄	KNiPO ₄ /0.5M KTFSI in Pyr ₁₃ TFSI/K metal	2.2	2.94	7.2 (21.1)
KMn ₄ (PO ₄) ₃	KMn ₄ (PO ₄) ₃ /0.5M KTFSI in Pyr ₁₃ TFSI/K metal	15.3	3.2	52.8 (168.8)
Beta-VOPO ₄	Beta-VOPO ₄ /0.5M KTFSI in Pyr ₁₃ TFSI/K metal	10	3.55	32.4 (114.8)
K ₂ VOP ₂ O ₇	K ₂ VOP ₂ O ₇ /0.5M KTFSI in Pyr ₁₃ TFSI/K metal	5	3.27	14.3 (46.7)
KFeP ₂ O ₇	KFeP ₂ O ₇ /0.5M KTFSI in Pyr ₁₃ TFSI/K metal	2	2.8	6.2 (17.4)
K ₂ FeP ₂ O ₇	K ₂ FeP ₂ O ₇ /0.5M KTFSI in Pyr ₁₃ TFSI/K metal	2	2.9	5.7 (16.5)
K ₂ MnP ₂ O ₇	K ₂ MnP ₂ O ₇ /0.5M KTFSI in Pyr ₁₃ TFSI/K metal	1	2.9	3.2 (9.1)
Tetragonal K ₂ CuP ₂ O ₇	K ₂ CuP ₂ O ₇ /0.5M KTFSI in Pyr ₁₃ TFSI/K metal	1.18	2.87	3.5 (10.0)
Orthorhombic K ₂ CuP ₂ O ₇	K ₂ CuP ₂ O ₇ /0.5M KTFSI in Pyr ₁₃ TFSI/K metal	2.2	2.9	6.4 (18.5)
K ₂ CoP ₂ O ₇	K ₂ CoP ₂ O ₇ /0.5M KTFSI in Pyr ₁₃ TFSI/K metal	×	×	×
K ₂ NiP ₂ O ₇	K ₂ NiP ₂ O ₇ /0.5M KTFSI in Pyr ₁₃ TFSI/K metal	1.7	2.95	5.2 (15.4)
Cu ₂ P ₂ O ₇	Cu ₂ P ₂ O ₇ /0.5M KTFSI in Pyr ₁₃ TFSI/K metal	1.8	2.63	7.5 (19.7)
K ₂ CoV ₂ O ₇	K ₂ CoV ₂ O ₇ /0.5M KTFSI in Pyr ₁₃ TFSI/K metal	×	×	×
NASICON Fe ₂ (SO ₄) ₃	Fe ₂ (SO ₄) ₃ /0.5M KTFSI in Pyr ₁₃ TFSI/K metal	19.8	3.52	60.7(213.5)
Yavapaiite KFe(SO ₄) ₂	KFe(SO ₄) ₂ /0.5M KTFSI in Pyr ₁₃ TFSI/K metal	61	3.37	176.4 (594.5)
Langbeinite K ₂ Mn ₂ (SO ₄) ₃	K ₂ Mn ₂ (SO ₄) ₃ /0.5M KTFSI in Pyr ₁₃ TFSI/K metal	2.5	2.91	7.6 (22.2)
Langbeinite K ₂ Co ₂ (SO ₄) ₃	K ₂ Co ₂ (SO ₄) ₃ /0.5M KTFSI in Pyr ₁₃ TFSI/K metal	2.9	2.2	9.6 (21.1)
Langbeinite K ₂ Ni ₂ (SO ₄) ₃	K ₂ Ni ₂ (SO ₄) ₃ /0.5M KTFSI in Pyr ₁₃ TFSI/K metal	32.8	2.1	110.5 (232.1)
Fedotovite K ₂ Cu ₃ O(SO ₄) ₃	K ₂ Cu ₃ O(SO ₄) ₃ /0.5M KTFSI in Pyr ₁₃ TFSI/K metal	5	3.7	15.9 (58.8)
Alpha-VOSO ₄	Alpha-VOSO ₄ /0.5M KTFSI in Pyr ₁₃ TFSI/K metal	19.6	2.2	66.0 (145.2)
KCoSO ₄ F	KCoSO ₄ F/0.5M KTFSI in Pyr ₁₃ TFSI/K metal	×	×	×
Fe ₂ O(SO ₄) ₂	Fe ₂ O(SO ₄) ₂ /0.5M KTFSI in Pyr ₁₃ TFSI/K metal	×	×	×
KCuSO ₄ F	KCuSO ₄ F/0.5M KTFSI in Pyr ₁₃ TFSI/K metal	10	4.2	

*Hardly any capacity could be obtained from K₂CoV₂O₇, K₂CoP₂O₇, KCoSO₄F, Fe₂O(SO₄)₂, KFeP₂O₇, KMnVO₄ polyanion-based compounds.

Supplementary Table 11. Lattice parameters and the corresponding voltage of $\text{K}_2\text{Ni}_2\text{TeO}_6$ during galvanostatic charge (electrochemical K-ion extraction) and following discharge (K-ion reinsertion). The a -lattice parameter decreases whilst the c -lattice parameter increases upon K^+ extraction, as is expected, with a minimal volume change (*ca.* 2.18%).

$\text{K}_{2-x}\text{Ni}_2\text{TeO}_6$ sample	Lattice	Symmetry	a_{hex}	c_{hex}	γ	V
state of (dis)charge			(Å)	(Å)	(°)	(Å³)
Pristine (before cycling)	Hexagonal	$P6_3/mcm$	5.2606(1)	12.4669(3)	120	298.79(1)
Charged to 4 V	Hexagonal	$P6_3/mcm$	5.1740(7)	12.6192(6)	120	292.57(2)
Charged to 4.7 V	Hexagonal	$P6_3/mcm$	5.1547(7)	12.7026(8)	120	292.29(4)
Discharged to 3 V	Hexagonal	$P6_3/mcm$	5.2097(2)	12.5071(3)	120	293.96(2)
Discharged to 1.5 V	Hexagonal	$P6_3/mcm$	5.2596(4)	12.4418(3)	120	298.08(2)

Supplementary Table 12. Bader charge of each atomic species in $\text{K}_{2-x}\text{Ni}_2\text{TeO}_6$ ($x = 0, 1$ and 2)

during galvanostatic charging (electrochemical K-ion extraction).

Atom	Bader Charge (averaged value) / $ e $		
	$x = 0$	$x = 1$	$x = 2$
K	0.838	0.886	
Ni ²⁺	1.291 (1.692)	1.300 (1.666)	
Ni ³⁺		1.394 (1.048)	1.413 (1.072)
Te	5.714	5.710	5.712
O	-1.662	-1.549	-1.423

^a Parentheses values are the magnetic moments μ_B .

Supplementary Note 1. Computational methodology for bond valency energy landscape (BVEL).

To gain insight on the K^+ ion migration channel dimensionality, bond-valency energy landscape (BVEL) method implemented in the BondSTR software with soft bond valency parameters ¹ of the FullProf Suite ² was employed and the diffusion pathways visualised with VESTA software ³. A distance of 10 Å was taken into account as the Coulomb and Morse-type interaction potential ranges. This empirical method avails plausible diffusion pathways under an adjusted cut-off energy, typically the activation energy (E_a). Although the qualitative E_a values of BVEL have unclear physical meaning, their good correlation with those of density functional theory (DFT) ⁴, deems the BVEL approach a legitimate tool to judge as to whether it is worthwhile to further examine using more cost demanding computational simulations (*viz.*, DFT or molecular dynamics (MD) *etc.*) including experiment. The calculated BVEL map drawn with the isosurface at $E_a = 0.35$ eV for $K_2Ni_2TeO_6$ is shown in **Supplementary Figure 10**. Bond valency calculations indicate diffusion of potassium ions through K1 and K2 sites in a rotary-like motion along the *ab* plane, depicting a two-dimensional circular K^+ diffusion pathway within the honeycomb structure akin to a rotary Wankel-type motor engine.

Supplementary Note 2. Computational methodology for density functional theory (DFT).

The dispersion-corrected density functional theory (DFT-D) calculations were performed using the generalised gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional ²¹ and projector augmented wave (PAW) pseudopotentials ²² as implemented in the Quantum-ESPRESSO (QE) Package ²³. DFT-D method can treat the interlayer van der Waals (vdW) interactions, correcting the PBE missing interaction tail; where Grimme's DFT-D2 ²⁴ type of vdW correction was used. The PAW pseudopotentials were generated under the valency electron configurations explicitly represented as follows: O as $2s^2 2p^4$, Mg as $2s^2 2s^6 3s^2$, K as $3s^2 3p^6 4s^1$, Ni as $3d^8 4s^2$, and Te as $5s^2 5p^4$. A plane-wave cut-off of 60 Rydberg (Ry) for the kinetic energy and 500 Ry for the charge density were used to expand the wave functions. Full cell relaxation for all the target structures were conducted with a tolerance of 10^{-10} Ry for total energy and 10^{-3} eV/Å for the residual forces on each ion. Spin-polarised GGA+ U approach was applied for $K_{2-x}Ni_2TeO_6$ ($x = 0, 1$ and 2) with an antiferromagnetic ordering of Ni ions similar to that of $Na_2Ni_2TeO_6$ ²⁵ adopting the $P6_3/mcm$ symmetry; where the effective Hubbard parameter $U_{\text{eff}} (= U - J)$ for Ni d orbitals was taken to be 6 eV ²⁶. The fact that no geometrical information pertaining to the fully de-potassiated end-member Ni_2TeO_6 was available, a model was made with the central Ni/Te/O layer shifted *ca.* 1/3 along the a and b -axis direction in order to avoid direct attachment of oxygen atoms along the c -axis belonging to the different layers. Based on the optimal structures, the partial density of states (PDOS) around the Fermi level (E_F) applied for a Gaussian smearing parameter of 0.01 Ry, Bader charge density analysis (Supplementary Table 12) ²⁷, and open-circuit voltage (OCV) as a reference to potassium metal, namely K^+ / K (see Supplementary Figure 16) were calculated using conventional protocols.

Supplementary Note 3. Computational methodology for DFT-based climbing-image nudged elastic band (DFT-NEB) method.

The activation energies (E_a) for $K_2Mg_2TeO_6$ were calculated using DFT-based climbing-image nudged elastic band (DFT-NEB) method including vdW correction with the GGA level of theory of the QE Package. A 10^{-2} eV / Å was chosen as the convergence threshold for ionic relaxation under the fixed lattice parameters. Prior to performing calculations, the vdW correction needed to reproduce the $P6_3/mcm$ symmetry, rather than $P6_322$ symmetry (as confirmed via experiment), was checked. Although similar formation energies for these symmetries were observed in $K_2Mg_2TeO_6$, the Na analogue ($Na_2Mg_2TeO_6$) tends to prefer more the $P6_322$ symmetry²⁸. The self-diffusion coefficient, D and ionic conductivity, σ of K^+ ion in $K_2Mg_2TeO_6$ were estimated using Nernst-Einstein relation²⁹:

$$\sigma T = (nq^2/k_B) D \quad (D = \rho \lambda^2 \nu^* \exp(-E_a/k_B T))^{30}$$

where, T is temperature, n the number density of charge carriers, q the movable ion's charge, k_B Boltzmann constant, ρ the geometric factor ≈ 1 , λ the hopping distance of 3.4 (4.8) Å for $P6_3/mcm$ ($P6_322$) symmetry structures of $K_2Mg_2TeO_6$, and ν^* the vibrational pre-factor $\approx 10^{13}$ Hz. Since it has been suggested from the results of the empirical-MD simulations that the high degree of movable ion-ion correlation prevailing necessitates a cooperative mechanism to be operative, such as that present in stoichiometric tellurium-oxides^{31,32}, it is sufficient to use the minimum unit-cell for DFT-NEB simulation as shown in **Supplementary Figure 12**. Here the K^+ ions at the top and bottom layers in the model were set to migrate in order to maintain the inversion symmetrical positions; thereby obviating the generation of the dipole moment within the cell.

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