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Exploring Two Dimensional $\text{Co}_{0.33}\text{In}_{2.67}\text{S}_{2.29}\text{Se}_{1.71}$ as Alloy Type Negative Electrode for Li-ion Battery with Olivine LiFePO_4 Cathode

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Abstract

We report the synthesis and Li-storage properties of two-dimensional $\text{Co}_{0.33}\text{In}_{2.67}\text{S}_{2.29}\text{Se}_{1.71}$ as an anode for Li-ion battery applications. Chemical vapour transport technique is adopted to prepare high quality $\text{Co}_{0.33}\text{In}_{2.67}\text{S}_{2.29}\text{Se}_{1.71}$ single crystals with high yield. Li-storage properties are assessed using a half-cell configuration in which the cell is cycled in the alloying region (0.005-1 V *vs.* Li) that provides better characteristics than the extended region (*i.e.* allowing the materials to undergo a conversion pathway) in terms of cycling stability and retention. This logically think us to evaluate the suitability of the prepared negative electrode to fabricate the practical cell *i.e.* full-cell with olivine phase LiFePO_4 cathode. The irreversible capacity loss observed in the negative electrode is effectively tackled by using an electrochemical pre-treatment with Li and subsequently assembled the full-cell by adjusting the loading of LiFePO_4 . The practical-cell, LiFePO_4 /pre-treated $\text{Co}_{0.33}\text{In}_{2.67}\text{S}_{2.29}\text{Se}_{1.71}$ displayed a very decent electrochemical activity and exhibits a maximum energy density of $\sim 103 \text{ Wh kg}^{-1}$ (including dead mass weight).

Keywords: 2 dimensional material; anode; alloying; energy density; pre-treating; olivine

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Introduction

Li-ion batteries (LIB) continue to conquer the battery market owing to their high volumetric and gravimetric energy density, light weight, lack of a memory effect and maintenance-free usage[1]. Also, LIBs are believed to be strong contenders to power zero emission transportation applications like electric vehicles and hybrid electric vehicles[2, 3]. Unfortunately, conventional graphitic anodes are unsafe to use in such high energy and high power configurations[4]. This is mainly because the low intercalation potential (< 0.1 V *vs.* Li) of graphite causes lithium plating and triggers the formation of dendrites when operating at high currents. Therefore, the search for an alternate anode to replace graphite has been widely taken up by the research community[4-6]. From this, transition metal based oxides and phosphate-based insertion anodes have been explored as intercalation hosts[4, 7-9]. The practical capacities of such anodes, however, have been found to be inferior (< 250 mAh g⁻¹), and the working potential is much higher (> 1 V *vs.* Li) than those of graphite, which dilutes the net energy density of the system. Besides intercalation, materials can undergo either conversion, alloy or combination of two type mechanisms is also proposed to replace traditional intercalation type graphite anodes[10-12]. Conversion and alloy type anodes exhibit lower redox potentials than transition metal oxide/phosphate-based materials and much higher practical capacities (> 500 mAh g⁻¹). However, such materials experience fatal issues like huge irreversible capacity loss and large volume variation upon charging and discharging, several

approaches have been proposed to mitigate these issues including spontaneous lithiation, stabilized lithium metal powder, chemical and electrochemical lithiation etc.[13-15] and pairing with practical LIB's with conventional cathodes[4].

We have made an attempt to explore the use of multi-component active elements, $\text{Co}_{0.33}\text{In}_{2.67}\text{S}_{2.29}\text{Se}_{1.71}$, as an anode for LIB applications which is more or less similar to those of Nexelion battery system composed of Sn-Co-C-Ti by Sony[16]. Previously, Si, Sn, Ge etc., based materials have been extensively investigated as alloy-type electrodes, but very little research has been completed for In-based electrodes[5, 17-21]. In $\text{Co}_{0.33}\text{In}_{2.67}\text{S}_{2.29}\text{Se}_{1.71}$, the transition metal Co involves the sustained Li storage via conversion pathway, whereas In undergoes both alloying and conversion reactions with Li. Multi-component reactions for Li storage is not new for LIB anodes, ZnFe_2O_4 is a perfect example, as well as Sn-Co-C-Ti, in which Zn involves both alloying and conversion reaction and Fe undergoes a conversion reaction[11, 22, 23]. Nevertheless, by limiting the testing potential, the active material can be allowed to buffer only in the alloying regime. Similarly, Hassoun *et al.*[24] studied an interesting system composed of Sn- Fe_2O_3 -Meso carbon micro beads, MCMB as an anode which exhibited all possible mechanisms like alloying, conversion and intercalation during the electrochemical reaction. In this present work, we report the first time, a In-based sulfo-selenide composite which has been evaluated as an anode material with different cut-off potentials for Li-storage. Detailed electrochemical studies have been conducted, investigating the interplay between alloying and conversion reactions involving In. Chemical vapour transport (CVT) was used to yield high-quality single crystals for charge storage applications[25-28]. Finally, a practical cell was fabricated with commercial LiFePO_4 as the cathode and pre-treated $\text{Co}_{0.33}\text{In}_{2.67}\text{S}_{2.29}\text{Se}_{1.71}$ as the anode.

Experimental section

Chemical vapour transport (CVT) technique was used to synthesize bulk layered compounds crystals of $\text{Co}_{0.33}\text{In}_{2.67}\text{S}_{2.29}\text{Se}_{1.71}$. Stoichiometric amounts of cobalt powder (Puratronic[®], ~22 mesh,

99.998%, Alfa Aesar), indium powder (~325 mesh, 99.99%, Alfa Aesar), sulphur powder (Puratronic®, 99.999%, Alfa Aesar) and selenium shots (99.99%, Alfa Aesar) were sealed in an evacuated quartz tube (10^{-5} Torr) with a small amount of iodine (I_2) as a transport agent (2 mg cc^{-1}). The sealed ampoule (tube) was placed in a two-zone furnace with a temperature profile of $750 - 700^\circ\text{C}$ for a period of 360 hours. Temperature profile and synthesis parameters for this material system were earlier described in detail by Memo *et al.*[29]. After the completion of this period, ampoule was allowed to cool naturally to room temperature. Later, the obtained product was carefully taken out from the ampoule for materials characterization and further studies.

Powder X-ray diffraction (P-XRD) data of crystalline flakes were obtained with a Bruker D8 advance diffractometer ($\text{CuK}\alpha = 1.5406 \text{ \AA}$ radiation at 45 kV, 30 mA). Single crystal X-ray diffraction (SC-XRD) was conducted using a Bruker SMART APEX II system. This was a 3-circle diffractometer used in a sealed Mo tube and a graphite monochromator to yield Mo $K_{\alpha 1}$ radiation. A crystal of $\text{Co}_{0.33}\text{In}_{2.67}\text{S}_{2.29}\text{Se}_{1.71}$ was ran, mounted using a Mitegen pip, at 23°C and found to be an inversion twin with a BASF parameter of 0.487 in the trigonal space group $P3m1$. While additional symmetry was tested for, none was found that didn't result in a hugely increased R-factor. It is assumed the small deviations in atomic coordinates, due to the heavy disorder observed within the structure, break any possible inversion symmetry. Absorption and scaling corrections were carried out using SAINT, SADABS and XPREP, whilst structure solution and refinement occurred using the WinGX programme suite and SHELXS and SHELXL refinement strategies[30-33]. Secondary electron imaging (SEI) of the obtained crystals were performed using a SEM-JSM-6360 instrument (JEOL). Elemental distributions over crystal surfaces were studied using energy- dispersive X-ray (EDAX) analysis, which provided semi- quantitative compositional information. Corresponding elemental EDAX mapping of the synthesized sample was performed using the attached detector. Transmission electron microscopy (TEM) for selected area electron diffraction (SAED) was performed using JOEL HR- TEM 2010.

CR2016 coin-cell was used to study the electrochemical properties of the $\text{Co}_{0.33}\text{In}_{2.67}\text{S}_{2.29}\text{Se}_{1.71}$ in both half-cell (*vs.* Li) and full-cell (*vs.* LiFePO_4) assemblies. The test electrodes were formulated with accurately weighed 10 mg of $\text{Co}_{0.33}\text{In}_{2.67}\text{S}_{2.29}\text{Se}_{1.71}$ in the presence of ethanol. The composite slurry was placed over 16 mm stainless steel mesh (Goodfellow, UK) and dried at 60 °C for the overnight before the conducting the coin-cell assembly. Half-cell performance was analyzed with metallic Li as the counter and reference electrode separated by Whatman paper (No. 1825-047) with 1 M LiPF_6 in ethylene carbonate (EC) and di-ethyl carbonate (DEC) as the electrolyte solution. In the case of practical LIB *i.e.* full-cell, the $\text{Co}_{0.33}\text{In}_{2.67}\text{S}_{2.29}\text{Se}_{1.71}$ electrode was electrochemically treated by means, two complete charge-discharge cycles (0.005-1 V *vs.* Li) have been conducted in the half-cell assembly @ Swagelok fittings. The usage of Swagelok fittings certainly useful to pre-treat the electrode without any physical damage. The mass loading of LiFePO_4 has been adjusted with respect to the $\text{Co}_{0.33}\text{In}_{2.67}\text{S}_{2.29}\text{Se}_{1.71}$ loading and paired in coin-cell by freshly filling the electrolyte solution. Although the mass loading may be varied, the composition remains constant throughout the analysis. Galvanostatic charge-discharge studies were performed with Arbin BT2000 battery tester at different cut-off potentials in ambient temperature conditions (25 °C).

Results and discussion

Previous work of Memo *et al.* [29] reported the existence of mixed sulfur-selenium layered phases in the CoIn_2S_4 - CoIn_2Se_4 system. On the similar lines, we have attempted to synthesize mixed sulfo-selenide layered compounds. Initially, SC-XRD measurement were performed to ascertain the formation of compound, stoichiometry between the constituents (Co, In, S and Se) and atomic structure. $\text{Co}_{0.33}\text{In}_{2.67}\text{S}_{2.29}\text{Se}_{1.71}$ was found in the space group P3m1 with a unit cell of $a = 3.8975(1)$ Å, $c = 12.5774(3)$ Å and a volume of 165.460(9) Å³.

The structure is a layered, solid solution, where the layers stack along the c -axis and are made up of indium octahedra that are linked to tetrahedra above and below through bridging

sulphur or selenium sites (Figure 1a). One of these tetrahedra has an indium at its centre, whilst the other is a mixed cobalt and indium site ($\text{Co}_{0.33}\text{In}_{0.66}$). All of the cobalt and indium centres are furnished with mixed occupancy sites of sulphur and selenium that were allowed to refine to slightly different atomic coordinates with anisotropic thermal displacement parameters. The sulphur and selenium remained extremely close during refinement, so to keep the sulphur's thermal parameters behaving correctly, all of sulphur atoms thermal displacement parameters were restrained together using an EADP command. The refinement finally converged to yield: $R_1 = 2.25\%$, $wR_2 = 5.68\%$ and a $GOF = 1.054$. P-XRD data (Figure 1b) was also obtained and indexed from the obtained **cif** file (Supporting Information).

SEM/EDAX measurements were performed to investigate the semi-quantitative analysis of the prepared compound, as shown in Figure 2. Figure 2a shows a stoichiometric ratio that is in agreement with the SC-XRD data. The homogeneous nature of the substitutional solid-solution compound was established by performing elemental EDAX mapping of a typical flake of the as-grown sample (Figure 2b). To further reaffirm the atomic structure, transmission electron microscopy data and select area electron diffraction (SAED) were collected and analysed, confirming the hexagonal symmetry ($P3m1$) of atoms in the $\text{Co}_{0.33}\text{In}_{2.67}\text{S}_{2.29}\text{Se}_{1.71}$ crystals (Figure 2c & d).

Li-storage properties of the $\text{Co}_{0.33}\text{In}_{2.67}\text{S}_{2.29}\text{Se}_{1.71}$ was studied by half-cell assembly between 0.005-3 V *vs.* Li at a constant current density of 80 mA g⁻¹ and given in Figure 3. Li-insertion is clearly evident during the initial stages (<1.5 V *vs.* Li) of the discharge process[34] (eqn. i) and continues lithiation results the structural destruction of the active material (eqn. ii). Such destruction of the crystalline phase is clearly evident from the derivative of the discharge curve *i.e.* differential capacity profile. A small plateau at ~0.7 V *vs.* Li is associated with the decomposition of the electrolyte solution and subsequent formation of solid electrolyte interphase (SEI) layer. This SEI formation is mostly an irreversible process which predominantly composed of oligomeric

layers, inorganic by-products etc.[35, 36]. The cell delivered a discharge capacity of $\sim 930 \text{ mAh g}^{-1}$ (16.55 mol. Li) and it is higher than the theoretical limitations (14 mol. Li). As mentioned, the excess consumption of Li is mainly associated with the SEI formation process and irreversible as well. Nevertheless, the irreversibility and consumption is a common process for conversion and alloy type negative electrodes during the first discharge[4, 37]. Long distinct plateau close to the reference electrode potential is associated with the Li_3In alloy formation according to eqn. (iii)

Upon charge, the appearance of redox peaks located at ~ 0.3 and $\sim 0.6 \text{ V vs. Li}$ corresponds to the de-alloying process of Li_3In . Further, a very broad oxidative potential above 1.5 V vs. Li is mainly because of the oxidation of the Co and In into its sulfo-selenides (eqn. iv & v). However, the charge capacity of only $\sim 587 \text{ mAh g}^{-1}$ is retained and it corresponds to the 10.4 mol. Li. Further, a drastic fade in capacity is noted upon cycling, for example the cell rendered the capacity of $\sim 71 \text{ mAh g}^{-1}$ after 100 cycles ($\sim 12\%$ retention). This poor performance is mainly because of the combined mechanism of alloying and conversion process which cause large variation in the unit cell parameters and results the pulverization of the electrode. This certainly leads to the detachment of the active materials from the current collectors. Surface modification and making the hollow structured active material is one of the efficient approaches to improve the cycling profiles, but suppression in the volumetric capacity has to be compromised. Therefore, we limit the half-cell to buffer only in the alloying regime ($0.005\text{-}1 \text{ V vs. Li}$) and the corresponding profiles are given in Figure 4. As expected, the first discharge characteristics remain same, but the entirely different

charge profiles are registered. The half-cell delivered a capacity of ~ 970 and ~ 307 mAh g⁻¹ for first discharge and charge, respectively. A very stable cycling profiles are noted for Li/Co_{0.33}In_{2.67}S_{2.29}Se_{1.71} half-cell compared to the extended region and retained $\sim 72\%$ capacity after 90 cycles. We believe the restricted cycling certainly provides the enhanced cycleability. Moreover, the presence of metallic Co⁰ in the sulfo-selenide promotes the electrical conductivity of the matrix[38, 39]. So, eventually enhanced electrochemical profiles are noted. Moreover, such narrow potential window is preferred for the fabrication of practical batteries with conventional cathodes.

This enhanced performance of Co_{0.33}In_{2.67}S_{2.29}Se_{1.71} in half-cell assembly within the alloying region logically led us to fabricate the practical LIB with olivine-type LiFePO₄ as the cathode. However, huge irreversible capacity is one of the main hurdles to fabricate the practical LIB. In this line, a half-cell assembly is fabricated with Swagelok fittings and tested for two complete cycles[25]. This pre-treating process will mitigate the irreversibility observed in the first discharge and also ensures the re-productibility of the half-cell performance. The pre-treated Co_{0.33}In_{2.67}S_{2.29}Se_{1.71} electrode has been carefully removed from the Swagelok fittings and paired with appropriate loading of LiFePO₄ in coin-cell. The electrolyte solution is also freshly topped up during the cell assembly to ensure the sufficient amount of solution. The mass loading has been adjusted based on the electrochemical performance of Co_{0.33}In_{2.67}S_{2.29}Se_{1.71} and LiFePO₄ with metallic Li in half-cell assembly at the constant current density of 80 mA g⁻¹ (Figure S1). Accordingly, the anode to cathode ratio has been fixed to 1:2.58 (5 mg: 12.9 mg). In the full-cell assembly, applied current and capacity is calculated based on the anode mass loading, but the values are calculated based on the total mass loading of the active materials (17.9 mg). The full-cell, LiFePO₄/Co_{0.33}In_{2.67}S_{2.29}Se_{1.71} delivered a capacity of ~ 94 mAh g⁻¹ at the current density of 50 mA g⁻¹ (Figure 5). Apparently, increasing the current rate tends to decrease the reversibility and it is common for the LIB irrespective of the negative/positive electrode and its Li-storage mechanism[40]. Because less participation/surface of the active material only involved in the electrochemical reaction at higher rates which cause for declining the reversibility. Irrespective of

the applied current rate, a marginal fade in the capacity is noted for the full-cell, $\text{LiFePO}_4/\text{Co}_{0.33}\text{In}_{2.67}\text{S}_{2.29}\text{Se}_{1.71}$.

Energy and power density value have also been calculated for the full-cell, $\text{LiFePO}_4/\text{Co}_{0.33}\text{In}_{2.67}\text{S}_{2.29}\text{Se}_{1.71}$ and given in Figure 6. Since the energy density is calculated by multiplying the capacity and working potential. Accordingly, the cell delivered the maximum energy density of $\sim 310 \text{ Wh kg}^{-1}$ at a power density of 0.164 kW kg^{-1} . As mentioned, the obtained energy density is based on the active material loading *i.e.* anode and cathode. If we consider the dead mass weight like a current collector, conductive additive, binder, electrolyte etc., the resultant value must be divided by the factor 3. Therefore, the net energy density of the $\text{LiFePO}_4/\text{Co}_{0.33}\text{In}_{2.67}\text{S}_{2.29}\text{Se}_{1.71}$ cell is estimated to be $\sim 103 \text{ Wh kg}^{-1}$ at lower rates. The obtained value is consistent with the reported values in the literature for other configurations based on LiFePO_4 [3, 6, 16]. At high power rates (1.48 kW kg^{-1}), the $\text{LiFePO}_4/\text{Co}_{0.33}\text{In}_{2.67}\text{S}_{2.29}\text{Se}_{1.71}$ cell rendered the energy density of $\sim 71 \text{ Wh kg}^{-1}$ (based on active materials weight). The obtained values are better than the graphitic anode based assemblies. Recyclability is another important criterion for the practical LIB's and the cycling studies were conducted. Figure 6b represents the plot of normalized capacity *vs.* cycle number at a current density of 250 mA g^{-1} . Interestingly, the cell exhibits the very high coulombic efficiency which is clearly evident from the cycling profile. As experienced during the rate performance studies, the capacity fading is observed irrespective of the applied current densities. The same trend is also reflected during the extended cycling, for example, the cell rendered $\sim 64\%$ of its initial values after 100 cycles. Although the observed fading is slightly higher than its half-cell assembly. Such contrasting profiles of the active material is common for half-cell and full-cell assemblies[41]. Moreover, this study clearly suggests that the importance of testing the active material in full-cell assembly rather than testing with half-cell in a routine way. Continuous growth of surface films on the anode and associated sluggish kinetics is the prime reason for the fade in capacity upon cycling which is clearly supported by the impedance

measurements (Figure S2). Further studies are in progress to make this In-based alloy-type material into commercial reality, specifically improving the cycleability.

Conclusion

We successfully demonstrated the fabrication of high-performance LIB using alloy type negative electrode based on In ($\text{Co}_{0.33}\text{In}_{2.67}\text{S}_{2.29}\text{Se}_{1.71}$). However, allowing a material to buffer only in the alloying region results rendered excellent stability, but the reversibility has to be sacrificed. This stable performance within the alloying region thinks us to assemble the practical LIB using commercial LiFePO_4 . The irreversible capacity loss has been mitigated by conducting electrochemical pre-treatment. The $\text{LiFePO}_4/\text{Co}_{0.33}\text{In}_{2.67}\text{S}_{2.29}\text{Se}_{1.71}$ cell delivered the maximum energy density of $\sim 103 \text{ Wh kg}^{-1}$ and it is consistent with the previous configurations based on the olivine phase. This results certainly provide the new avenues for the exploration of the In-based negative electrodes for constructing high-performance Li-ion power packs.

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References

- [1] J. Goodenough, Rechargeable batteries: challenges old and new, *Journal of Solid State Electrochemistry* 16(6) (2012) 2019-2029.
- [2] E.J. Cairns, P. Albertus, Batteries for Electric and Hybrid-Electric Vehicles, *Annual Review of Chemical and Biomolecular Engineering* 1(1) (2010) 299-320.

- [3] D. Andre, S.-J. Kim, P. Lamp, S.F. Lux, F. Maglia, O. Paschos, B. Stiaszny, Future generations of cathode materials: an automotive industry perspective, *Journal of Materials Chemistry A* 3(13) (2015) 6709-6732.
- [4] V. Aravindan, Y.-S. Lee, S. Madhavi, Research Progress on Negative Electrodes for Practical Li-Ion Batteries: Beyond Carbonaceous Anodes, *Advanced Energy Materials* 5(13) (2015) 1402225.
- [5] M.N. Obrovac, V.L. Chevrier, Alloy Negative Electrodes for Li-Ion Batteries, *Chemical Reviews* 114(23) (2014) 11444-11502.
- [6] M.M. Thackeray, C. Wolverton, E.D. Isaacs, Electrical energy storage for transportation-approaching the limits of, and going beyond, lithium-ion batteries, *Energy & Environmental Science* 5(7) (2012) 7854-7863.
- [7] V. Aravindan, J. Sundaramurthy, P. Suresh Kumar, Y.-S. Lee, S. Ramakrishna, S. Madhavi, Electrospun nanofibers: A prospective electro-active material for constructing high performance Li-ion batteries, *Chemical Communications* 51(12) (2015) 2225-2234.
- [8] V. Aravindan, Y.-S. Lee, R. Yazami, S. Madhavi, TiO₂ polymorphs in 'rocking-chair' Li-ion batteries, *Materials Today* 18(6) (2015) 345-351.
- [9] S. Patoux, C. Masquelier, Lithium Insertion into Titanium Phosphates, Silicates, and Sulfates, *Chemistry of Materials* 14(12) (2002) 5057-5068.
- [10] P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, J.M. Tarascon, Nano-sized transition-metal oxides as negative-electrode materials for lithium-ion batteries, *Nature* 407(6803) (2000) 496-499.
- [11] D. Bresser, S. Passerini, B. Scrosati, Leveraging valuable synergies by combining alloying and conversion for lithium-ion anodes, *Energy & Environmental Science* 9(11) (2016) 3348-3367.
- [12] S. Jayaraman, V. Aravindan, M. Ulaganathan, W.C. Ling, S. Ramakrishna, S. Madhavi, Ultralong Durability of Porous α -Fe₂O₃ Nanofibers in Practical Li-Ion Configuration with LiMn₂O₄ Cathode, *Advanced Science* 2(5) (2015) 1500050.

- [13] V. Aravindan, Y.-S. Lee, S. Madhavi, Best Practices for Mitigating Irreversible Capacity Loss of Negative Electrodes in Li-Ion Batteries, *Advanced Energy Materials* 7(17) (2017) 1602607.
- [14] V. Aravindan, P. Sennu, Y.-S. Lee, S. Madhavi, Practical Li-Ion Battery Assembly with One-Dimensional Active Materials, *The Journal of Physical Chemistry Letters* 8(17) (2017) 4031-4037.
- [15] V. Aravindan, Y.S. Lee, Electrochemical Activity of Hematite Phase in Full-Cell Li-ion Assemblies, *Advanced Energy Materials* 8(11) (2018) 1702841.
- [16] V. Aravindan, J. Gnanaraj, Y.S. Lee, S. Madhavi, LiMnPO_4 - A next generation cathode material for lithium-ion batteries, *Journal of Materials Chemistry A* 1(11) (2013) 3518-3539.
- [17] Y. Zhang, C. Jiang, S. Zhuang, M. Lu, Y. Cai, Mesoporous In_2O_3 nanofibers assembled by ultrafine nanoparticles as a high capacity anode for Li-ion batteries, *RSC Advances* 6(55) (2016) 49782-49786.
- [18] D.-W. Kim, I.-S. Hwang, S.J. Kwon, H.-Y. Kang, K.-S. Park, Y.-J. Choi, K.-J. Choi, J.-G. Park, Highly Conductive Coaxial SnO_2 - In_2O_3 Heterostructured Nanowires for Li Ion Battery Electrodes, *Nano Letters* 7(10) (2007) 3041-3045.
- [19] J. Choi, J. Jin, J. Lee, J.H. Park, H.J. Kim, D.-H. Oh, J.R. Ahn, S.U. Son, Columnar assembly and successive heating of colloidal 2D nanomaterials on graphene as an efficient strategy for new anode materials in lithium ion batteries: the case of In_2S_3 nanoplates, *Journal of Materials Chemistry* 22(22) (2012) 11107-11112.
- [20] X. Yang, C.Y. Chan, H.T. Xue, J. Xu, Y.-B. Tang, Q. Wang, T.L. Wong, C.-S. Lee, One-pot synthesis of graphene/ In_2S_3 nanoparticle composites for stable rechargeable lithium ion battery, *CrystEngComm* 15(33) (2013) 6578-6584.
- [21] G. Han, Z.-G. Chen, D. Ye, B. Wang, L. Yang, Y. Zou, L. Wang, J. Drennan, J. Zou, In_3Se_4 and S-doped In_3Se_4 nano/micro-structures as new anode materials for Li-ion batteries, *Journal of Materials Chemistry A* 3(14) (2015) 7560-7567.

- [22] D. Bresser, E. Paillard, R. Kloepsch, S. Krueger, M. Fiedler, R. Schmitz, D. Baither, M. Winter, S. Passerini, Carbon Coated ZnFe_2O_4 Nanoparticles for Advanced Lithium-Ion Anodes, *Advanced Energy Materials* 3(4) (2013) 513-523.
- [23] A. Varzi, D. Bresser, J. von Zamory, F. Müller, S. Passerini, $\text{ZnFe}_2\text{O}_4\text{-C/LiFePO}_4\text{-CNT}$: A Novel High-Power Lithium-Ion Battery with Excellent Cycling Performance, *Advanced Energy Materials* 4(10) (2014) 1400054.
- [24] R. Verrelli, J. Hassoun, High capacity tin–iron oxide-carbon nanostructured anode for advanced lithium ion battery, *Journal of Power Sources* 299 (2015) 611-616.
- [25] A. Chaturvedi, V. Aravindan, P. Hu, R.R. Prabhakar, L.H. Wong, C. Kloc, S. Madhavi, Synthesis of SnS_2 single crystals and its Li-storage performance with LiMn_2O_4 cathode, *Applied Materials Today* 5 (2016) 68-72.
- [26] A. Chaturvedi, E. Edison, N. Arun, P. Hu, C. Kloc, V. Aravindan, S. Madhavi, Two Dimensional TiS_2 as a Promising Insertion Anode for Na-Ion Battery, *ChemistrySelect* 3(2) (2018) 524-528.
- [27] A. Chaturvedi, P. Hu, V. Aravindan, C. Kloc, S. Madhavi, Unveiling two-dimensional TiS_2 as an insertion host for the construction of high energy Li-ion capacitors, *Journal of Materials Chemistry A* 5(19) (2017) 9177-9181.
- [28] A. Chaturvedi, P. Hu, C. Kloc, Y.-S. Lee, V. Aravindan, S. Madhavi, High energy Li-ion capacitors using two-dimensional $\text{TiSe}_{0.6}\text{S}_{1.4}$ as insertion host, *Journal of Materials Chemistry A* 5(37) (2017) 19819-19825.
- [29] A. Memo, W. Kwarteng-Acheampong, H. Haeuseler, Materials with layered structures XIII: electrical and optical properties of layered chalcogenides in the system $\text{CoIn}_2\text{S}_4\text{--CoIn}_2\text{Se}_4$, *Materials Research Bulletin* 38(6) (2003) 1057-1061.
- [30] G. Sheldrick, SHELXL-97, Program for crystal structure refinement; University of Göttingen: Göttingen, Germany, 1997, There is no corresponding record for this reference (2006).

- [31] G. Sheldrick, Crystal structure refinement with SHELXL, *Acta Crystallographica Section C* 71(1) (2015) 3-8.
- [32] L. Farrugia, WinGX and ORTEP for Windows: an update, *Journal of Applied Crystallography* 45(4) (2012) 849-854.
- [33] Bruker, APEX2, SAINT. Bruker AXS Inc., Madison, Wisconsin, USA. (2012).
- [34] C.M. Julien, M. Balkanski, Lithium reactivity with III–VI layered compounds, *Materials Science and Engineering: B* 100(3) (2003) 263-270.
- [35] E. Peled, S. Menkin, Review—SEI: Past, Present and Future, *Journal of The Electrochemical Society* 164(7) (2017) A1703-A1719.
- [36] X.-B. Cheng, R. Zhang, C.-Z. Zhao, F. Wei, J.-G. Zhang, Q. Zhang, A Review of Solid Electrolyte Interphases on Lithium Metal Anode, *Advanced Science* 3(3) (2016) n/a-n/a.
- [37] J. Cabana, L. Monconduit, D. Larcher, M.R. Palacín, Beyond Intercalation-Based Li-Ion Batteries: The State of the Art and Challenges of Electrode Materials Reacting Through Conversion Reactions, *Advanced Materials* 22(35) (2010) E170-E192.
- [38] P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, J.M. Tarascon, Searching for new anode materials for the Li-ion technology: time to deviate from the usual path, *Journal of Power Sources* 97–98(0) (2001) 235-239.
- [39] P. Sennu, M. Christy, V. Aravindan, Y.-G. Lee, K.S. Nahm, Y.-S. Lee, Two-Dimensional Mesoporous Cobalt Sulfide Nanosheets as a Superior Anode for a Li-Ion Battery and a Bifunctional Electrocatalyst for the Li–O₂ System, *Chemistry of Materials* 27(16) (2015) 5726-5735.
- [40] K. Zaghib, J.B. Goodenough, A. Mauger, C. Julien, Unsupported claims of ultrafast charging of LiFePO₄ Li-ion batteries, *Journal of Power Sources* 194(2) (2009) 1021-1023.
- [41] J.-H. Kim, N.P.W. Pieczonka, L. Yang, Challenges and Approaches for High-Voltage Spinel Lithium-Ion Batteries, *ChemPhysChem* 15(10) (2014) 1940-1954.

Figure 1. Structural studies of $\text{Co}_{0.33}\text{In}_{2.67}\text{S}_{2.29}\text{Se}_{1.71}$: (a, b) $\text{Co}_{0.33}\text{In}_{2.67}\text{S}_{2.29}\text{Se}_{1.71}$ shown down the y-axis (Left, a) and down the z-axis (Right, b). It is a layered solid solution stacking along the z-axis. Each layer is made from one central indium octahedra which is sandwiched between two tetrahedra, one of which is indium based and the other is a mixed site with $\text{Co}_{0.33}\text{In}_{0.66}$. Cobalt, indium, sulphur and selenium atoms are shown as blue, pink, yellow and green spheres respectively, whilst indium based polyhedra are shown in pink and Cobalt/Indium mixed site polyhedra are shown as blue. (c) P-XRD pattern of the as-grown $\text{Co}_{0.33}\text{In}_{2.67}\text{S}_{2.29}\text{Se}_{1.71}$ crystalline flakes indexed with the obtained **cif** file (Supporting Information).

Figure 2. (a) Semi-quantitative analysis of as-grown $\text{Co}_{0.33}\text{In}_{2.67}\text{S}_{2.29}\text{Se}_{1.71}$, (b) EDS elemental mapping of a typical as-synthesized crystalline flakes $\text{Co}_{0.33}\text{In}_{2.67}\text{S}_{2.29}\text{Se}_{1.71}$, (c) transmission electron microscopy image of the dispersed sample after sonication in ethanol, and (d) corresponding select area electron diffraction pattern (SAED).

Figure 3. Electrochemical performance of Li/Co_{0.33}In_{2.67}S_{2.29}Se_{1.71} cell between 0.005-3 V *vs.* Li at current density of 80 mA g⁻¹: (a) typical galvanostatic charge-discharge curves for first three cycles, Inset: corresponding differential capacity profiles, and (b) plot of capacity *vs.* cycle number

Figure 4. Electrochemical performance of Li/Co_{0.33}In_{2.67}S_{2.29}Se_{1.71} cell between 0.005-1 V *vs.* Li at current density of 80 mA g⁻¹: (a) typical galvanostatic charge-discharge curves for first three cycles, Inset: corresponding differential capacity profiles, and (b) plot of capacity *vs.* cycle number

Figure 5. Electrochemical performance of $\text{LiFePO}_4/\text{pre-treated Co}_{0.33}\text{In}_{2.67}\text{S}_{2.29}\text{Se}_{1.71}$ cell between 2.5-3.8 V at various current densities: (a) typical galvanostatic charge-discharge curves, and (b) plot of discharge capacity *vs.* cycle number at various current rates

Figure 6. (a) Ragone plot of LiFePO₄/pre-treated Co_{0.33}In_{2.67}S_{2.29}Se_{1.71} cell derived from Figure 5 and the values are based on the total active material loading, and (b) cycling profile of LiFePO₄/Co_{0.33}In_{2.67}S_{2.29}Se_{1.71} cell at current density of 250 mA g⁻¹ along with the Columbic efficiency

Supporting Information

Figure S1. Electrochemical performance of Li/LiFePO₄ cell between 2.5-4 V *vs.* Li at current density of 80 mA g⁻¹: (a) typical galvanostatic charge-discharge curves for two three cycles, and (b) plot of capacity *vs.* cycle number, Inset: corresponding differential capacity profiles.

Figure S2. Electrochemical impedance spectroscopy of $\text{LiFePO}_4/\text{pre-treated Co}_{0.33}\text{In}_{2.67}\text{S}_{2.29}\text{Se}_{1.71}$ cell recorded before (after the pre-treating process) and after cycling.

Table 1. Crystal data and structure refinement.

Identification code	shelx
Empirical formula	Co _{0.33} In _{2.67} S _{2.29} Se _{1.71}
Formula weight	534.73
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Trigonal
Space group	P 3 m 1
Unit cell dimensions	a = 3.89750(10) Å α = 90°.
	b = 3.89750(10) Å β = 90°.
	c = 12.5774(3) Å γ = 120°.
Volume	165.460(9) Å ³
Z	1
Density (calculated)	5.366 Mg/m ³
Absorption coefficient	20.045 mm ⁻¹
F(000)	235
Crystal size	0.1 x 0.08 x 0.02 mm ³
Theta range for data collection	3.239 to 36.320°.
Index ranges	-6 ≤ h ≤ 6, -6 ≤ k ≤ 6, -20 ≤ l ≤ 20
Reflections collected	3926
Independent reflections	734 [R(int) = 0.0294]
Completeness to theta = 25.242°	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.4383 and 0.2467
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	734 / 61 / 37
Goodness-of-fit on F ²	1.054
Final R indices [I > 2σ(I)]	R1 = 0.0225, wR2 = 0.0532
R indices (all data)	R1 = 0.0273, wR2 = 0.0568
Absolute structure parameter	0.49(6)
Extinction coefficient	n/a
Largest diff. peak and hole	1.303 and -1.264 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$).

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
In(1)	3333	6667	7885(1)	20(1)
In(2)	-3333	3333	4886(3)	18(1)
In(3)	10000	10000	1902(3)	15(1)
Co(3)	10000	10000	1670(11)	9(2)
Se(1)	0	0	8739(9)	22(2)
S(1)	0	0	8580(20)	15(2)
Se(2)	3333	6667	5990(17)	17(2)
S(2)	3333	6667	5910(30)	15(2)
Se(3)	3333	6667	11152(11)	30(3)
S(3)	3333	6667	11030(30)	15(2)
Se(4)	0	0	3780(50)	8(3)
S(4)	0	0	3800(40)	15(2)

Table 3. Bond lengths [Å] and angles [°].

In(1)-Se(2)	2.38(2)
In(1)-S(1)#1	2.415(11)
In(1)-S(1)#2	2.415(11)
In(1)-S(1)	2.415(11)
In(1)-S(2)	2.49(4)
In(1)-Se(1)	2.494(5)
In(1)-Se(1)#1	2.494(5)
In(1)-Se(1)#2	2.494(5)
In(2)-S(2)#3	2.591(19)
In(2)-S(2)	2.591(19)
In(2)-S(2)#4	2.591(19)
In(2)-S(4)	2.63(2)
In(2)-Se(4)#3	2.64(3)
In(2)-Se(4)#1	2.64(3)
In(2)-Se(4)	2.64(3)
In(2)-Se(2)#3	2.644(12)
In(2)-Se(2)	2.644(12)
In(2)-Se(2)#4	2.644(12)
In(3)-Se(4)#2	2.37(7)
In(3)-Se(3)#5	2.440(6)
In(3)-Se(3)#6	2.440(6)
In(3)-Se(3)#7	2.440(6)
In(3)-S(3)#5	2.502(19)
In(3)-S(3)#6	2.502(19)
In(3)-S(3)#7	2.502(19)
Co(3)-Se(3)#5	2.343(6)
Co(3)-Se(3)#6	2.343(6)
Co(3)-Se(3)#7	2.343(6)
Co(3)-S(3)#5	2.389(15)
Co(3)-S(3)#6	2.389(15)
Co(3)-S(3)#7	2.389(15)
Co(3)-Se(4)#2	2.66(7)
Se(2)-In(1)-S(1)#1	111.3(7)
Se(2)-In(1)-S(1)#2	111.3(7)
S(1)#1-In(1)-S(1)#2	107.6(7)

Se(2)-In(1)-S(1)	111.3(7)
S(1)#1-In(1)-S(1)	107.6(7)
S(1)#2-In(1)-S(1)	107.6(7)
Se(2)-In(1)-S(2)	0.000(3)
S(1)#1-In(1)-S(2)	111.3(7)
S(1)#2-In(1)-S(2)	111.3(7)
S(1)-In(1)-S(2)	111.3(7)
Se(2)-In(1)-Se(1)	115.5(3)
S(1)#1-In(1)-Se(1)	105.3(4)
S(1)#2-In(1)-Se(1)	105.3(4)
S(1)-In(1)-Se(1)	4.2(8)
S(2)-In(1)-Se(1)	115.5(3)
Se(2)-In(1)-Se(1)#1	115.5(3)
S(1)#1-In(1)-Se(1)#1	4.2(8)
S(1)#2-In(1)-Se(1)#1	105.3(4)
S(1)-In(1)-Se(1)#1	105.3(4)
S(2)-In(1)-Se(1)#1	115.5(3)
Se(1)-In(1)-Se(1)#1	102.8(3)
Se(2)-In(1)-Se(1)#2	115.5(3)
S(1)#1-In(1)-Se(1)#2	105.3(4)
S(1)#2-In(1)-Se(1)#2	4.2(8)
S(1)-In(1)-Se(1)#2	105.3(4)
S(2)-In(1)-Se(1)#2	115.5(3)
Se(1)-In(1)-Se(1)#2	102.8(3)
Se(1)#1-In(1)-Se(1)#2	102.8(3)
S(2)#3-In(2)-S(2)	97.6(9)
S(2)#3-In(2)-S(2)#4	97.6(9)
S(2)-In(2)-S(2)#4	97.6(9)
S(2)#3-In(2)-S(4)	178.5(9)
S(2)-In(2)-S(4)	83.4(8)
S(2)#4-In(2)-S(4)	83.4(8)
S(2)#3-In(2)-Se(4)#3	83.7(8)
S(2)-In(2)-Se(4)#3	178.1(16)
S(2)#4-In(2)-Se(4)#3	83.7(8)
S(4)-In(2)-Se(4)#3	95.3(3)
S(2)#3-In(2)-Se(4)#1	83.7(8)

S(2)-In(2)-Se(4)#1	83.7(8)
S(2)#4-In(2)-Se(4)#1	178.1(16)
S(4)-In(2)-Se(4)#1	95.3(3)
Se(4)#3-In(2)-Se(4)#1	95.0(16)
S(2)#3-In(2)-Se(4)	178.1(16)
S(2)-In(2)-Se(4)	83.7(8)
S(2)#4-In(2)-Se(4)	83.7(8)
S(4)-In(2)-Se(4)	0(2)
Se(4)#3-In(2)-Se(4)	95.0(16)
Se(4)#1-In(2)-Se(4)	95.0(16)
S(2)#3-In(2)-Se(2)#3	2.0(11)
S(2)-In(2)-Se(2)#3	96.3(3)
S(2)#4-In(2)-Se(2)#3	96.3(3)
S(4)-In(2)-Se(2)#3	179.5(11)
Se(4)#3-In(2)-Se(2)#3	85.0(9)
Se(4)#1-In(2)-Se(2)#3	85.0(9)
Se(4)-In(2)-Se(2)#3	180.0(12)
S(2)#3-In(2)-Se(2)	96.3(3)
S(2)-In(2)-Se(2)	2.0(11)
S(2)#4-In(2)-Se(2)	96.3(3)
S(4)-In(2)-Se(2)	84.7(5)
Se(4)#3-In(2)-Se(2)	180.0(12)
Se(4)#1-In(2)-Se(2)	85.0(9)
Se(4)-In(2)-Se(2)	85.0(9)
Se(2)#3-In(2)-Se(2)	95.0(5)
S(2)#3-In(2)-Se(2)#4	96.3(3)
S(2)-In(2)-Se(2)#4	96.3(3)
S(2)#4-In(2)-Se(2)#4	2.0(11)
S(4)-In(2)-Se(2)#4	84.7(5)
Se(4)#3-In(2)-Se(2)#4	85.0(9)
Se(4)#1-In(2)-Se(2)#4	180.0(12)
Se(4)-In(2)-Se(2)#4	85.0(9)
Se(2)#3-In(2)-Se(2)#4	95.0(5)
Se(2)-In(2)-Se(2)#4	95.0(5)
Se(4)#2-In(3)-Se(3)#5	112.7(3)
Se(4)#2-In(3)-Se(3)#6	112.7(3)

Se(3)#5-In(3)-Se(3)#6	106.0(4)
Se(4)#2-In(3)-Se(3)#7	112.7(3)
Se(3)#5-In(3)-Se(3)#7	106.0(4)
Se(3)#6-In(3)-Se(3)#7	106.0(4)
Se(4)#2-In(3)-S(3)#5	115.9(9)
Se(3)#5-In(3)-S(3)#5	3.2(12)
Se(3)#6-In(3)-S(3)#5	104.2(4)
Se(3)#7-In(3)-S(3)#5	104.2(4)
Se(4)#2-In(3)-S(3)#6	115.9(9)
Se(3)#5-In(3)-S(3)#6	104.2(4)
Se(3)#6-In(3)-S(3)#6	3.2(12)
Se(3)#7-In(3)-S(3)#6	104.2(4)
S(3)#5-In(3)-S(3)#6	102.3(11)
Se(4)#2-In(3)-S(3)#7	115.9(9)
Se(3)#5-In(3)-S(3)#7	104.2(4)
Se(3)#6-In(3)-S(3)#7	104.2(4)
Se(3)#7-In(3)-S(3)#7	3.2(12)
S(3)#5-In(3)-S(3)#7	102.3(11)
S(3)#6-In(3)-S(3)#7	102.3(11)
Se(3)#5-Co(3)-Se(3)#6	112.6(4)
Se(3)#5-Co(3)-Se(3)#7	112.6(4)
Se(3)#6-Co(3)-Se(3)#7	112.6(4)
Se(3)#5-Co(3)-S(3)#5	3.4(13)
Se(3)#6-Co(3)-S(3)#5	111.0(4)
Se(3)#7-Co(3)-S(3)#5	111.0(4)
Se(3)#5-Co(3)-S(3)#6	111.0(4)
Se(3)#6-Co(3)-S(3)#6	3.4(13)
Se(3)#7-Co(3)-S(3)#6	111.0(4)
S(3)#5-Co(3)-S(3)#6	109.3(10)
Se(3)#5-Co(3)-S(3)#7	111.0(4)
Se(3)#6-Co(3)-S(3)#7	111.0(4)
Se(3)#7-Co(3)-S(3)#7	3.4(13)
S(3)#5-Co(3)-S(3)#7	109.3(10)
S(3)#6-Co(3)-S(3)#7	109.3(10)
Se(3)#5-Co(3)-Se(4)#2	106.2(5)
Se(3)#6-Co(3)-Se(4)#2	106.2(5)

Se(3)#7-Co(3)-Se(4)#2	106.2(5)
S(3)#5-Co(3)-Se(4)#2	109.6(10)
S(3)#6-Co(3)-Se(4)#2	109.6(10)
S(3)#7-Co(3)-Se(4)#2	109.6(10)
In(1)#4-Se(1)-In(1)	102.8(3)
In(1)#4-Se(1)-In(1)#8	102.8(3)
In(1)-Se(1)-In(1)#8	102.8(3)
In(1)#4-S(1)-In(1)	107.6(7)
In(1)#4-S(1)-In(1)#8	107.6(7)
In(1)-S(1)-In(1)#8	107.6(7)
In(1)-Se(2)-In(2)#9	121.7(4)
In(1)-Se(2)-In(2)	121.7(4)
In(2)#9-Se(2)-In(2)	95.0(5)
In(1)-Se(2)-In(2)#2	121.7(4)
In(2)#9-Se(2)-In(2)#2	95.0(5)
In(2)-Se(2)-In(2)#2	95.0(5)
In(1)-S(2)-In(2)#9	119.7(7)
In(1)-S(2)-In(2)	119.7(7)
In(2)#9-S(2)-In(2)	97.6(9)
In(1)-S(2)-In(2)#2	119.7(7)
In(2)#9-S(2)-In(2)#2	97.6(9)
In(2)-S(2)-In(2)#2	97.6(9)
Co(3)#10-Se(3)-Co(3)#11	112.6(4)
Co(3)#10-Se(3)-Co(3)#12	112.6(4)
Co(3)#11-Se(3)-Co(3)#12	112.6(4)
Co(3)#10-Se(3)-In(3)#10	6.6(3)
Co(3)#11-Se(3)-In(3)#10	109.6(4)
Co(3)#12-Se(3)-In(3)#10	109.6(4)
Co(3)#10-Se(3)-In(3)#11	109.6(4)
Co(3)#11-Se(3)-In(3)#11	6.6(3)
Co(3)#12-Se(3)-In(3)#11	109.6(4)
In(3)#10-Se(3)-In(3)#11	106.0(4)
Co(3)#10-Se(3)-In(3)#12	109.6(4)
Co(3)#11-Se(3)-In(3)#12	109.6(4)
Co(3)#12-Se(3)-In(3)#12	6.6(3)
In(3)#10-Se(3)-In(3)#12	106.0(4)

In(3)#11-Se(3)-In(3)#12	106.0(4)
Co(3)#10-S(3)-Co(3)#11	109.3(10)
Co(3)#10-S(3)-Co(3)#12	109.3(10)
Co(3)#11-S(3)-Co(3)#12	109.3(10)
Co(3)#10-S(3)-In(3)#10	6.3(3)
Co(3)#11-S(3)-In(3)#10	106.1(11)
Co(3)#12-S(3)-In(3)#10	106.1(11)
Co(3)#10-S(3)-In(3)#11	106.1(11)
Co(3)#11-S(3)-In(3)#11	6.3(3)
Co(3)#12-S(3)-In(3)#11	106.1(11)
In(3)#10-S(3)-In(3)#11	102.3(11)
Co(3)#10-S(3)-In(3)#12	106.1(11)
Co(3)#11-S(3)-In(3)#12	106.1(11)
Co(3)#12-S(3)-In(3)#12	6.3(3)
In(3)#10-S(3)-In(3)#12	102.3(11)
In(3)#11-S(3)-In(3)#12	102.3(11)
In(3)#4-Se(4)-In(2)#9	121.6(12)
In(3)#4-Se(4)-In(2)#8	121.6(12)
In(2)#9-Se(4)-In(2)#8	95.0(16)
In(3)#4-Se(4)-In(2)	121.6(12)
In(2)#9-Se(4)-In(2)	95.0(16)
In(2)#8-Se(4)-In(2)	95.0(16)
In(3)#4-Se(4)-Co(3)#4	0.0
In(2)#9-Se(4)-Co(3)#4	121.6(12)
In(2)#8-Se(4)-Co(3)#4	121.6(12)
In(2)-Se(4)-Co(3)#4	121.6(12)
In(3)#4-S(4)-In(2)#9	121.2(9)
In(3)#4-S(4)-In(2)#8	121.2(9)
In(2)#9-S(4)-In(2)#8	95.6(11)
In(3)#4-S(4)-In(2)	121.2(9)
In(2)#9-S(4)-In(2)	95.6(11)
In(2)#8-S(4)-In(2)	95.6(11)
In(3)#4-S(4)-Co(3)#4	0.0
In(2)#9-S(4)-Co(3)#4	121.2(9)
In(2)#8-S(4)-Co(3)#4	121.2(9)
In(2)-S(4)-Co(3)#4	121.2(9)

Symmetry transformations used to generate equivalent atoms:

#1 x,y+1,z #2 x+1,y+1,z #3 x-1,y,z #4 x-1,y-1,z

#5 x,y,z-1 #6 x+1,y+1,z-1 #7 x+1,y,z-1 #8 x,y-1,z

#9 x+1,y,z #10 x-1,y,z+1 #11 x,y,z+1 #12 x-1,y-1,z+1

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for apoorva_ciss2d_attempt2_hex07_final. The anisotropic

displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
In(1)	17(1)	17(1)	27(1)	0	0	8(1)
In(2)	15(1)	15(1)	24(1)	0	0	7(1)
In(3)	17(1)	17(1)	11(2)	0	0	9(1)
Co(3)	12(2)	12(2)	3(5)	0	0	6(1)
Se(1)	26(3)	26(3)	16(2)	0	0	13(1)
S(1)	15(3)	15(3)	15(2)	0	0	7(2)
Se(2)	18(3)	18(3)	15(2)	0	0	9(2)
S(2)	15(3)	15(3)	15(2)	0	0	7(2)
Se(3)	34(3)	34(3)	21(4)	0	0	17(1)
S(3)	15(3)	15(3)	15(2)	0	0	7(2)
Se(4)	5(5)	5(5)	15(2)	0	0	3(3)
S(4)	15(3)	15(3)	15(2)	0	0	7(2)