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Supporting Information

P3-Type $K_{0.45}Co_{1/12}Mg_{1/12}Mn_{5/6}O_2$ as a Superior Cathode Material for Potassium-Ion Batteries with High Structural Reversibility Ensured by the Co–Mg Co-Substitution

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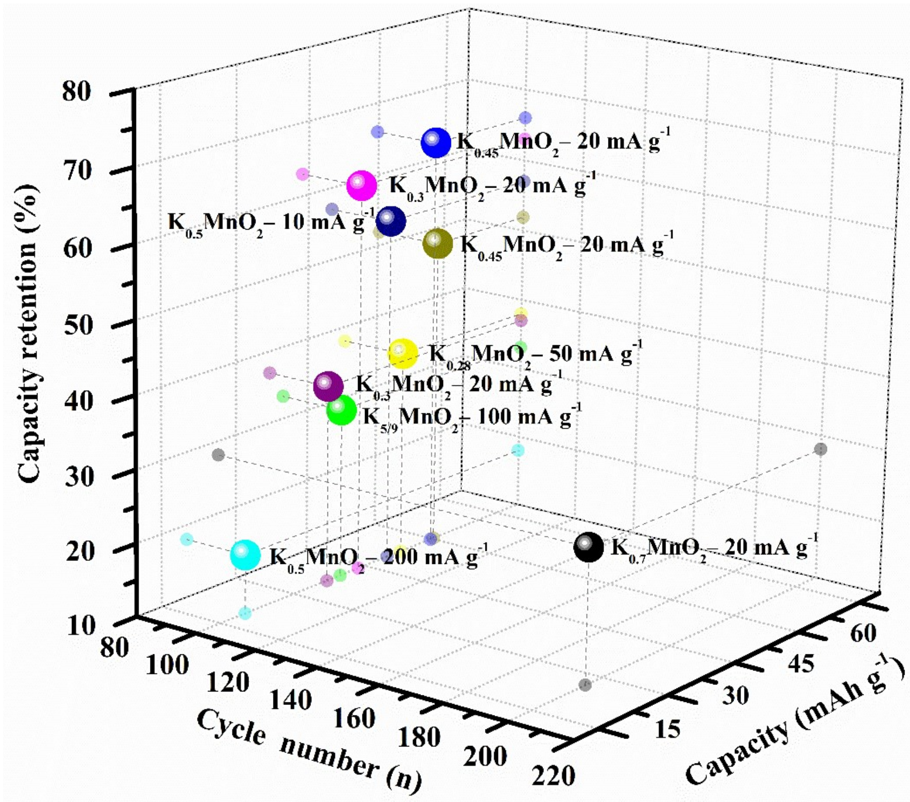


Figure S1. Electrochemical performance of the K_xMnO_2 in PIBs.[1–9]

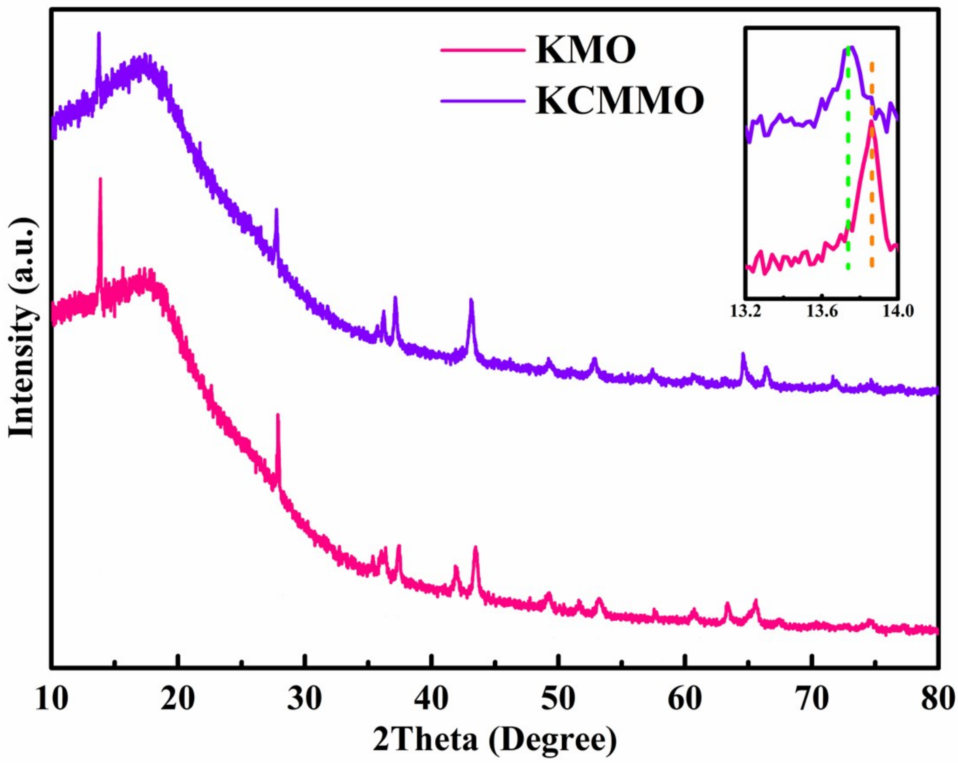


Figure S2. XRD patterns of $K_{0.45}Co_{1/12}Mg_{1/12}Mn_{5/6}O_2$ (KCMMO) and $K_{0.45}MnO_2$ (KMO) collected by sealing the samples with a Polyimide film.

Table S1. The refined crystal sites and atom occupancies from Rietveld refinement results for $K_{0.45}Co_{1/12}Mg_{1/12}Mn_{5/6}O_2$ tested at 25 ℃.

Atom	x	y	z	Occ.
K	0.723	0	0.522	0.45
Co	0	0	0	0.083
Mg	0	0	0	0.083
Mn	0	0	0	0.833
O1	0.365	0	0.136	0.232
O2	0.723	0	0.522	0.902
O3	0	0	0.5	0.864
Monoclinic C2/m (12)	a=5.068	b=2.872	c=7.180	V=102.0 Å^3
R=9.88%	E=3.31%		P=43	EPS=0.5

Table S2. The refined crystal sites and atom occupancies from Rietveld refinement results for $K_{0.45}Co_{1/12}Mg_{1/12}Mn_{5/6}O_2$ tested at 300 ℃.

Atom	x	y	z	Occ.
K	0	0	0.836	0.45
Co	0	0	0	0.083
Mg	0	0	0	0.083
Mn	0	0	0	0.833
O1	0	0	0.382	1
O2	0	0	0.618	1
Hexagonal R3m (160)	a=2.893	b=2.893	c=19.338	V=140.2 Å^3
R=5.86%	E=3.31%		P=25	EPS=0.5

Table S3. The refined crystal sites and atom occupancies from Rietveld refinement results for $K_{0.45}MnO_2$ tested at 25 °C.

Atom	x	y	z	Occ.
K	0.723	0	0.522	0.45
Mn	0	0	0.136	1
O1	0.365	0	0.382	0.232
O2	0.723	0	0.522	0.902
O3	0	0	0.5	0.864
Monoclinic C2/m (12)	a=5.167	b=2.843	c=7.119	V=101.9 Å^3
R=17.14%	E=2.78%		P=56	EPS=0.5

Table S4. The refined crystal sites and atom occupancies from Rietveld refinement results for $K_{0.45}MnO_2$ tested at 300 ℃.

Atom	x	y	z	Occ.
K	0	0	0.836	0.45
Mn	0	0	0	1
O1	0	0	0.382	1
O2	0	0	0.618	1
Hexagonal R3m (160)	a=2.918	b=2.918	c=19.394	V=143.1 Å^3
R=5.33%	E=2.30%		P=26	EPS=0.5

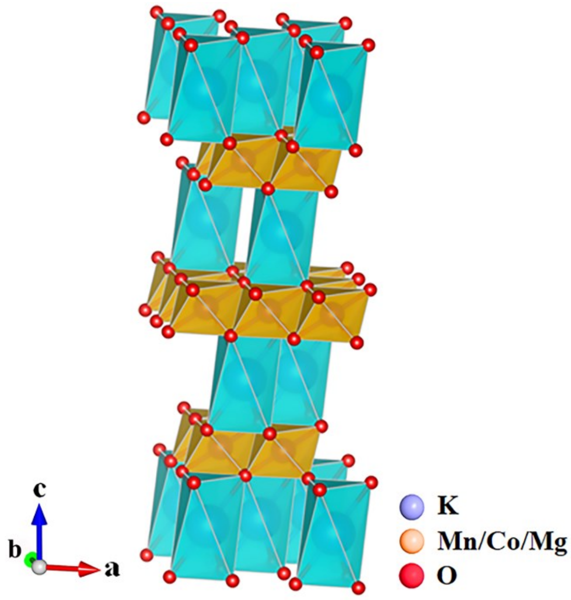
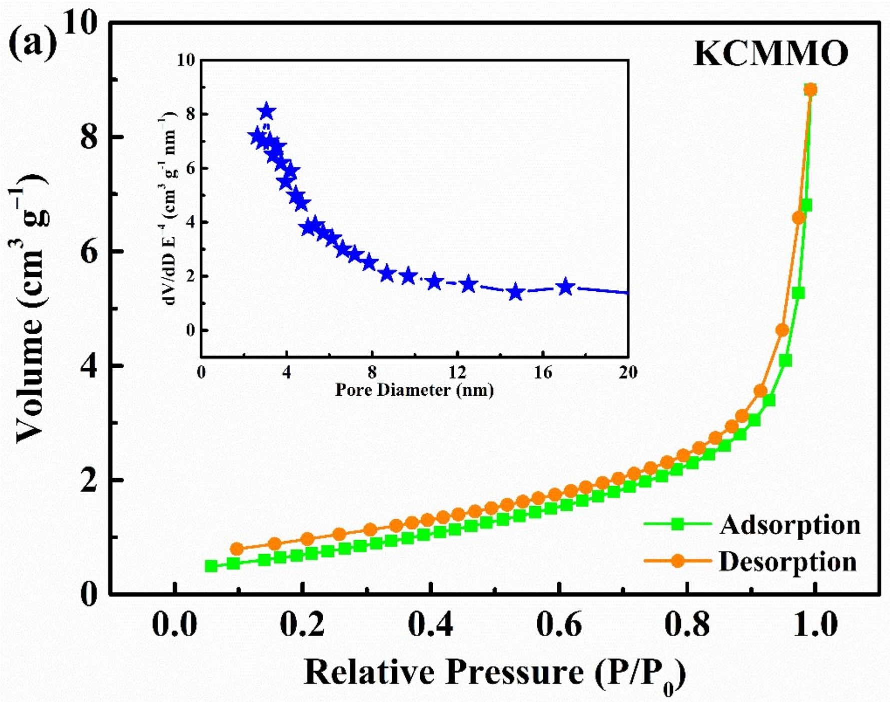


Figure S3. Schematic crystal structure of P3 type.



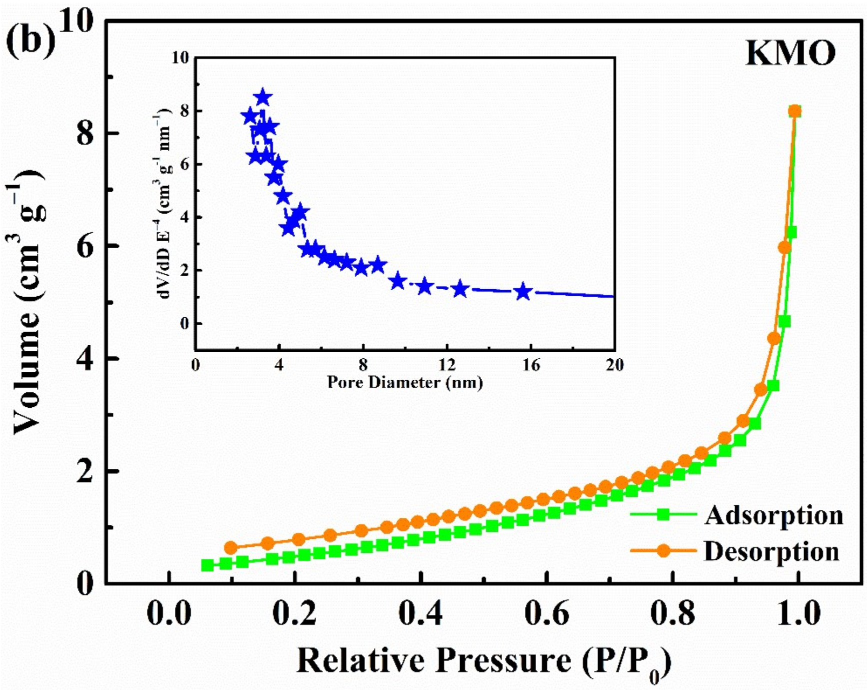


Figure. S4 Nitrogen adsorption-desorption isotherms and pore size distribution for KCMMO (a) and KMO (b) samples.

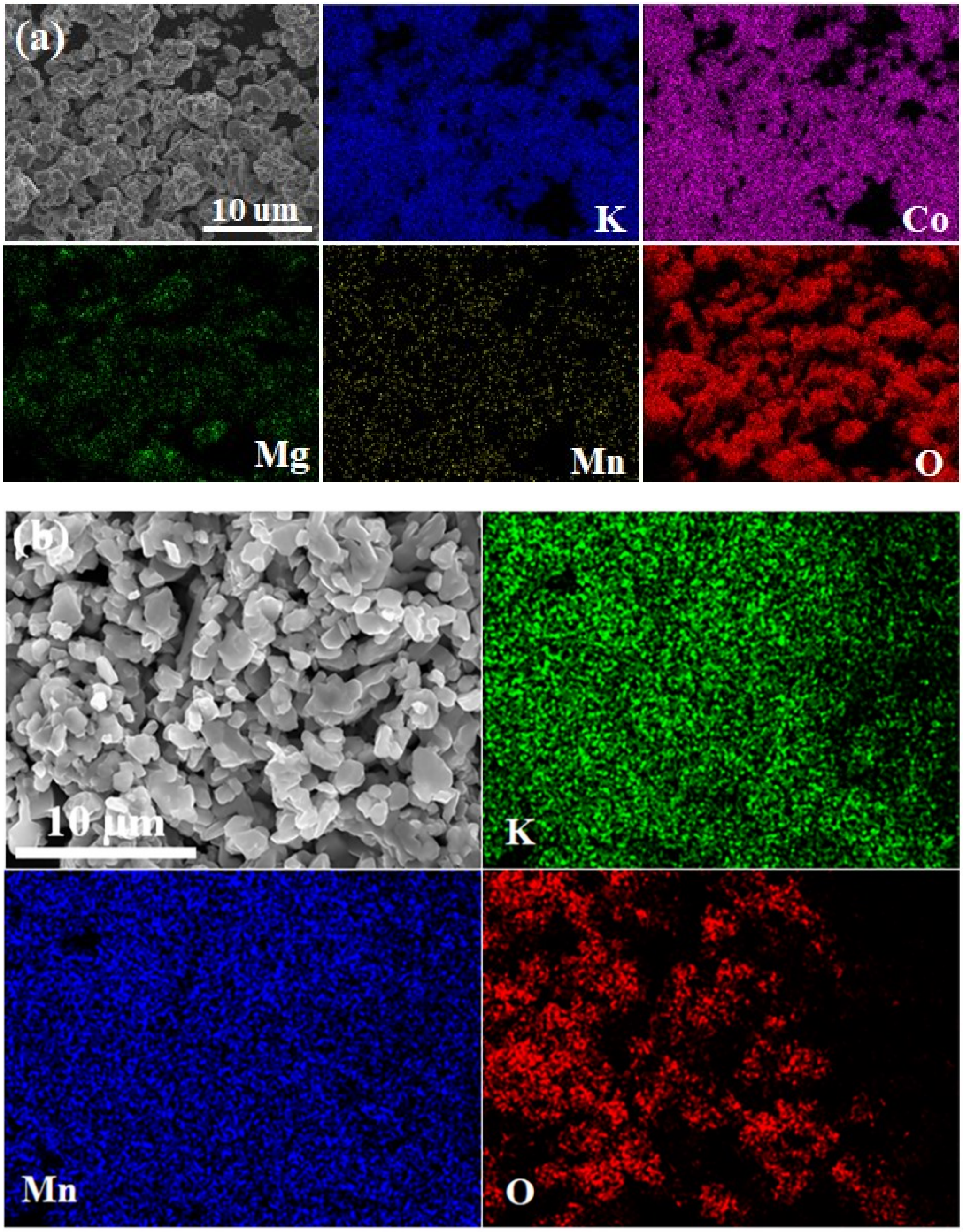


Figure S5. SEM images and EDS mappings of (a) KCMMO and (b) KMO.

Table S5. Theoretical/tested ICP element contents (at %).

Samples	K	Mn	Co	Mg
KMO	0.45/0.42	1.00/0.97	-	-
KCMMO	0.45/0.42	0.833/0.834	0.083/0.082	0.083/0.081

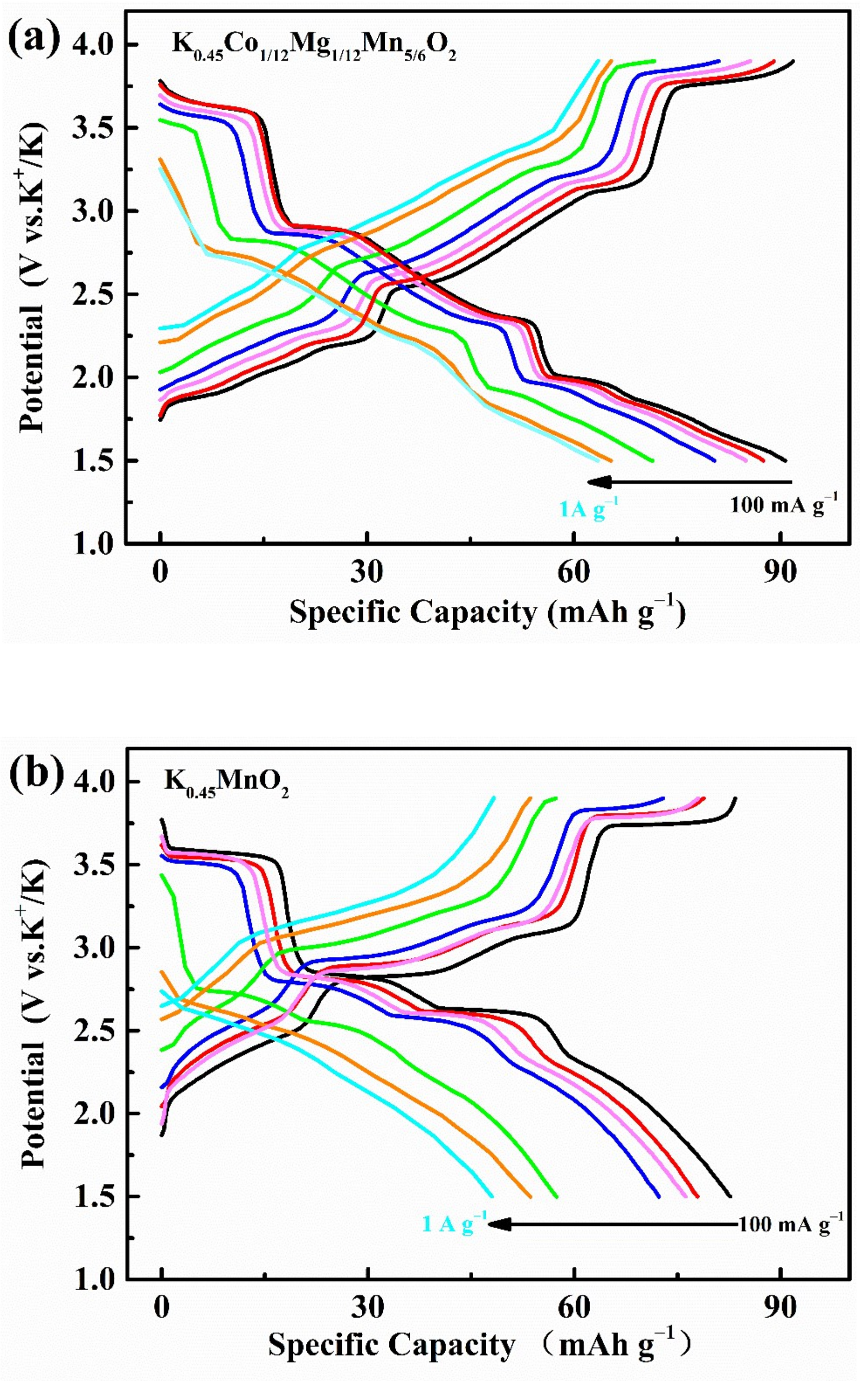


Figure S6. Voltage profiles at different rates for (a) KCMMO and (b) KMO in the voltage range of 1.5–3.9 V.

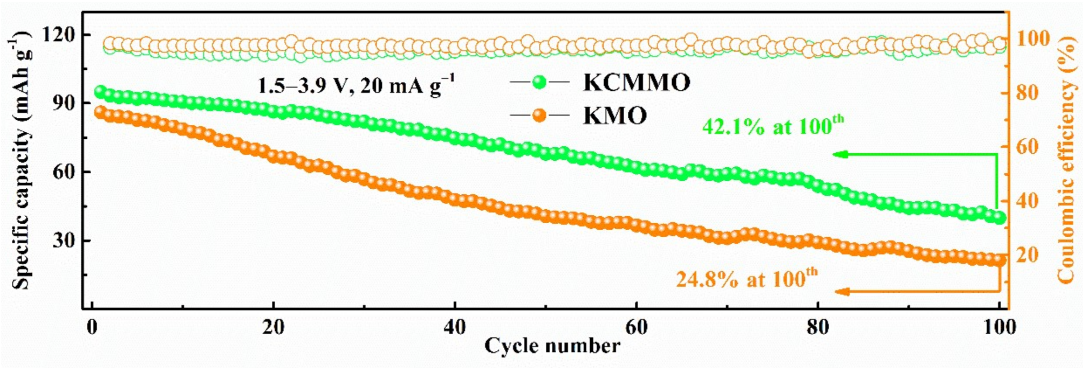


Figure S7. Cycle performances for KCMMO and KMO at 20 mA g^{-1}.

Table S6. Comparison of the 1st discharge capacity of Mn-based oxide cathode materials for PIBs

Sample	Initial discharge specific capacity / mAh g^{-1}	Voltage range / V	Current density / mA g^{-1}	References
KCMMO	96.5	1.5–3.9	20	This work
$K_{5/9}Mn_{5/9}Ti_{4/9}O_2$	85.6	1.5–4.2	20	2
$K_{0.45}Ni_{0.1}Co_{0.1}Mn_{0.8}O_2$	89.2	1.5–4.0	20	10
$K_{0.45}Ni_{0.1}Co_{0.1}Mg_{0.05}Mn_{0.75}O_2$	80.8	1.5–4.0	20	10
$K_{0.45}Ni_{0.1}Co_{0.1}Al_{0.05}Mn_{0.75}O_2$	84.5	1.5–4.0	20	10
$K_{0.67}Ni_{0.17}Co_{0.17}Mn_{0.66}O_2$	76.5	2.0–4.3 V	20	11
$K_{0.4}Mn_{0.7}Ni_{0.3}O_2$	93.7	2.0–3.9 V	100	12
$K_{0.48}Ni_{0.2}Co_{0.2}Mn_{0.6}O_2$	57	1.5–4.2 V	40	13
$K_{0.48}Mn_{0.4}Co_{0.6}O_2$	65	1.0–4.2 V	10	14
$K_{0.37}Na_{0.3}Ni_{0.17}Co_{0.17}Mn_{0.66}O_2$	86.1	2.0–4.2	20	15
$K_{0.5}MnO_2$	106	1.5–3.9	5	16
$K_{0.5}Mn_{0.72}Ni_{0.15}Co_{0.13}O_2$	82.9	1.5–4.0	10	17
$K_{0.5}[Mn_{0.85}Ni_{0.1}Co_{0.05}]O_2$	96	1.5–3.9	20	18

Table S7. Comparison of K^+ Diffusion Coefficients (D_{K^+}) obtained by GITT of Mn-based oxide cathode materials for PIBs.

Sample	D_{K^+} / $cm^2\ s^{-1}$	References
KCMMO	10^{-10} to 10^{-8}	This work
$K_{0.7}MnO_2$	10^{-14} to 10^{-10}	1
$K_{0.7}Mn_{0.7}Mg_{0.3}O_2$	10^{-12} to 10^{-10}	1
$K_{0.5}MnO_2$	10^{-14} to 10^{-13}	4
$K_{0.28}MnO_2{\cdot}0.15H_2O$	10^{-12} to 10^{-8}	6
$K_{0.28}MnO_2$	10^{-13} to 10^{-9}	6
$K_{0.45}Ni_{0.1}Co_{0.1}Mg_{0.05}Mn_{0.75}O_2$	10^{-14} to 10^{-13}	10
$K_{0.64}Na_{0.04}[Ni_{1/3}Mn_{2/3}]O_2$	10^{-12} to 10^{-10}	19

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