

Cite this: *J. Mater. Chem. A*, 2024, **12**, 11390Effects of sulfate modification of stoichiometric and lithium-rich LiNiO<sub>2</sub> cathode materials†Bo Dong,<sup>id</sup>\*<sup>ad</sup> Andrey D. Poletayev,<sup>id</sup><sup>bd</sup> Jonathon P. Cottom,<sup>id</sup><sup>bdgh</sup> Javier Castells-Gil,<sup>id</sup><sup>ad</sup> Ben F. Spencer,<sup>id</sup><sup>e</sup> Cheng Li,<sup>f</sup> Pengcheng Zhu,<sup>id</sup><sup>cd</sup> Yongxiu Chen,<sup>id</sup><sup>cd</sup> Jaime-Marie Price,<sup>id</sup><sup>ad</sup> Laura L. Driscoll,<sup>ad</sup> Phoebe K. Allan,<sup>id</sup><sup>ad</sup> Emma Kendrick,<sup>id</sup><sup>cd</sup> M. Saiful Islam<sup>id</sup>\*<sup>bdg</sup> and Peter R. Slater<sup>id</sup>\*<sup>ad</sup>

Lithium nickel oxide, LiNiO<sub>2</sub>, has attracted considerable interest as a high energy cathode for next generation lithium-ion batteries. Nevertheless, shortcomings such as significant cycling capacity decay and low stability in ambient atmosphere have hindered its practical application, and consequently most work has focused on the more stable Mn and Co doped analogues Li(Ni,Mn,Co)O<sub>2</sub>. Here, we report an investigation of an alternative strategy, sulfate modification, in the LiNiO<sub>2</sub> system. We show that improved performance can be achieved, attributed to the dual effect of a low level of bulk doping and the presence of a self-passivation Li<sub>2</sub>SO<sub>4</sub> layer formed beyond the solid solution limit. *Ab initio* simulations suggest that the behavior is similar to that of other high valent dopants such as W and Mo. These dual effects contribute to the improved air stability and enhanced electrochemical performance for the sulfate modified lithium-rich LiNiO<sub>2</sub>, leading to high initial capacities (~245 mA h g<sup>-1</sup> at 25 mA g<sup>-1</sup>, and ~205 mA h g<sup>-1</sup> at 100 mA g<sup>-1</sup>) and better capacity retention. Overall, the results show that polyanion modification represents an excellent alternative low-cost strategy to improve the performance of lithium nickel oxide cathode materials.

Received 12th January 2024  
Accepted 3rd April 2024

DOI: 10.1039/d4ta00284a

rsc.li/materials-a

## 1. Introduction

Lithium-ion batteries (LIBs) dominate the energy storage market for portable electronics and electrical vehicles (EVs) due to their high energy densities.<sup>1–4</sup> Ni-rich lithium transition metal oxides, such as LiNi<sub>x</sub>Co<sub>y</sub>Al<sub>1–x–y</sub>O<sub>2</sub> (NCA) and LiNi<sub>x</sub>Mn<sub>y</sub>Co<sub>1–x–y</sub>O<sub>2</sub> (NMC) have attracted great interest and are extensively applied in the field.<sup>5–7</sup> However, the high and volatile cost of Co hinders their long-term sustainability and motivates research into higher Ni content, lower Co content NMC

(NMC811, LiNi<sub>0.8</sub>Mn<sub>0.1</sub>Co<sub>0.1</sub>O<sub>2</sub>) materials. Ultimately a key aim is to eliminate Co to give LiNiO<sub>2</sub> (LNO), which is considered as the promising next generation cathode due to its high theoretical capacity of ~270 mA h g<sup>-1</sup> and high average voltage of 3.8 V vs. Li metal.<sup>8,9</sup>

However, the intrinsic problems with this stoichiometric LNO phase, such as moisture instability at ambient atmosphere, detrimental phase transitions and particle cracking at high states of charge remain unresolved.<sup>10,11</sup> During delithiation, several phase transitions of Li<sub>1–x</sub>NiO<sub>2</sub> occur during the charging process, which includes hexagonal (H1, 0 ≤ x ≤ 0.25) to monoclinic (M, 0.25 ≤ x ≤ 0.55), monoclinic (M) to hexagonal (H2, 0.55 ≤ x ≤ 0.75), and hexagonal (H2) to hexagonal (H3, 0.75 ≤ x ≤ 1).<sup>12–15</sup> In particular, the H2–H3 phase transition of Li<sub>1–x</sub>NiO<sub>2</sub> above 4.1 V triggers the shrinkage of the unit cell and large volume change due to the large difference of *c* parameters of H2 (*c* = 14.404(1) Å) and H3 (*c* = 13.363(6) Å) phases.<sup>16,17</sup> The resulting microcracks of active cathode material leads to further side reactions of cathode and electrolyte, which accelerates the capacity fade of LiNiO<sub>2</sub>.<sup>18</sup> To mitigate these issues, most attempts have focused on dopant incorporation and surface modification to stabilise the material.<sup>19–22</sup>

It has been demonstrated that Ti or Zr doped LiNiO<sub>2</sub> have limited solid solution ranges, with a small amount of dopant incorporation into the bulk structure and with the remaining dopant forming surface layers (such as Li<sub>2</sub>TiO<sub>3</sub> and Li<sub>2</sub>ZrO<sub>3</sub>) on

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† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d4ta00284a>



the  $\text{LiNiO}_2$  particles.<sup>23,24</sup> In other work, Al or Mg doping of  $\text{LiNiO}_2$  was found to dramatically reduce the amount of residual surface lithium carbonate in ambient atmosphere owing to strong  $\text{TM}(\text{Al}/\text{Mg})\text{-O}$  bonding, which inhibits the reaction between water/carbon dioxide and  $\text{LiNiO}_2$ .<sup>25–27</sup> High-valence dopants, such as W and Mo, have also been examined in  $\text{LiNiO}_2$ .<sup>28–32</sup> *In situ* XRD results have indicated that W doped  $\text{LiNiO}_2$  modified the H2–H3 phase transition into a more gradual solid solution reaction during cycling, and the resulting enhancement of cycling stability was attributed to an alleviation of the structural stress and abrupt lattice changes.<sup>28</sup>

All these previous studies have involved doping with cations of similar octahedral size to Ni. As an alternative to such cation incorporation, polyanion doping is a less widely used strategy in altering the structural, chemical or physical properties of inorganic materials. This methodology has attracted much interest in perovskite oxide electrodes for solid oxide fuel cells, where results illustrate that transition-metal octahedra  $\text{TMO}_6$  can be replaced with tetrahedral  $\text{MO}_4$  ( $M = \text{Si}, \text{S}, \text{P}$ ) or trigonal planar  $\text{MO}_3$  ( $C, B$ ) to create materials with improved properties.<sup>33–41</sup>

In this work, we examine the effect of sulfate modification in  $\text{LiNiO}_2$  and Li-rich  $\text{LiNiO}_2$ , and the corresponding effect on the structural and electrochemical properties using a combined experimental and modelling approach. The formation of Li-rich phases with Ni-rich compositions has been challenging so far, producing poorly ordered materials. The aim of polyanion doping was also to introduce tetrahedral ions with higher charge and oxygen vacancies in order to help to stabilise a Li-rich phase that is otherwise challenging to isolate.<sup>42</sup> Our results show enhanced electrochemical performance on sulfate incorporation compared to undoped materials prepared under comparable conditions.

## 2. Results and discussion

### 2.1 Phase formation and crystal structures

**2.1.1 X-ray/neutron diffraction and spectroscopy.** We first investigated the incorporation of the polyanion dopant,  $\text{SO}_4^{2-}$ , in Li-stoichiometric  $\text{LiNiO}_2$  (LNO).  $\text{LiNiO}_2$  and sulfate doped  $\text{LiNi}_{1-x}\text{S}_x\text{O}_{2-\delta}$ , were initially made *via* the conventional solid state route at 700–725 °C/12 h in  $\text{O}_2$ . As shown in Fig. 1, the XRD patterns of sulfate doped  $\text{LiNiO}_2$  show a single layered phase for  $x = 0.025$ . As shown in Table 1, the cell volume of sulfate doped  $\text{LiNiO}_2$  increased compared to that of the undoped sample, which is consistent with the suggested partial reduction in line with prior work on sulfate doped perovskite systems. The intensity ratio  $I_{003}/I_{104}$  between the (003) and (104) reflections has been intensively used in LNO as an indicator of the Li/Ni antisites defect: the higher the  $I_{003}/I_{104}$  ratio, indicates a more perfect layered  $\text{LiNiO}_2$  structure without anti-site disorder. Sulfate doped samples indeed show an increase in the  $I_{003}/I_{104}$  ratio (Table 2), which suggests improved structural ordering in the material.

Following these initial results and given that the doping was expected to lower the anion content (total anion charge), and the dopant (normally  $\text{S}^{6+}$ ) has a higher charge than Ni, the possible stabilisation of higher Li content/lower Ni content phases was investigated. Sulfate doped Li-rich  $\text{LiNiO}_2$  (S-LRNO)



Fig. 1 XRD patterns of  $\text{LiNiO}_2$  and S doped  $\text{LiNiO}_2$  (solid state synthesis route).

Table 1 Cell parameters of polyanion doped  $\text{LiNiO}_2$

Composition	$a = b$ (Å)	$c$ (Å)	$V$ (Å <sup>3</sup> )
$\text{LiNiO}_2$	2.8814(1)	14.2079(1)	102.16(2)
$\text{LiNi}_{0.975}\text{S}_{0.025}\text{O}_{2-x}$	2.8817(1)	14.2155(1)	102.23(2)

Table 2  $I_{003}/I_{104}$  of polyanion doped  $\text{LiNiO}_2$

Composition	$I_{003}/I_{104}$
$\text{LiNiO}_2$	1.569
$\text{LiNi}_{0.975}\text{S}_{0.025}\text{O}_{2-x}$	2.834

were made under similar conditions used for LNO to increase the capacity. As shown in Fig. 2a (XRD data), the S-free control  $\text{Li}_{1.1}\text{Ni}_{0.85}\text{O}_2$  shows a majority layered phase with unknown impurity peaks at lower two theta angles. In contrast, when adding a small amount of sulfate,  $\text{Li}_{1.1}\text{Ni}_{0.875}\text{S}_{0.025}\text{O}_{2-\delta}$  shows a single-phase sample, indicating the benefits of sulfate in stabilising the phase formation. A small amount of  $\text{Li}_2\text{SO}_4$  impurity was detected with increasing sulfate content ( $\text{Li}_{1.1}\text{Ni}_{0.85}\text{S}_{0.05}\text{O}_{2-\delta}$ ), suggesting only a low-level incorporation of sulfate in the Li-rich  $\text{LiNiO}_2$  system. The presence of a small amount of bulk sulfate and a surface  $\text{Li}_2\text{SO}_4$  layer for this sample is supported by the XPS/HAXPES data (see later).

Structural refinement of  $\text{Li}_{1.1}\text{Ni}_{0.85}\text{S}_{0.05}\text{O}_{2-\delta}$  using neutron diffraction data was performed, with the profile fits shown in Fig. 2b. Weight fractions of  $\text{Li}_2\text{SO}_4$ ,  $\text{Li}_2\text{CO}_3$  and  $\text{Li}_{1.1}\text{Ni}_{0.85}\text{S}_{0.05}\text{O}_{2-\delta}$  were refined to give 95.9% S-LRNO, 2.0%  $\text{Li}_2\text{SO}_4$  and 2.1%  $\text{Li}_2\text{CO}_3$ , which is consistent to XRD results. 0.03 S was then added to the Li2/Ni2 site (Ni layer), and constraints of the same  $U_{\text{iso}}$  and full occupancy were made for Li1/Ni1; and Li2/Ni2/S1. The atomic position of O1 was refined followed by  $U_{\text{isos}}$  of all atoms which were fixed after convergence. The occupancies of Li1/Ni1, Li2/Ni2 (to give the occupancy of S1) and O1 were refined. A final refinement of the  $U_{\text{iso}}$  of all atoms showed only a small change





Fig. 2 (a) XRD patterns of  $\text{Li}_{1.1}\text{Ni}_{0.85}\text{O}_2$ ,  $\text{Li}_{1.1}\text{Ni}_{0.875}\text{S}_{0.025}\text{O}_{2-x}$  and  $\text{Li}_{1.1}\text{Ni}_{0.85}\text{S}_{0.05}\text{O}_{2-x}$  (solid state synthesis route). (b) Observed, calculated and difference profiles from structural refinement of  $\text{Li}_{1.1}\text{Ni}_{0.85}\text{S}_{0.05}\text{O}_{2-x}$  using neutron diffraction data (c) XAS data of  $\text{Li}_{1.1}\text{Ni}_{0.85}\text{S}_{0.05}\text{O}_{2-x}$ .

and the final parameters are shown in Table 3. From these data, the refined composition was determined to be  $\text{Li}_{1.047(3)}\text{Ni}_{0.922(3)}\text{S}_{0.031}\text{O}_{1.98(2)}$ , consistent with the formation of a higher Li content/lower Ni content phase.

In support of sulfate doping, the Ni K-edge XAS also indicates a small shift for the sulfate doped sample, where the normalised absorption of S-LRNO is shifted to lower energy compared to that of  $\text{LiNiO}_2$  (Fig. 2c). The slight shift of the Ni K-

Table 3 Structural parameters of  $\text{Li}_{1.1}\text{Ni}_{0.85}\text{S}_{0.05}\text{O}_{2-x}$  from Rietveld refinement using neutron diffraction data<sup>a</sup>

Atom	x	y	z	Mult.	Occupancy	$U_{\text{iso}}$ ( $\text{\AA}^2$ )
Li1	0	0	0	3	0.978(2)	0.016
Ni1	0	0	0	3	0.022(2)	0.016
S1	0	0	0.5	3	0.031	0.002
Li2	0	0	0.5	3	0.069(1)	0.002
Ni2	0	0	0.5	3	0.900(1)	0.002
O1	0	0	0.242(1)	6	0.992(4)	0.011

<sup>a</sup> Space group:  $R\bar{3}m$ ,  $a = b = 2.8777(1)$   $\text{\AA}$ ,  $c = 14.1938(1)$   $\text{\AA}$ ,  $V = 101.79(1)$   $\text{\AA}^3$ .

edge for S-LRNO suggests the partial reduction of  $\text{Ni}^{3+}$  in the bulk material. In order to evaluate the surface states, XPS data were collected. Here, the Ni 2p spectrum (Fig. S1†) is dominated by the spin-orbit doublet characterized by binding energies of the Ni 2p<sub>3/2</sub> and Ni 2p<sub>1/2</sub> core levels of 855.2 and 872.6 eV, respectively. The spectra also show broad satellites at 862.7 and 879.2 eV. All of these binding energy values are representative of the nickel environments in  $\text{LiNiO}_2$ .<sup>43,44</sup>

HAXPES and XPS spectra were collected to investigate the presence of S dopant in the bulk and on the surface of S-LRNO, respectively. XPS and HAXPES spectra of S 2p of S-LRNO are shown in Fig. 3a and b. The S 2p signal is a spin-orbit doublet and each chemical state consists of two peaks. The S 2p (XPS) can be fitted with two components at  $\sim 169.2$  eV and  $\sim 170.5$  eV, corresponding to a metal sulfate, here attributed to  $\text{Li}_2\text{SO}_4$ .<sup>45</sup> The HAXPES did not show the S 2p response but the signal from S 1s was detected. Two components at  $\sim 2477.9$  eV and  $\sim 2480.0$  eV can be used to fit S 1s spectra. However, since 1s core levels are singlet states, the two peaks in the S 1s peak suggest more than one chemical state, which may be related to sulfate in a different environment to surface  $\text{Li}_2\text{SO}_4$  (*i.e.* bulk incorporation).

The recorded O 1s spectra from XPS and HAXPES are shown in Fig. 3c and d. The O 1s spectra (XPS) are fitted to two oxygen contributions at  $\sim 528.9$  eV and  $\sim 531.8$  eV, and the O 1s spectra (HAXPES) are fitted to three components at  $\sim 528.4$  eV,  $\sim 531.4$  eV and  $\sim 533.9$  eV. The components at  $\sim 528$  eV and  $\sim 531$  eV are assigned to metal-oxygen bonds and carbonate groups, respectively.<sup>46,47</sup> The O 1s contribution above  $\sim 533$  eV can be assigned to either water or sulfate bonds (both are located in this region).<sup>48</sup> Previous studies of sulfate incorporation into perovskite oxides have indicated associated oxygen vacancies are introduced.<sup>33</sup> The refinement of the structure for S-LRNO, however, reveals only a very small amount of oxygen vacancies in this case. Computational modelling (below) also suggests that generating oxygen vacancies within the layered structure is a high-energy, *i.e.*, unfavorable process. Hence, given that the amount of oxygen vacancies appears to be very low, their presence is difficult to detect by either XPS or HAXPES.

The chemical stability in ambient atmosphere of polyanion modified LNO was examined by exposing both undoped and





Fig. 3 XPS and HAXPES spectra of S-LRNO (solid state route). (a) XPS spectra of S 2p, (b) HAXPES spectra of S 1s, (c) XPS spectra of O 1s, and (d) HAXPES spectra of O 1s.



Fig. 4 XRD patterns of (a)  $\text{LiNiO}_2$  and (b)  $\text{Li}_{1.1}\text{Ni}_{0.85}\text{S}_{0.05}\text{O}_{2-\delta}$  (solid state route) after the exposure in air after 1, 15 and 30 days.

sulfate doped samples to air. The XRD results, as shown in Fig. 4a, shows a clear degradation in the undoped LNO sample with the detection of additional peaks at  $\sim 36$  and  $\sim 44^\circ$  after exposing to air for 2 weeks (zoomed-in region is shown in Fig. S2<sup>†</sup>). In contrast, sulfate modified LRNO showed no change under the same conditions (Fig. 4b), illustrating the improved stability in ambient atmosphere of this phase.

**2.1.2 Atomic-scale insights from *ab initio* simulations.** The defect chemistry of incorporation of S and excess Li into  $\text{LiNiO}_2$  was further investigated by DFT simulations. To form Li-rich  $\text{LiNiO}_2$ , the excess Li is accommodated on the Ni site. Within the disproportionated structure of LNO,<sup>49</sup> the  $\text{Li}_{\text{Ni}}$  defect carries minimal structural distortions *versus* a high-spin Ni (octahedral volume  $11.2 \text{ \AA}^3$  vs.  $10.9 \text{ \AA}^3$ ) and induces a rearrangement of Ni spins around itself that is consistent with having one extra electron relative to a high-spin (formally “2+”) Ni. This is in contrast with the common expectation of a double negative effective charge relative to a spin-half (formally “3+”) nickel. A single negative charge on an excess Li on Ni ( $\text{Li}_{\text{Ni}}$ ) relative to the lattice is consistent regardless of which site (high-spin, half-spin, or zero-spin) is substituted with Li to initialize the calculation in the spin-disproportionated structure. To maintain charge neutrality upon the inclusion of a  $\text{Li}_{\text{Ni}}$  defect, the compensating hole is accommodated as a hole polaron.<sup>49</sup>

At the conditions of synthesis ( $700^\circ\text{C}$ ,  $1 \text{ atm O}_2$ ) where layered LNO is in equilibrium with disordered rocksalt from which it is synthesized, the lowest-energy incorporation of



**Table 4** Computed incorporation energies for select intrinsic defects in spin-disproportionated LiNiO<sub>2</sub> at synthesis conditions (700 °C, 1 atm O<sub>2</sub>)

Defect	Incorporation energy (eV)	Compensation
Li <sub>Ni</sub>	0.30	h <sub>Ni</sub>
V <sub>O</sub>	1.40	e <sub>Ni</sub>
Ni <sub>Li</sub> <sup>49</sup>	-0.12	e <sub>Ni</sub>

dilute Li<sub>Ni</sub> defects into the disproportionated structure is 0.30 eV (Table 4), which decreases with the supplied Li excess (increase in  $\mu_{\text{Li}}$ ).<sup>42,50</sup> The logical limit of such excess Li incorporation is Li<sub>2</sub>NiO<sub>3</sub>, where Li<sub>Ni</sub> defects fully substitute one of three Ni sub-lattices, and all remaining Ni atoms have zero spin and are formally in a “4+” charge state. However, experimental attempts have only approached this limit with substantial Ni disorder and reduction;<sup>26</sup> layered Li<sub>2</sub>NiO<sub>3</sub> has to our knowledge not been synthesized.

Turning to sulfate doping, the predicted lowest-energy site for the bulk incorporation of dilute S is S<sub>Ni</sub> at 2.92 eV during synthesis (Table 5). The dopant S<sub>Ni</sub> is surrounded and compensated by additional high-spin nickels, which approximate Ni<sup>2+</sup>. Such compensation additionally relieves the mechanical stress created by extremely short S–O bonds ( $\approx 1.69$  Å) of the S<sub>Ni</sub> by surrounding it with enlarged Ni octahedra. We find it further instructive to compare the energetics of incorporation of sulfur with other common high-valence dopants such as W and Mo, which are known to phase-separate at interfaces and grain boundaries.<sup>31,32</sup> The incorporation energies for Mo<sub>Ni</sub> and W<sub>Ni</sub> are both under 1 eV, and the dopant–oxygen bond lengths are much closer to those of the parent nickel octahedra at 1.93 Å.

The association of S<sub>Ni</sub> with oxygen vacancies (formation energy 1.40 eV on their own) is not favorable: the loss of coordination by the surrounding nickel offsets the favorability of approaching tetrahedral S, with an association energy of 0.85 eV (Table 6). This contrasts with polyanion doping of perovskites, where each oxygen anion is two-coordinate, and fewer metal–oxygen bonds are broken to accommodate the sulphur. The association of excess Li<sub>Ni</sub> with S<sub>Ni</sub> is only favorable by 20 meV (Table 6); such an effect does not translate to finite temperatures when the octahedra are dynamically disordered. Surface

**Table 6** Computed association energies for defect complexes in spin-disproportionated LiNiO<sub>2</sub> at synthesis conditions (700 °C, 1 atm O<sub>2</sub>). Negative is favorable, for consistency with Tables 4 and 5

Complex	Association energy (eV)
Li–Ni exchange	-0.05
S <sub>Ni</sub> + Li <sub>Ni</sub>	-0.02
S <sub>Ni</sub> + Ni <sub>Li</sub>	0.20
S <sub>Ni</sub> + Li–Ni exchange	0.23
S <sub>Ni</sub> + V <sub>O</sub>	0.85

**Fig. 5** (a) Initial charge–discharge curves of LNO and S-LRNO synthesised by the solid state method between 2 and 4.3 V at 25 mA g<sup>-1</sup> (after the formation cycle). (b) The cycling performance of LNO and S-LRNO at 25 mA g<sup>-1</sup>.**Table 5** Computed incorporation energies for select high-valence dopants in spin-disproportionated LiNiO<sub>2</sub> at synthesis conditions (700 °C, 1 atm O<sub>2</sub>). Bond lengths are cited for dopant–oxygen bonds

Dopant	Incorporation energy (eV)	Chemical potential (eV)	Reference phase	Bond length (Å)
Mo <sub>Ni</sub>	0.84	-6.29	Li <sub>4</sub> MoO <sub>5</sub> (ref. 31)	1.93
W <sub>Ni</sub>	0.91	-7.16	Li <sub>4</sub> WO <sub>5</sub>	1.93
S <sub>Ni</sub>	2.92	-4.52	Li <sub>2</sub> SO <sub>4</sub>	1.69
S <sub>Ni(104)</sub>	6.93	-4.52	Li <sub>2</sub> SO <sub>4</sub>	1.59
S <sub>Ni(012)</sub>	4.57	-4.52	Li <sub>2</sub> SO <sub>4</sub>	1.57
S <sub>Ni(100)</sub>	4.56	-4.52	Li <sub>2</sub> SO <sub>4</sub>	1.59
S <sub>Ni(110)</sub>	4.96	-4.52	Li <sub>2</sub> SO <sub>4</sub>	1.57



incorporation at Ni sites has similarly unfavorable energetics (Table 5), although the figures are approximate due to the multitude of possibilities for compensation *via* polarons, O, and Li.

However, since  $\text{Li}_2\text{SO}_4$  forms a eutectic with  $\text{Li}_2\text{CO}_3$ ,<sup>51</sup> its addition can facilitate lithiation and crystallisation during the solid state synthesis of LNO at the experimental temperatures used here, which are below the melting point of  $\text{Li}_2\text{CO}_3$ . This positive effect is demonstrated by a small decrease in the full width at half maximum of XRD peaks in the sulfate modified sample prepared using the solid state route, as shown in Fig. S3.†

## 2.2 Electrochemical performance

**2.2.1 Solid state method.** The electrochemical properties of solid state reaction prepared  $\text{Li}_{1.1}\text{Ni}_{0.85}\text{S}_{0.05}\text{O}_{2-x}$  (S-LRNO) and  $\text{LiNiO}_2$  (LNO) were evaluated in the voltage range of 2.0–4.3 V. Fig. 5a shows the initial galvanostatic charge/discharge curves (after the formation cycle) as a function of capacity at  $25 \text{ mA g}^{-1}$  current density (charge rate  $\approx C/10$ ). The initial discharge capacities of S-LRNO increased to  $203 \text{ mA h g}^{-1}$  compared to  $176 \text{ mA h g}^{-1}$  for LNO. The formation cycle (Fig. S4 and S5)† at

$25 \text{ mA g}^{-1}$  indicates 11.5% and 7.8% capacity loss for LNO and S-LRNO respectively. The H2–H3 two-phase plateau is more prevalent in the S-LRNO sample compared to that of LNO. S-LRNO showed a higher voltage on both charging and discharging processes, leading to a higher energy density than that of LNO. Slightly reduced hysteresis and improved lower-voltage plateau were also observed for S-LRNO, demonstrating the benefits of sulfate modification. The cycling performance of selected cells was further evaluated at  $25 \text{ mA g}^{-1}$  for 100 cycles (Fig. 5b). After 100 cycles, the discharge capacities of  $\text{Li}_{1.1}\text{Ni}_{0.85}\text{S}_{0.05}\text{O}_{2-x}$  were  $\sim 170 \text{ mA h g}^{-1}$  compared to  $130 \text{ mA h g}^{-1}$  for LNO, illustrating the improved capacity retention (83.7% for S-LRNO and 73.8% for LNO) for the sulfate modified system.

To confirm the importance of sulfate incorporation in addition to surface coating, a separate experiment to introduce  $\text{Li}_2\text{SO}_4$  as a coating was examined. Here the  $\text{Li}_{1.1}\text{Ni}_{0.85}\text{O}_2$  was ball milled (500 rpm/1 h) with 5%  $\text{Li}_2\text{SO}_4$  which is the equivalent sulfate content in the structure (sample named as coated-LRNO), and reheated at  $700 \text{ }^\circ\text{C}/12 \text{ h}$  in  $\text{O}_2$ . As shown in Fig. 6a, the XRD pattern of ball milled  $\text{Li}_{1.1}\text{Ni}_{0.85}\text{O}_2$  (with  $\text{Li}_2\text{SO}_4$ ) showed a layered phase with  $\text{Li}_2\text{SO}_4$  impurity and a few unknown peaks. The electrochemical performance of



Fig. 6 (a) XRD patterns of  $\text{Li}_{1.1}\text{Ni}_{0.85}\text{O}_{2-x}$  and  $\text{Li}_2\text{SO}_4$  ball milled  $\text{Li}_{1.1}\text{Ni}_{0.85}\text{O}_{2-x}$ . (b) Charge–discharge curves of solid state route synthesised LRNO, S-LRNO and LRNO with 5% $\text{Li}_2\text{SO}_4$  between 2 and 4.3 V at  $25 \text{ mA g}^{-1}$  (after the formation cycle).



Fig. 7 (a) Initial charge–discharge curves LNO and S-LRNO synthesised by the co-precipitation route between 2 and 4.3 V at  $25 \text{ mA g}^{-1}$  (after the formation cycle). (b) The cycling performance of LNO and S-LRNO at  $100 \text{ mA g}^{-1}$ .



$\text{Li}_{1.1}\text{Ni}_{0.85}\text{O}_2$  (LRNO) and the 5%  $\text{Li}_2\text{SO}_4$  coated  $\text{Li}_{1.1}\text{Ni}_{0.85}\text{O}_2$  (coated-LRNO) was examined using the same conditions to that of S-LRNO. As shown in Fig. 6b, both LRNO and coated-LRNO showed poorer performance compared to that of S-LRNO, indicating the sulfate incorporation assisted with the formation of the lithium-excess phase. In addition, while the discharge capacities of coated-LRNO improved a little compared to LRNO, the values are much lower than S-LRNO (Fig. 6b and S6†), which further supports the successful sulfate incorporation in the original sample. The improved electrochemical performance could result from both the limited sulfate dopant in the structure and the  $\text{Li}_2\text{SO}_4$  passivating layers which is spontaneously formed beyond the solid solution limitation, in addition to the  $\text{Li}_2\text{SO}_4$ - $\text{Li}_2\text{CO}_3$  eutectic effects facilitating high lithiation and crystallization in the solid state synthesis (as mentioned in the modelling section).

**2.2.2 Co-precipitation method.** Following promising results from solid state synthesis, a co-precipitation route, which is the preferred industrial route, was further investigated to enhance the performance, as illustrated previously for undoped stoichiometric  $\text{LiNiO}_2$ .<sup>20</sup> The LNO prepared using the co-precipitation route exhibited a (003/104) ratio of 1.679 which is higher than that of the sample prepared using the solid state route, demonstrating a more ordered structure. For both LNO and S-LRNO samples, the use of a co-precipitation route was

shown to improve the electrochemical performance under cycling between 2.0 V and 4.3 V at  $25 \text{ mA g}^{-1}$  (Fig. 7a). The discharge capacity of S-LRNO increases to  $\sim 245 \text{ mA h g}^{-1}$  compared to  $\sim 223 \text{ mA h g}^{-1}$  for LNO, with the former value representing an excellent initial capacity significantly exceeding traditional Mn and Co doped systems,  $\text{Li}(\text{Ni},\text{Mn},\text{Co})\text{O}_2$ . A higher average voltage with similar voltage hysteresis was seen for S-LRNO during intercalation above 3.5 V, and a slightly increased hysteresis was seen at lower voltage for S-LRNO. The cycling performance of selected cells was also conducted at  $100 \text{ mA g}^{-1}$  (charge rate  $\approx C/2$ , initial discharge capacity  $\sim 205 \text{ mA h g}^{-1}$ ), which was chosen to represent a commercially relevant rate. The results showed that the discharge capacity of S-LRNO after 100 cycles remained  $\sim 171 \text{ mA h g}^{-1}$  (Fig. 7b). Although a first cycle loss of  $\sim 12.3\%$  in S-LRNO at  $100 \text{ mA g}^{-1}$  was observed (Fig. S7 and S8†), 83.4% capacity retention was achieved which is higher than 80.5% for LNO over 100 cycles.

Rate capabilities of co-precipitated LNO and S-LRNO were then tested in the voltage range of 2.0–4.3 V at current densities of 25, 50, 100, 200, 400 and  $25 \text{ mA g}^{-1}$  for 5 cycles (Fig. 8a). The discharge capacities of co-precipitated S-LRNO and LNO reached 230 and  $209 \text{ mA h g}^{-1}$  at  $25 \text{ mA g}^{-1}$ , 207 and  $176 \text{ mA h g}^{-1}$  at  $50 \text{ mA g}^{-1}$ , 192 and  $165 \text{ mA h g}^{-1}$  at  $100 \text{ mA g}^{-1}$ , 176 and  $145 \text{ mA h g}^{-1}$  at  $200 \text{ mA g}^{-1}$ , 161 and  $117 \text{ mA h g}^{-1}$  at  $400 \text{ mA g}^{-1}$  respectively. The S-LRNO sample exhibits higher



Fig. 8 (a) The cycling performance of LNO and S-LRNO prepared using co-precipitation route at different rates. (b) EIS of LNO and S-LRNO prepared using co-precipitation route at the 1st cycle. (c) GITT of LNO and S-LRNO prepared using co-precipitation route on charging at the initial cycle (after formation cycles).



Table 7 EIS fitting parameters for LNO and S-LRNO

Parameter	LNO	S-LRNO
$R_i$ ( $\Omega$ )	1.5	1.4
$R_{CT}$ ( $\Omega$ )	160	119

discharge capacities than those of the pristine LNO at all cycling rates, illustrating the improved rate capability of the sulfate modified sample.

Electrochemical impedance spectroscopy analysis for both samples are shown in Fig. 8b. The smaller semicircle was seen in S-LRNO than that of LNO, indicating a smaller internal resistance. By fitting the Nyquist plots with the equivalent circuit, the S-LRNO shows a charge transfer resistance of 119  $\Omega$  which is lower than 160  $\Omega$  in LNO (Table 7). To investigate the influence of sulfate modification on the kinetic behavior of  $\text{Li}^+$ , GITT (galvanostatic intermittent titration technique) was carried out to determine the apparent diffusion capability of  $\text{Li}^+$  in the initial cycle (after formation cycles). The  $D_{\text{Li}}$  calculated from the GITT curve as a function of the state of charge during charging are shown in Fig. 8c, where the measured solid-state diffusion coefficient is mainly in the range of  $10^{-12}$  to  $10^{-11}$ . The sulfate doped sample exhibits an increased  $D_{\text{Li}}$  value compared to LNO, indicating faster kinetics for Li ion in the doped sample. Although the SEM analyses of LNO and S-LRNO

prepared using the co-precipitation route revealed comparable morphology of particles (Fig. 9), the observed enhancements in rate capability and lithium transport kinetics in S-LRNO could be attributed to the excess lithium ions in the structure; this feature helps to promote the formation of face-sharing or edge-sharing lithium octahedra, leading to reduced lithium ion hopping distance and lower activation energy.

The structural transitions during the cycling of doped and undoped LRNO prepared using co-precipitation routes was evaluated using  $dQ/dV$  curves, as shown in Fig. 10; H1–M, M–H2, and H2–H3 phase transitions were observed for both materials, which is consistent with literature.<sup>11</sup> In contrast to the quickly decaying H2–H3 phase transition in undoped LNO, this transition has been preserved after long-term cycling for sulfate doped samples, as shown in Fig. 9d. This result suggests that structural changes during the cycling for the sulfate modified phase are more reversible, which most likely accounts for the improved long-term capacity. In this respect, it has been reported that high valence dopants, such as  $\text{Mo}^{6+}$  and  $\text{W}^{6+}$ , in  $\text{LiNiO}_2$ , could facilitate the merging of the Li-rich and Li-poor phases into a single phase during the H2–H3 phase transition, resulting in better structural stability.<sup>28,31</sup> Other studies have shown that high valence dopants help to suppress primary particle growth during synthesis and impart mechanical toughness to counteract the high internal strain.<sup>32,52</sup> The introduction of excess  $\text{Zr}^{4+}$



Fig. 9 SEM images of samples at 50 000 $\times$  magnification (a) LNO prepared by solid state route (b) S-LRNO prepared by solid state route (c) LNO prepared by co-precipitation route (d) S-LRNO prepared by co-precipitation route.





Fig. 10  $dQ/dV$  curves of (a)  $\text{LiNiO}_2$  and (b)  $\text{Li}_{1.1}\text{Ni}_{0.85}\text{S}_{0.05}\text{O}_{2-x}$  prepared through co-precipitation route; (c) comparison of  $\text{LiNiO}_2$  and  $\text{Li}_{1.1}\text{Ni}_{0.85}\text{S}_{0.05}\text{O}_{2-x}$  at 1st cycle. (d) Comparison of  $\text{LiNiO}_2$  and  $\text{Li}_{1.1}\text{Ni}_{0.85}\text{S}_{0.05}\text{O}_{2-x}$  at 75th cycle showing the clear preservation of H2–H3 transition in the latter.



Fig. 11 SEM images of (a) pristine  $\text{LiNiO}_2$ ; (b) pristine  $\text{Li}_{1.1}\text{Ni}_{0.85}\text{S}_{0.05}\text{O}_{2-x}$  (c)  $\text{LiNiO}_2$  after 200 cycles. (d)  $\text{Li}_{1.1}\text{Ni}_{0.85}\text{S}_{0.05}\text{O}_{2-x}$  after 200 cycles.



into the LiNiO<sub>2</sub> cathode was shown to result in simultaneous doping and coating with Li<sub>2</sub>ZrO<sub>3</sub>, enhancing the phase transition and thermal stability,<sup>23</sup> similar to what we observe for sulfate doping (small incorporation with Li<sub>2</sub>SO<sub>4</sub> coating). The SEM images of S-LRNO and LNO before and after 200 cycles are shown in Fig. 11, where cracking was observed for LNO whereas S-LRNO showed better particle preservation, illustrating further the benefits of sulfate modification.

### 3. Conclusions

Polyanion (sulfate) modified LiNiO<sub>2</sub> and Li-rich LiNiO<sub>2</sub> were synthesised through solid state and co-precipitation methods. Although the solid solution of sulfate doping appears to be limited in line with modelling results, a self-passivation Li<sub>2</sub>SO<sub>4</sub> layer formed beyond the solid solution, which contributed to the improvement in air stability and to the electrochemical performance of sulfate modified Li-rich LiNiO<sub>2</sub> (S-LRNO).

Such improved electrochemical performance as well as better capacity retention for S-LRNO was observed for samples prepared using both solid state and co-precipitation methods. The initial 245 mA h g<sup>-1</sup> discharge capacity (at 25 mA g<sup>-1</sup>) for co-precipitation synthesised S-LRNO represents a significant improvement to conventional Mn and Co co-doped NMC systems. High capacities were also observed at higher rates (205 mA h g<sup>-1</sup> initial discharged capacity at 100 mA g<sup>-1</sup>), with improved capacity retention compared to the unmodified system and attributed to the improved preservation of the H2–H3 transition. Overall, this work highlights that as an alternative design strategy, polyanion modification can effectively improve the electrochemical properties of lithium nickel oxide cathode materials, which has the potential to be easily applied to other cathode systems.

### 4. Experimental

#### 4.1 Synthesis

For the solid state synthesis method, Li<sub>2</sub>CO<sub>3</sub> (99.9%, Alfa Aesar), Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (%, Sigma-Aldrich), (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·H<sub>2</sub>O (99%, Sigma-Aldrich), (NH<sub>4</sub>)H<sub>2</sub>PO<sub>4</sub> (99%, Sigma-Aldrich) and SiO<sub>2</sub> (99%, Sigma-Aldrich) were used as reagents. Li<sub>1+z</sub>Ni<sub>1-z-x</sub>M<sub>x</sub>O<sub>2-y</sub> (M = S, P, Si) samples from intimately ground stoichiometric amounts of starting reagents were heated initially to 650 °C for 12 hours at a rate of 2.5 °C min<sup>-1</sup> to fully decompose starting reagents. A 2.5% excess Li<sub>2</sub>CO<sub>3</sub> was added to the mixture to compensate for Li loss during the synthesis. The mixture was milled (ZrO<sub>2</sub> containers and balls) with hexane solvent for 30 minutes using a Pulverisette 5 planetary ball mill to yield fine powders. The powders were pressed into pellets and reheated one or multiple times at 700–725 °C for 12 hours in dry O<sub>2</sub> with a rate of 5 °C min<sup>-1</sup> to obtain the final product, which is stored in an Ar-filled glove box.

For co-precipitation method, Ni(OH)<sub>2</sub> precursor were synthesised by precipitation from an aqueous solution of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and NaOH. Then (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·H<sub>2</sub>O (99%, Sigma-Aldrich), Ni(OH)<sub>2</sub> (as prepared) and LiOH·H<sub>2</sub>O (99%, Sigma-Aldrich) were mixed with 5–10% excess LiOH·H<sub>2</sub>O by ball milling in a zirconia pot at 500 rpm for 1 hour. The mixture was

heated to 350 °C for 12 hours at 2.5 °C min<sup>-1</sup> and followed by heating to 700 °C for 12 hours at 5 °C min<sup>-1</sup> in O<sub>2</sub> to obtain the final product. The sample was allowed to cool down to room temperature and stored in an Ar-filled glove box.

#### 4.2 X-ray diffraction

A Bruker D8 X-ray diffractometer (XRD) with CuKα radiation and linear position sensitive detector was used to collect X-ray diffraction data. Patterns were recorded over the 2θ range 15° to 80° with a 0.02° step size. Structural refinement was carried out using the XRD data with the GSAS suite of Rietveld refinement software.<sup>53</sup>

#### 4.3 Neutron diffraction

The neutron diffraction experiment was performed on the POWGEN instrument at the Spallation Neutron Source (SNS), Oak Ridge National Laboratory. Approximately 1 g of powder was loaded into a PAC vanadium can with 6 mm diameter. The sample cans were loaded into POWGEN sample changer (PAC) and the diffraction data was collected at 293 K for around 2 hour, followed by the standard data reduction routine. The center wavelength was 0.8 Å, covering a *d* spacing range of 6.2 Å > *d* > 0.1 Å.

#### 4.4 Electrochemical testing

The active materials and carbon black (TimCal, C65) were dried at 110 °C for 24 h in a vacuum oven before use. The slurry was prepared by mixing 80% active materials, 10% carbon black and 10% polyvinylidene fluoride (PVDF, PI-KEM) in *N*-methyl-2-pyrrolidone (NMP, Sigma) using a Thinky mixer, before coating onto an aluminum foil in a dry room. The cathode was dried at 120 °C for 24 h in the vacuum oven and punched into 14.8 mm disks. The electrode disks were weighed and the mass loading of active materials on cathodes was 3–4 mg cm<sup>-2</sup>. Li metal (Aldrich) was used as anode, which was rolled and punched into 15 mm disks. The composition of the electrolyte (R&D 281, Soulbrain) was 1.0 M LiPF<sub>6</sub> in EC:EMC (ethylene carbonate/methyl carbonate, 3/7 V/V) with 1 wt% VC (vinylene carbonate) as an electrolyte additive. Microporous trilayer membrane (PP/PE/PP) (H1609, Celgard) was used as the separator.

The half cells using the components above were assembled with CR2032 coin cells in an argon-filled glove box and all electrochemical measurements were conducted on the BCS805 cell tester (Bio-logic). Galvanostatic charge/discharge with potential limitation (GVPL) measurement was conducted at constant current density of 25 mA g<sup>-1</sup>, 50 mA g<sup>-1</sup> or 100 mA g<sup>-1</sup> in the voltage range between 2 and 4.3 V vs. Li/Li<sup>+</sup>. Electrochemical impedance spectroscopy (EIS) measurement was performed in half-cell using an amplitude of 5 mV in the frequency range from 10<sup>-2</sup> to 10<sup>5</sup> Hz. For the data analysis, EC-Lab software was used for the equivalent circuit models fitting.

For galvanostatic intermittent titration technique (GITT) measurement, the cells were charged and discharged at 25 mA g<sup>-1</sup> with a rest (3 h) to achieve full equilibrium voltage. Fundamental ideas calculating diffusion coefficients from GITT technique have originated from the research work by Weppner



and Huggins.<sup>54</sup> Here we adopted the transformed sand equation to calculate the diffusion of  $\text{Li}^+$  in the active particle materials from the following eqn (1).

$$D_{\text{Li}^+} = \frac{4}{\pi} \left( \frac{iV_m}{nFS} \right)^2 \left( \frac{dE/d\delta}{dE/dt^{0.5}} \right)^2 \quad (1)$$

Herein,  $i$  denotes the current passing through the electrode with the unit of amps (A);  $V_m$  is the molar volume of active materials ( $\text{cm}^3 \text{mol}^{-1}$ );  $n$  stands for the transferred electrons in the 'reaction' ( $n = 1$ );  $F$  and  $S$  are Faraday constant ( $\text{C mol}^{-1}$ ) and active surface area between electrode and electrolyte ( $\text{m}^2$ ); the gradient  $dE/d\delta$  is the slope of the coulometric titration curve, which is found by plotting the steady state voltages  $E(V)$  measured after each titration step. The gradient  $dE/dt^{0.5}$  means the slope of the linearized plot of the potential  $E(V)$  during the current pulse of duration.

The rate tests for LNO and S-LRNO prepared using coprecipitation routes were performed in half cells using different current densities at 25, 50, 100, 200, 400  $\text{mA g}^{-1}$  within the voltage window of 2 to 4.3 V vs.  $\text{Li/Li}^+$ .

#### 4.5 X-ray absorption spectroscopy (XAS), X-ray photoelectron spectroscopy (XPS) and hard X-ray photoelectron spectroscopy (HAXPES)

Hard X-ray absorption spectroscopy (XAS) data at the Ni K-edge of  $\text{NiO}$ ,  $\text{LiNiO}_2$  and S-LNRO were measured at the beamline, Diamond Light Source. X-ray photoelectron spectroscopy (XPS) and hard X-ray photoelectron spectroscopy (HAXPES) were measured on one instrument (HAXPES-Lab, Scienta Omicron GmbH). Hard X-ray photoelectron spectroscopy (HAXPES) was performed using monochromated Ga  $K\alpha$  metal jet X-ray radiation (9252 eV, 3.57 mA emission at 250 W, micro-focussed to 50  $\mu\text{m}$ ) and an EW-4000 high voltage electron energy analyser (HAXPES-Lab, Scienta Omicron GmbH); the instrument has a base vacuum pressure of  $5 \times 10^{-10}$  mbar.<sup>55,56</sup> The entrance slit width used was 1.5 mm, and the pass energies used for survey and core level spectra were 500 and 100 eV respectively, with total energy resolutions of 2.0 and 0.6 eV respectively.<sup>55</sup> The HAXPES instrument also has a monochromated Al  $K\alpha$  X-ray source (1486 eV, 20 mA emission at 300 W) for surface sensitive XPS at the same sample position. Charge neutralisation for insulating samples is achieved using a low energy electron flood source as required (FS40A, PreVac). Binding energy scale calibration was performed using Au 4f7/2 at 84 eV of a clean gold reference sample, else C 1s at 285 eV BE if the flood source is used. Analysis and curve fitting was performed using Voigt-approximation peaks using CasaXPS.<sup>57</sup> Core level relative sensitivity factors for HAXPES quantification were calculated according to references.<sup>56,58</sup>

#### 4.6 Computational methods

All calculations were performed within the density functional theory (DFT) framework using the Vienna *ab initio* Simulation Package (VASP).<sup>59–62</sup> Following our work on undoped  $\text{LiNiO}_2$ ,<sup>49</sup> the calculations were performed using the meta-generalized gradient approximation  $r^2\text{SCAN}$  functional with the revised

Vydrov–van Voorhis ( $r\text{VV10}$ ) non-local dispersion correction.<sup>63</sup> All calculations were after convergence tests performed with a plane-wave cutoff of 700 eV, projector augmented wave (PAW) pseudopotentials to describe the core electrons,<sup>64</sup> and  $k$ -point spacing of  $0.25 \text{ \AA}^{-1}$ . The convergence criteria were set to  $\leq 10^{-5}$  eV for energies and  $\leq 10^{-2}$  eV  $\text{\AA}^{-1}$  for forces. Unless otherwise stated, the relaxation calculations were started from the spin-disproportionated hexagonal structure;<sup>49</sup> zigzag  $P2_1/c$  structure was also computed.

The chemical potentials of the elements ( $\mu_{\text{O}}$ ,  $\mu_{\text{Li}}$ ,  $\mu_{\text{Ni}}$ ,  $\mu_{\text{S}}$ ) have a direct impact on the calculated defect formation energies. All chemical potentials were chosen to represent the conditions of the material synthesis, where the partial pressure of oxygen and temperature are set by the phase equilibrium between the forming LNO phase and a disordered rocksalt  $\text{Li}_x\text{Ni}_{1-x}\text{O}_2$  ( $x < 1$ ) phase at 700 °C and 1 atm  $\text{O}_2$ , which yields  $\mu_{\text{Li}} = -3.00$  eV and  $\mu_{\text{Ni}} = -1.35$  eV.<sup>49</sup> The chemical potentials of extrinsic dopants were set by a phase equilibrium with another phase, such as  $\text{Li}_2\text{SO}_4$  for S, at the same temperature and oxygen pressure ( $\mu_{\text{S}} = -4.52$  eV, Table 5). The magnetic moments of the Ni ions were used as simple proxies for their charge states. Such DFT based methods have been applied to a wide range of Li-ion cathode materials.<sup>65–69</sup>

## Author contributions

Bo Dong: conceptualization, data curation, formal analysis, investigation, methodology, visualization, writing – original draft, writing – review & editing. Andrey Poletayev: data curation, formal analysis, investigation, methodology, visualization, writing – original draft, writing – review & editing. Jonathon P. Cottom: data curation, formal analysis, writing – original draft. Javier Castells-Gil: data curation, formal analysis, writing – original draft. Ben Spencer: data curation, formal analysis, writing – original draft. Cheng Li: data curation, formal analysis, writing – original draft. Pengcheng Zhu: data curation, formal analysis, writing – original draft. Yongxiu Chen: data curation, formal analysis, writing – original draft. Jaime-Marie Price: data curation, formal analysis. Laura L. Driscoll: data curation, formal analysis. Phoebe K. Allan: resources, supervision, writing – review & editing. Emma Kendrick: resources, supervision, writing – review & editing. M. Saiful Islam: conceptualization, funding acquisition, investigation, methodology, project administration, resources, supervision, writing – original draft, writing – review & editing. Peter R. Slater: conceptualization, funding acquisition, investigation, methodology, project administration, resources, supervision, writing – original draft, writing – review & editing.

## Conflicts of interest

The authors declare no conflict of interest.

## Acknowledgements

We would like to thank the Faraday Institution CATMAT (FIRG016, EP/S003053/1) and NEXTRUDE (FIRG015) projects



for funding. We would like to thank the Diamond Light Source for the award of beam time as part of the Energy Materials Block Allocation Group SP14239. The XPS/HAXPES work was supported by the Henry Royce Institute, funded through EPSRC grants EP/R00661X/1, EP/P025021/1 and EP/P025498/1. We are also grateful to the HEC Materials Chemistry Consortium (EP/R029431) for the use of Archer2 high-performance computing (HPC) facilities, and for the Faraday Institution's Michael HPC resource. A portion of this research used resources at the Spallation Neutron Source, as appropriate, a DOE Office of Science User Facility operated by the Oak Ridge National Laboratory. J. C.-G. thanks the Generalitat Valenciana for his GVA APOSTD Fellowship (CIAPOS/2021/272). Raw experimental data can be found at <https://doi.org/10.25500/edata.bham.00001084>.

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