Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Insight into Lithium Transport in Lithium Nitridometallate Battery Materials from Muon Spin Relaxation

Andrew S. Powell†, Zltaka Stoeva†, James S. Lord‡, Ronald I. Smith‡, Duncan H. Gregory§* and Jeremy J. Titman†*

†*School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, UK*

‡*ISIS Facility, Rutherford Appleton Laboratory, Chilton, Oxfordshire OX11 0QX, UK*

§*WESTChem, School of Chemistry, University of Glasgow, Glasgow, G12 8QQ, UK*

Supplementary Information

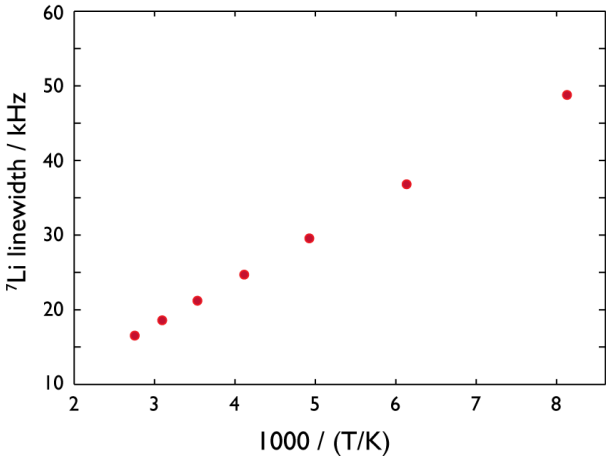

Figure S1. ^{7}Li NMR linewidth of $Li_{3-x-y}Co_xN$ with nominal x = 0.4 (**2**) as a function of temperature showing Curie-Weiss behaviour.

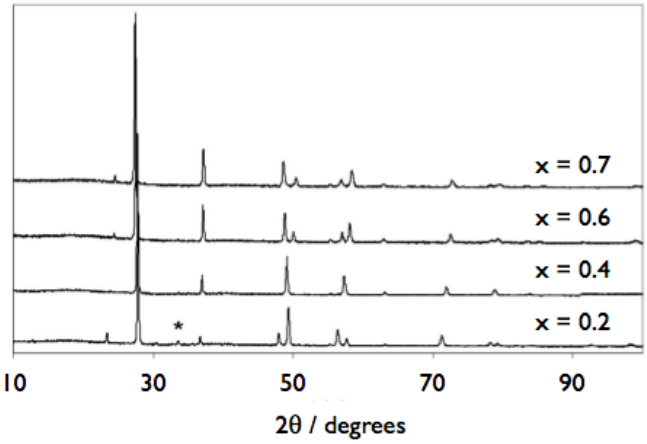

Figure S2. PXD patterns for the series $Li_{3-x-y}Co_xN$, as a function of nominal composition and including an additional sample with x = 0.7 which was not subsequently characterized by PND. The asterisk denotes a

reflection from a $LiNH_2$ impurity in the case of x=0.2. Note there are no reflections from Co metal in any of the PXD patterns.

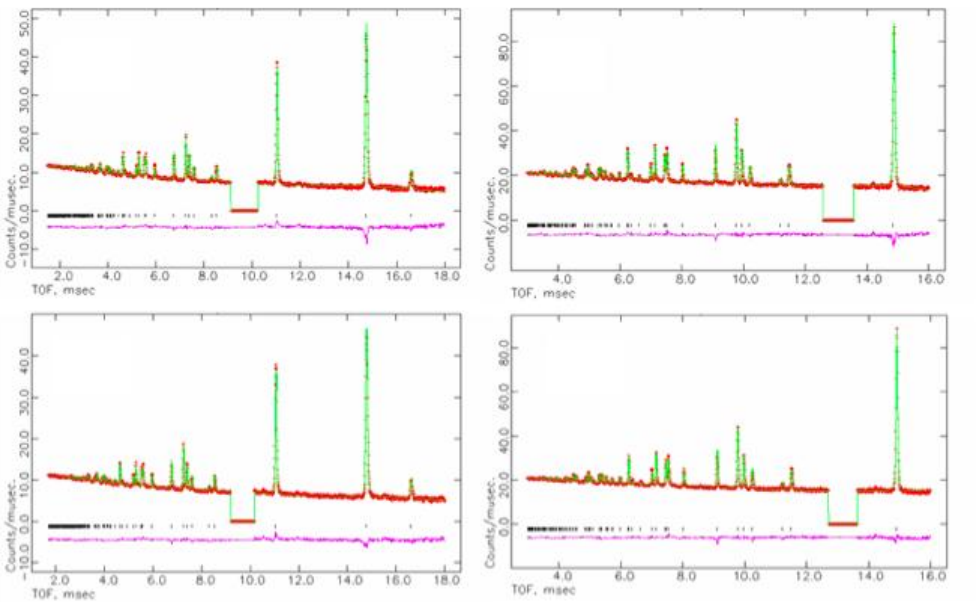

Figure S3. Profile plots for the Rietveld refinement against neutron diffraction data for a representative sample ($Li_{3-x-y}Co_xN$ with x = 0.58, **3**): top: 2K left: histogram 1, right: histogram 2, bottom: 250 K, left: histogram 1, right: histogram 2. (Red) crosses show observed data points, solid (green) lines represent the calculated diffraction patterns, and (black) tick marks represent the calculated positions of the reflections.

Sample, nominal composition,	**1**, x = 0.2	**2**, x = 0.4	**3**, x = 0.6
T / K	250		
(**Li**,**Co**) (0, 0, 0.5)			
Co occupancy	0.202(3)	0.428(2)	0.581(2)
$U_{11} = U_{22}$	0.037(2)	0.063(5)	0.003(1)
U_{33}	0.003(2)	0.013(8)	0.004(2)
U_{12}	0.019(9)	0.044(2)	0.0015(5)
Li 2×(0.3333, 0.6667, 0)			
Occupancy	0.980(8)	0.880(6)	0.782(7)
$U_{11} = U_{22}$	0.0079(6)	0.0153(6)	0.0185(8)
U_{33}	0.046(2)	0.098(2)	0.078(2)
U_{12}	0.0039(3)	0.0076(3)	0.0093(4)
N (0, 0, 0)			
Occupancy	1	1	1
$U_{11} = U_{22}$	0.0066(1)	0.0211(1)	0.0152(1)
U_{33}	0.0085(2)	0.0206(3)	0.0115(2)
U_{12}	0.00331(6)	0.01055(7)	0.00759(6)

Table S1. Refined atomic parameters obtained from PND for three $Li_{3-x-y}Co_xN$ materials.

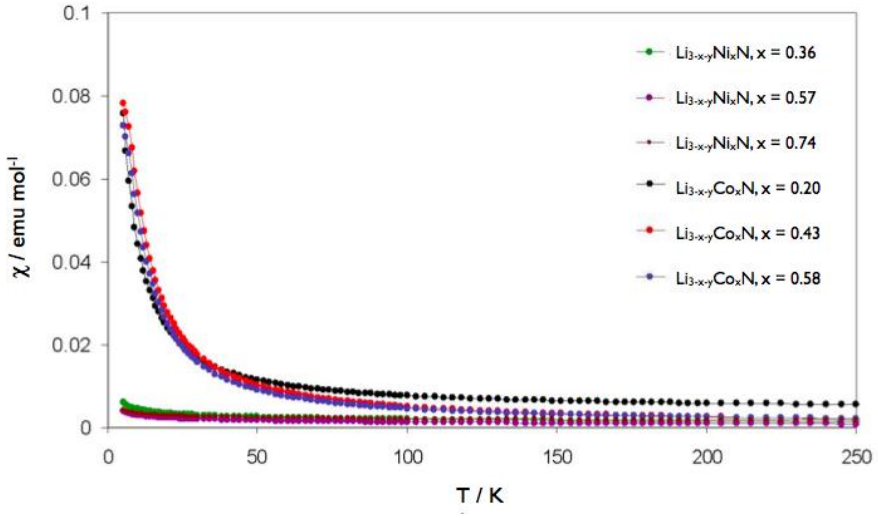

Figure S4. Temperature variation of the magnetic susceptibility of $Li_{3-x-y}Co_xN$ materials **1 – 3**, compared with data[13] for three representative members of the corresponding Ni-substituted series.

Calculated Values of the Kubo-Toyabe Depolarization Rate. Values of the depolarization rate can be calculated for a powder sample by summing over the dipolar interactions between the muon and each nuclear spin j in the surrounding crystal lattice according to:

$$\Delta^2 = \kappa I(I+1)\left(\frac{\mu_0}{4\pi}\right)^2 h^2\gamma_\mu^2\gamma_n^2\sum_j 1/r_j^6 \qquad (1)$$

where the pre-factor κ is 2/3 for the spin-1/2 case where the quadrupolar interaction is zero. For quadrupolar spins the nuclear moments precess about the electric field gradient (EFG) vector which, in materials of cubic symmetry, extends radially from the muon. Since the local field arises only from the projection onto the EFG axis, this overestimates the contribution to Δ from nuclei with I > 1/2. If the quadrupolar interaction dominates then κ is 4/9 for integer spins (^{14}N and ^{6}Li) and 8/15 and 92/189 for half-integer spins with I = 3/2 (^{7}Li) and 7/2 (^{59}Co) respectively.[i] Note that this treatment neglects the component of the EFG arising from the hexagonal $Li_{3-x-y}Co_xN$ structure which is oriented along the *c* axis. In addition, for small quadrupolar interactions the transverse components of the nuclear spin still contribute to some extent and the effect on Δ is therefore smaller. For the disordered Co-substituted materials, an average value is given in which each local muon environment was weighted according to the Li occupancies. No correlation was assumed between the positions of the Co atoms in the Li(1) plane and the Li(2) vacancies.

(i) Schenck, A. "Muon Spin Rotation Spectroscopy", Adam Hilger Ltd, Bristol, UK , 1984.