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Lithium Rich Composition of Li_2RuO_3 and $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$ Layered Materials as Li-Ion Battery Cathode

S. Sarkar, P. Mahale, and S. Mitra^z

Department of Energy Science and Engineering, Indian Institute of Technology Bombay, Powai Mumbai 400076, India

Li_2MO_3 -based layered structures play an important role in lithium rich composites to realize high energy density cathode for lithium-ion batteries. However, detailed storage mechanism in lithium rich composition is still not clear due to complicated redox chemistry and their synergy effect. In the present work, we report electrochemical property of Li_2RuO_3 and Li_2IrO_3 and their solid solution $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$ ($0 \leq x \leq 1$). Despite having the same structure they differ in space group (C2/c for Li_2RuO_3 and C2/m for Li_2IrO_3), however; show the similar electrochemistry against lithium. The solid solution of $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$ compositions show a mix behavior depending upon the concentration of the specific phase. Electrochemical performance clarified that specific $\text{Li}/\text{Li}_2\text{Ru}_{0.90}\text{Ir}_{0.10}\text{O}_3$ composition shows better cyclic behavior with 198.30 mAh g^{-1} discharge capacity at 40 mA g^{-1} current rate. During this study, few underlying points observed here are 1) high voltage oxidation process is mainly due to O_2 removal during de-lithiation, 2) the amount of O_2 removal decreases as a function of Ir component in the solid solution increases and more importantly 3) we suspect there will be Ru-Ir bond formation along with Ru-Ru and Ir-Ir bonds. These strong metal-metal bonding in the metal oxide plane shifts the electronic energy levels, as a consequence, oxygen removal is somewhat restricted. Therefore, the objective of this project is to extract knowledge from these two layered materials and use further to design new excellent cathode materials.
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LiCoO_2 -based cathode has been widely used in lithium-ion battery due to its stability and well-ordered layered structure which helps in faster lithium-ion kinetics.^{1,2} Since a large scale production of lithium-ion battery focuses mainly on low cost process and environmental safety, hence earth abundant transition metals like iron, manganese and nickel will be of great choice to design or use in any new electrodes. In literature, several LiMO_2 layered type compositions have been studied including $\text{LiNi}_{1/3}\text{Mn}_{1/2}\text{O}_2$ and $\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$ which are regarded as high potential cathode material and with obvious reasons they have attracted much attention in the research community.³⁻⁵ Apart from these two compositions, another composition like Li_2MO_3 which can be represented like $\text{Li}[\text{Li}_{1/3}\text{M}_{2/3}]\text{O}_2$ -layered structure attracted a great deal among the researchers lately.⁶⁻⁸ The composition like Li_2MnO_3 can have high lithium storage capability (theoretically) of 460 mAh g^{-1} , which is much higher than that of existing cathode like LiCoO_2 , LiMn_2O_4 and LiFePO_4 etc. This rocksalt-type layered material has not been considered earlier due to a few fundamental reasons that includes a) high insulating nature and b) the improbability of further oxidation of Mn^{4+} .⁹⁻¹² However, few literature witnessed the capability of such materials to store lithium and exhibit good or reasonable cycling stability over large potential window by using unique materials processing strategies.¹²⁻¹⁴

A great discovery originated after Delmas and coworkers have introduced a revolutionary approach to overcome few issues of Li_2MnO_3 phase and to achieve a high potential and high energy density cathode is by combining Li_2MnO_3 phase with other layered phase like LiMO_2 .¹⁵ Few compositions of such combination showed a unique pathway to create high energy density lithium battery cathode and achieved high storage capacity > 200 mAh g^{-1} with good cyclic stability.^{12,16,17} But, at the same time, the above mentioned approach opened up with few scientific questions like the composition could be considered as homogenous solid solutions or with short range ordered phases which are associated with complicated redox chemistry. Since such ambiguity still persists along with complex phase change during the intercalation/de-intercalation process, which attracts scientific community to devote their research toward lithium rich composition.

With this Li_2MnO_3 - LiMO_2 composition, most approaches so far reported different synthesis strategies including various temperature annealing-cooling cycle processes and changing metal cation with lithium to achieve the best composition in terms of electrochemistry. However, very few attempts have been addressed so far to find out the complex storage mechanism. In recent literature, an attempt to address such complex issues using other transition metal center like

Ru, Sn other than Mn has been reported.¹⁸ The authors have claimed and showed the reaction mechanism with the use of Ru and Sn based composite where Sn^{4+} is difficult to oxidize under the same electrochemical conditions.¹⁸ Since the redox behavior of Mn is completely different from Ru, the complex storage mechanism of $\text{Li}_2\text{RuSnO}_3$ composition cannot be extended directly to LiMnMO_3 systems.

At this conjunction, we have taken composition like Li_2RuO_3 with varying Li_2IrO_3 to form solid solutions. Considering the first few reports in this category, 1) Li_2IrO_3 has been published by Kobayashi et al.,¹⁹ 2) Moore et al. demonstrated the electrochemical behavior of Li_2RuO_3 cathode for lithium-ion batteries.²⁰ More recently, Li_2RuO_3 has been studied by Sathiya et al.²¹ and an excellent electrochemical performance of $\text{Li}_2\text{Ru}_{1-y}\text{Mn}_y\text{O}_3$ has been reported. However, to the best of our knowledge Ru-Ir-based Li_2MO_3 cathode material has not been reported till date. Li_2RuO_3 is monoclinic structure with space group of C2/c as proposed by James et al.,²² whereas Li_2IrO_3 has monoclinic symmetry with space group of C2/m.²³ It is quite interesting to note that the ionic radii of Ru^{4+} and Ir^{4+} are 0.62 Å and 0.63 Å, respectively¹⁹ and due to compatible ionic radii, the solid solution among Ru-Ir is possible in Li_2MO_3 phase. Moreover, unlike Li_2MnO_3 cathode where Mn^{4+} is redox inactive, Ru^{4+} and Ir^{4+} both are redox active. Due to the redox activity of both Ir and Ru, the electrochemistry and the charge/discharge mechanism of Li_2RuO_3 and Li_2IrO_3 are quite different from Li_2MnO_3 . The strategy here is to study the electrochemistry of end member of the solid solution individually and then compare the electrochemistry with $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$ compositions. Thus, exploration of Li_2MO_3 , where M = Ru and Ir are present and its solid solution formation as lithium-ion battery cathode may result in fundamental understanding in this class of materials which shall contribute to further battery electrode development.

Material Synthesis

Synthesis of Li_2RuO_3 powder.— Starting materials for the Li_2RuO_3 synthesis are lithium carbonate (Li_2CO_3 , Sigma Aldrich, 99%), ruthenium chloride (RuCl_3 , Sigma Aldrich, 99.98%). At first, RuCl_3 was annealed at 550°C for 5 h in air atmosphere to form RuO_2 (black) powder. The as-prepared RuO_2 and Li_2CO_3 were mixed in stoichiometric amount and wet milled with isopropyl alcohol (IPA, synthesis grade) as solvent with approximately 1:10 weight ratio of powder to stainless steel (SS) balls. The milling was performed for 10 h at 250 rpm. After ball milling, the sample was dried at 65°C for over-night in air oven. The as-prepared sample was then heated at 850–950°C for 10 h duration in air atmosphere to form Li_2RuO_3 powder.

^zE-mail: sagar.mitra@iitb.ac.in

Synthesis of Li_2IrO_3 powder.— The synthesis of Li_2IrO_3 was similar to the synthesis of Li_2RuO_3 , only ruthenium source needs to be replaced by iridium source. Iridium oxide (IrO_2 , Sigma Aldrich, 99.9%) was used as the starting material. The lithium and iridium sources were ball milled and then calcined at 950°C for 10 h to obtain Li_2IrO_3 black colored powder.

Synthesis of $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$ powder (where $x = 0.01, 0.1, 0.25, 0.50$, and 0.75).— All the compositions of $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$ were carried out by high temperature solid state synthesis method. For $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$ material synthesis, stoichiometric amount of Li_2CO_3 , as-prepared RuO_2 and IrO_2 were mixed and ball-milled for 10 h at 250 rpm in wet medium (IPA was used as solvent). The as-prepared sample was heated for 10 h at 950°C in air atmosphere to form desired compositions.

Structural and morphological characterization.— X-ray powder diffraction (XRD) was performed using a Philips X'pert X-ray diffractometer equipped with a $\text{Cu-K}\alpha$ radiation source. Morphological analysis was carried out by field emission gun scanning electron microscope (FEG-SEM, Carl-Zeiss, Ultra 55).

Electrochemical characterization.— Electrochemical charge/discharge experiments were carried out using CR2032 type coin cell or Swagelok type test cell in Arbin charge/discharge station (BT 2000, USA). At first, electrode materials were prepared by mixing of $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$ with conducting carbon (Super C-65, Timcal) and polyvinylidene difluoride (PVDF, Sigma Aldrich) as binder in the weight ratio of 70:20:10, respectively. The slurry was prepared by adding few drops of N-methylpyrrolidone (NMP, Fisher Scientific) in the mixture and then tape cast on Al foil. The tape cast foil was dried at 65°C for 12 h. The dried films were used as working electrodes to test lithium-ion battery performance in half cell configuration. The cells were assembled in argon filled glove box where lithium metal foil and $\text{LiRu}_{1-x}\text{Ir}_x\text{O}_3$ were punched out as circular disks, borosilicate glass fiber was used as separator, and 1 M LiPF_6 dissolved in EC/DMC (1:1) (LP-30, Merck) as electrolyte. All the electrochemical tests were conducted in constant temperature at $20 \pm 2^\circ\text{C}$ and controlled humidity condition. Cyclic voltammetric (CV) experiments were performed at 0.1 mV s^{-1} scan rate in Bio-logic VMP-3 unit. For galvanostatic intermittent titration technique (GITT) experiment (Bio-logic VMP-3), the cell was charged and discharged for 30 min at a rate of 10 mA g^{-1} followed by residence time of 30 min. All the electrochemical measurements were carried out in the potential window of 2.0 V–4.6 V.

Results and Discussion

Li_2RuO_3 Cathode material for lithium storage.— The Li_2RuO_3 phase was prepared by high temperature solid state reaction from stoichiometric amounts of RuO_2 and Li_2CO_3 as precursors and the structure has been confirmed by XRD study. As we mentioned earlier, RuO_2 was prepared separately and analyzed first. Figure 1 shows the X-ray diffraction (XRD) of as-synthesized RuO_2 prepared from decomposition of RuCl_3 at 550°C . The XRD shows well-ordered RuO_2 tetragonal phase with $\text{P4}_2/\text{mm}$ space group (JCPDS # 88-0322). The inset Figure (Figure 1) shows the morphology of RuO_2 material. The growth of RuO_2 particles shows a multi-faceted morphology. The estimated particle size of RuO_2 varies from 50–60 nm with occasional aggregation to larger particles of size ~ 90 –100 nm.

The as-prepared RuO_2 was used for the preparation of Li_2RuO_3 cathode material. The XRD of Li_2RuO_3 material synthesized at various temperatures is shown in Figure 2. The XRD pattern for the sample prepared at 850°C shows less ordered monoclinic phase (space group C2/c). However, on annealing at higher temperature more ordering was observed with larger particle-size (inset of Figure 2). Also, an increase in relative intensity ratio of $I_{(002)}/I_{(020)}$ was observed with the increase in synthesis temperature. The intensity ratio of $I_{(002)}/I_{(020)}$ varies as 0.82, 2.93, 3.36 for 850°C , 900°C and 950°C , respectively

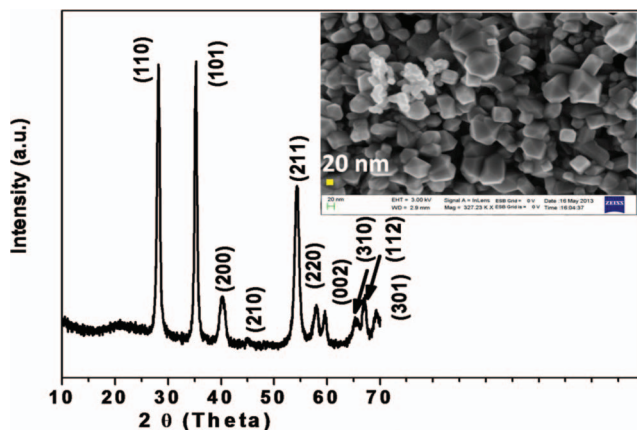


Figure 1. X-ray diffraction pattern of RuO_2 powder prepared at 550°C (Inset: FEG-SEM micrograph of RuO_2).

which indicates more crystal ordering at higher temperature. The inset of Figure 2 shows the morphology of Li_2RuO_3 at different temperature of annealing process. Li_2RuO_3 particles grow with multi-faceted morphology with varying the shape as observed from FEG-SEM study. The estimated particle size of Li_2RuO_3 was $\sim 2 \mu\text{m}$ with slight increase in grain size as a function of temperature (which increases slightly with the temperature) was observed.

As we know, Li_2RuO_3 is a layered material with alternate layers of Li^+ and Ru^{4+} in the rock-salt crystal structure where oxygen forms the cubic close pack lattice (Figure 3a). More interestingly, Ru^{4+} makes a quadruple bond with neighboring Ru^{4+} in honey comb lattice of edge sharing RuO_6 present as layers in Li_2RuO_3 . Due to this significant metal-metal bonding between Ru^{4+} – Ru^{4+} , the layered oxide exhibits good electronic and ionic conductivity and displays better electrochemical activity than Li_2MnO_3 .^{21,24} To explain the bonding in Ru-system; molecular orbital theory was used to demonstrate the formation of quadruple bonding (Figure 3b). The three occupied t_{2g} orbitals of Ru combine to forms σ , π ; σ bonding and anti-bonding molecular orbital as described in the schematics (Figure 3b).²⁵

During charging, de-insertion of lithium-ion is balanced by corresponding oxidation of $\text{Ru}^{4+}/\text{Ru}^{5+}$ in Li_2RuO_3 at average

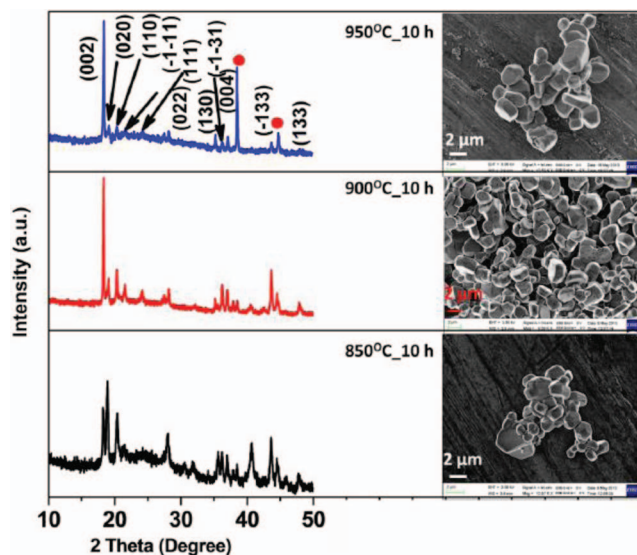


Figure 2. X-ray diffraction pattern of Li_2RuO_3 prepared at various temperatures (Inset: FEG-SEM micrograph of Li_2RuO_3) and red dots in XRD pattern: aluminum substrate.

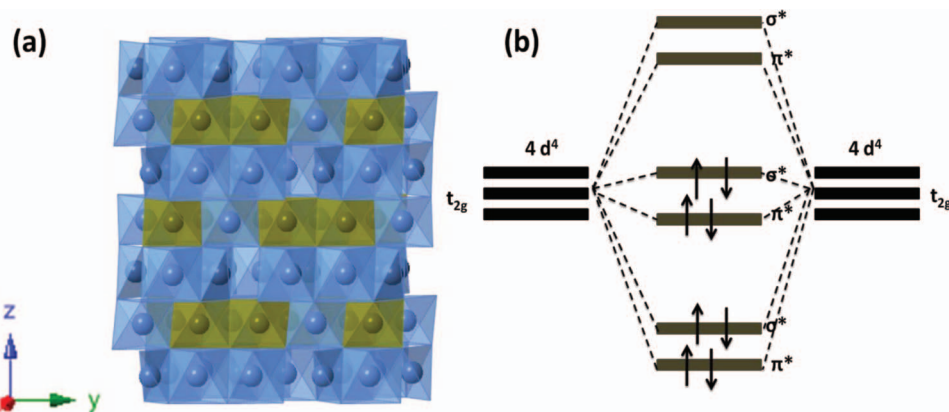


Figure 3. a) Orbital diagram of Ru^{4+} - Ru^{4+} metal-metal quadruple bond, and b) Crystal structure of Li_2RuO_3 along [100] plane (blue polyhedron: Li, and yellow polyhedron: Ru).

plateau ~ 3.65 V vs. Li^+/Li . The charge/discharge profile of Li_2RuO_3 along with various synthesis temperatures is shown in the Figure 4a. The charge capacity of Li_2RuO_3 increases with the increase in annealing temperature which is consistent with XRD study revealing the ordering of Li_2RuO_3 crystal in terms of the change in the relative

intensity ratio of $I_{(002)}/I_{(020)}$. The initial charge capacity of samples prepared at 850°C , 900°C , and 950°C were observed to be ~ 189.4 mAh g^{-1} , 208.7 mAh g^{-1} and 234.86 mAh g^{-1} , respectively under similar electrochemical conditions. The current observation estimated the number of lithium ions de-inserted from Li_2RuO_3 host matrix per formula unit to be ~ 1.45 for sample annealed at 950°C . However, as mentioned above that oxidation of Ru^{4+} to Ru^{5+} is possible which leads to the conclusion that removal of one lithium-ion from the host is feasible. Therefore, the extra capacity that arises (0.45 Li per metal cation) could be due to several other reasons described by various researchers.^{26–28} To describe a possible mechanism for extra charge storage here, we can draw a parallel conclusion between iso-structural Li_2MnO_3 and Li_2RuO_3 . However, unlike ruthenium, manganese cannot be oxidized beyond (+4) state in an octahedral oxygen environment, nevertheless; lithium extraction in Li_2MnO_3 has been reported not by oxidation of Mn^{4+} but by two other possible phenomenon which can be extended to account for excess lithium removal beyond $x = 1$ in $\text{Li}_{2-x}\text{RuO}_3$. Since further oxidation of Ru^{4+} is not possible, these phenomenon can be extended for excess lithium removal beyond $x = 1$ in $\text{Li}_{2-x}\text{RuO}_3$. Robertson et al. have shown that one-for-one exchange of lithium-ion and H^+ occurs in Li_2MnO_3 at 55°C to form $\text{Li}_{2-x}\text{H}_x\text{MnO}_3$.²⁶ However, at lower temperature $\sim 30^\circ\text{C}$ initial charging is accompanied by oxygen loss from oxide lattice and during further charging lithium-ion is exchanged for H^+ . More-recently, Amalraj et al. have also showed removal of oxygen from Li_2MnO_3 structure at 30°C and proton exchange mechanism at 60°C with phase transformation from layered to both cubic spinel and layered structure.²⁷ Similarly, in Li_2RuO_3 charge and discharge processes leads to transformation Li_2RuO_3 to different phases. To identify these phases, ex-situ X-ray diffraction experiments have been performed at various stages of charge state as shown in Figure 4b. X-ray diffraction pattern of pristine Li_2RuO_3 shows no impurity, however, when one mole of Li^+ is removed from the host matrix, the signature peaks of monoclinic Li_2RuO_3 has changed to two other phases: $\text{Li}_{0.9}\text{RuO}_3$ [rhombohedral (JCPDS file # 85–2002)] and $\text{Li}_{1.4}\text{RuO}_3$ [monoclinic (JCPDS file # 85–2001)] with some signature peaks still resembled the pristine Li_2RuO_3 structure (unreacted). With further removal of Li-ion at the level of $x = 1.4$, the peaks are identical to the rhombohedral phase of $\text{Li}_{0.9}\text{RuO}_3$. It is noteworthy to mention here that during discharge at 2.2 V vs. Li^+/Li , XRD pattern showed the reappearance of pristine Li_2RuO_3 phase with small amount of impurity due to rhombohedral $\text{Li}_{0.9}\text{RuO}_3$ phase. However, on further discharge to 2 V vs. Li^+/Li both the phases Li_2RuO_3 and $\text{Li}_{0.9}\text{RuO}_3$ co-exist. It is evident from ex-situ XRD of Li_2RuO_3 after 50th cycle that $\text{Li}_{0.9}\text{RuO}_3$ phase is predominant. It can be concluded here that Li_2RuO_3 constantly changes its phase with the increase in cycle number. Similar to the charge capacity, discharge capacity of Li_2RuO_3 increases with the increase in synthesis (annealing) temperature. The

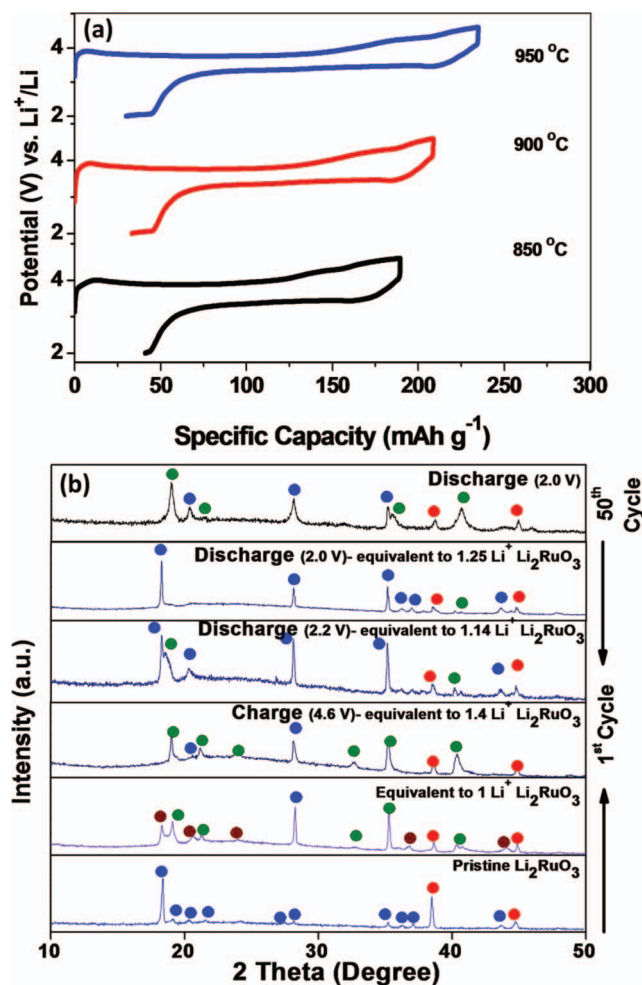


Figure 4. a) 1st Charge/discharge profile of Li_2RuO_3 prepared at various temperature (current rate: 20 mA g^{-1}), and (b) X-ray diffraction pattern of Li_2RuO_3 cathode at various stages of charge (blue dots: Li_2RuO_3 , green dots: $\text{Li}_{0.9}\text{RuO}_3$, dark red dots: $\text{Li}_{1.4}\text{RuO}_3$, and red dots: aluminum substrate).

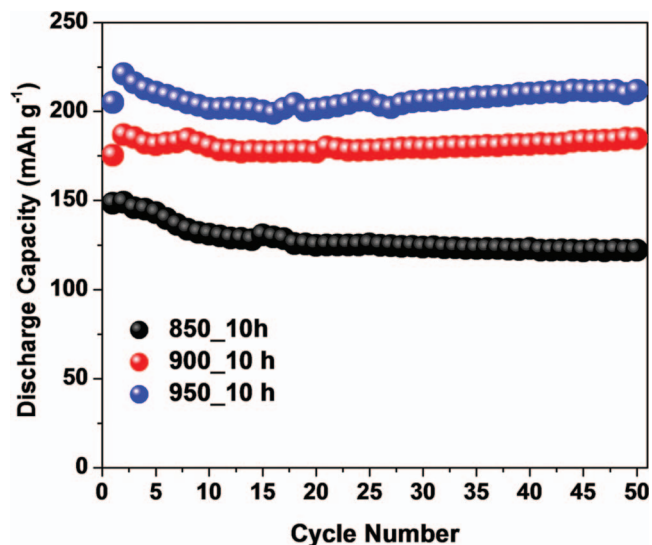


Figure 5. Discharge capacity of Li_2RuO_3 prepared at different temperature (current rate: 20 mA g^{-1}).

first discharge capacity of the samples prepared at 850°C , 900°C and 950°C were $148.36 \text{ mAh g}^{-1}$, 175 mAh g^{-1} , and 205 mAh g^{-1} , respectively. As evident from Figure 4a, the irreversible capacity loss decreases by increasing the synthesis (annealing) temperature and the losses are 29.86 mAh g^{-1} , 33.7 mAh g^{-1} , and 41 mAh g^{-1} for 950°C , 900°C and 850°C , respectively. The origin of irreversible capacity loss in Li_2RuO_3 may be due to evolution of oxygen from the host matrix in initial charge cycles and more discussion on this will be done in later stage of this report. The cyclic performance of Li_2RuO_3 synthesized at different temperatures, was observed by plotting discharge capacity of Li_2RuO_3 as a function of cycle number at 20 mA g^{-1} current rate as shown in Figure 5 synthesized at various temperatures. Li_2RuO_3 samples annealed for 10 h at different temperatures have shown excellent capacity retention for 50 charge-discharge cycles.

Lithium storage performance of $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$.— The crystal structure of layered Li_2IrO_3 is shown in Figure 6a, where oxygen forms the cubic close pack lattice. Akin to Ru-Ru metal-metal bonds, Ir can also form quadruple bonds whose molecular orbital arrangement and bond formation is shown in Figure 6b (as schematic). Due to its ability to exist in multiple oxidation states, Ru-Ir bond formation and redox activity of this electrode material can show possible lithium storage capability. Being similar size, Ir can easily occupy Ru's lattice

space in monoclinic structure and vice-versa to form possible solid-solution between Ir-Ru in $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$. Further, Ir and Ru can form quadruple bonds i.e. $\text{Ir}^{4+}\text{-Ru}^{4+}$ metal-metal bonds together with existing $\text{Ir}^{4+}\text{-Ir}^{4+}$ and $\text{Ru}^{4+}\text{-Ru}^{4+}$ metal-metal bonds. Thus, preventing any drastic crystallographic change and thereby preserving the advantage of layered structure and the metal-metal bond.

Since, Li_2RuO_3 shows best performance when synthesized at 950°C for 10 h, therefore; similar synthesis condition was used for Li_2IrO_3 preparation and for solid-solution between Ir-Ru in $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$ with end members being Li_2RuO_3 and Li_2IrO_3 . Figure 7a shows the XRD pattern of $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$ (where $x = 0, 0.01, 0.10, 0.25, 0.50, 0.75$, and 1.0). Ru rich compounds were indexed with monoclinic phase with space group C2/c ($x = 0, 0.01$ and 0.10) and Ir-rich compounds with monoclinic phase with space group C2/m . We propose that the Ru rich compounds ($x = 0, 0.01$ and 0.10) have monoclinic phase with space group C2/c whereas samples having $x = 0.25$ and above possess monoclinic phase with space group C2/m . It was observed from Figure 7b that for the initial members ($x = 0.01$, and 0.10) the peaks for (002) are shifted toward lower 2θ value and the subsequent members show a shift toward higher 2θ value. This phenomenon can be well understood from Figure 7b, which suggests that Ir occupies Ru lattice sites for $x = 0.01$, and 0.10 compositions, thus might form solid-solution between Ir-Ru in $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$ with space group C2/c . Since, Ir has larger ionic radii compared to Ru, a probable shift in lower Bragg angle (2θ) is expected. However, with a progressive increase in Ir concentration, the peak shift toward higher 2θ value as smaller size of Ir occupies Ir lattice site in the crystal structure having C2/m space group. This is in accordance with the crystal information file (CIF) # 246025 where Li_2IrO_3 possess its first characteristic peak (001) at 18.391° (2θ value) and peak (002) for Li_2RuO_3 is at 18.229° (2θ value) (CIF #78721) which indicates that as characteristic “x” value increases there should be an obvious peak shift toward higher 2θ value. The as-prepared solid-solution of Ir-Ru at $x = 0.01$ and 0.10 exists with space group C2/c whereas for $x = 0.25, 0.50, 0.75$ and 1 sample has monoclinic phase with C2/m space group. It is noteworthy to mention that a system that exhibits solid-solution, it is essential that two end-member phase be iso-structural. Both the system represents monoclinic structure with C2/c space group for Li_2RuO_3 system and C2/m space group for Li_2IrO_3 . To understand the formation of solid solution between Ru-Ir in $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$, d_{spacing} of highest intense peak was plotted against composition (Figure 7c), which shows a positive departure from linearity as suggested by Vegard's law. The positive deviation from linearity of Vegard's law is possible due to immiscibility of Ru-Ir at 950°C temperature for 10 h. The possible explanation for immiscibility of Ru-Ir may be due to arrangement of atoms in random manner and clustered together to form Ru and Ir rich domains, even though solid solution between Ru-Ir in $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$ appears in macroscopic scale.

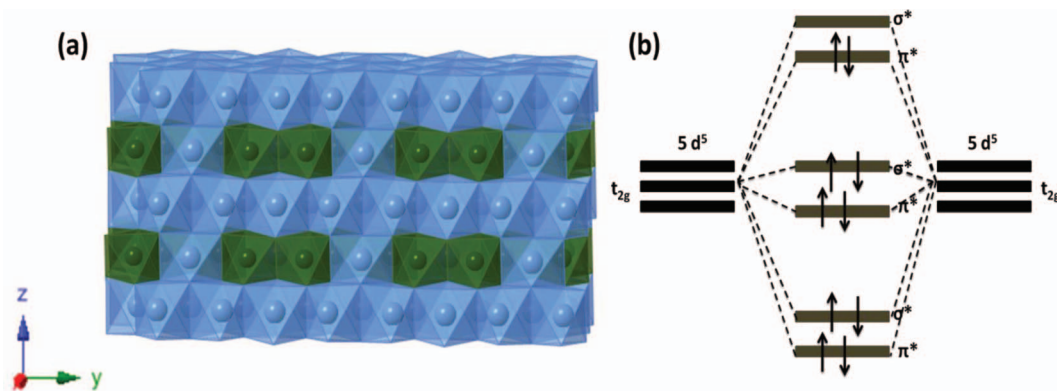


Figure 6. a) Orbital diagram of $\text{Ir}^{4+}\text{-Ir}^{4+}$ metal-metal bond, b) Crystal structure of Li_2IrO_3 along $[100]$ (blue polyhedron: Li, and green polyhedron: Ir).

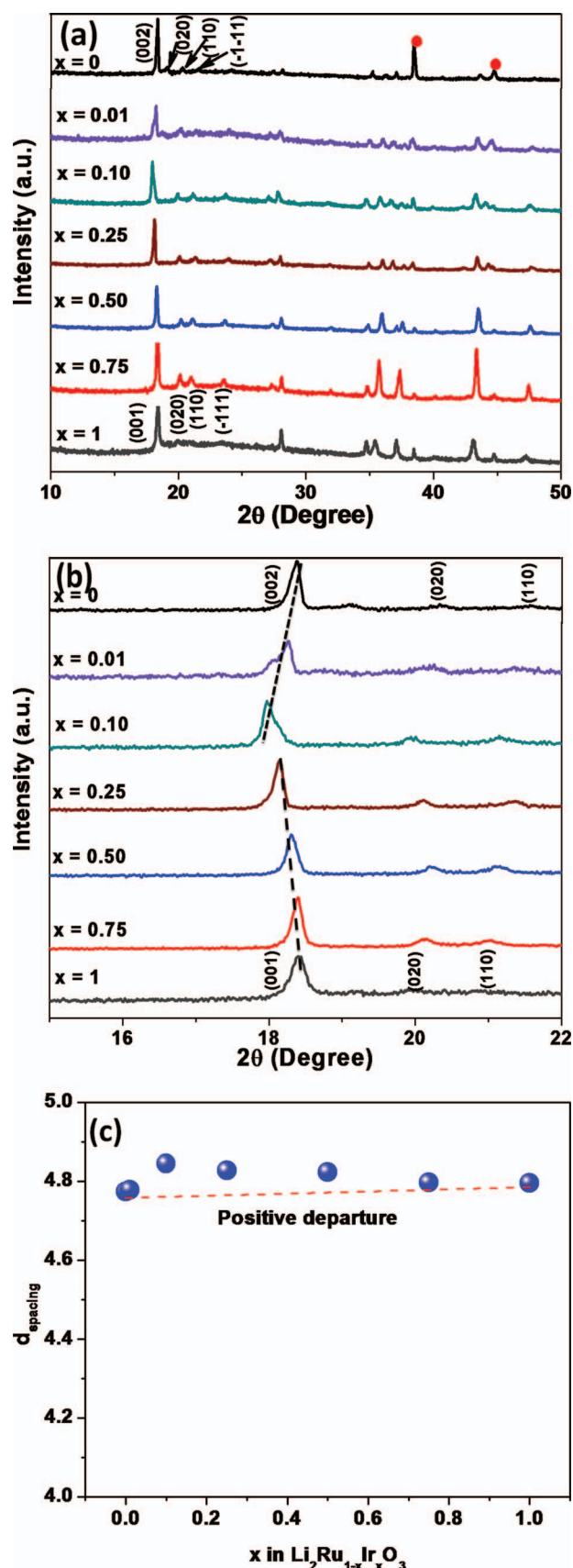


Figure 7. a) X-ray diffraction pattern of $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$ with varying composition “ x ” prepared by solid state reaction at 950°C for 10 h (red dots: aluminum substrate), b) Zoomed portion of XRD of $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$, and c) Positive departure from linearity of d_{spacing} for highest intensity peak ~ 18 for $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$.

The Figure 8 shows the morphology of $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$ synthesized at 950°C obtained from FEG-SEM experiments. As illustrated in Figure 8, the particle size of Li_2RuO_3 grows with Ir concentration for $x = 0.01$ and 0.10 where Ir occupies Ru sites in the monoclinic phase (C2/c), whereas, further increase in Ir concentration at $x = 0.25$ in $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$ particle size starts decreasing, this trend in decreasing particle size with increasing Ir concentration was prevalent in the entire sample range from $x = 0.25$ to $x = 1.0$. The exact reason behind the fact is unknown here and we will investigate it further in near future.

Figure 9 shows the 1st, 2nd, 25th and 50th charge/discharge profile of $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$ samples with varying composition “ x ” at 40 mA g^{-1} current rate in $2.0 \text{ V} - 4.6 \text{ V}$ vs. Li^+/Li potential window. The 1st charge plateau for $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$ occurs at average potential of 3.65 V , and 3.75 V vs. Li^+/Li for redox couple of $\text{Ru}^{4+/5+}$ and $\text{Ir}^{4+/5+}$, respectively; whereas 1st discharge plateau occurs at 3.34 V , and 3.54 V vs. Li^+/Li for $\text{Ru}^{4+/5+}$ and $\text{Ir}^{4+/5+}$, respectively which accounts for insertion/de-insertion of 1 Li^+ per formula unit of $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$. It is noteworthy to mention that at $\sim 4.0 \text{ V}$ vs. Li^+/Li region there is a steep increase in potential observed in the charge profile which could be due to the evolution of oxygen from the $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$ lattice. This also explains the excess removal of lithium beyond 1 Li^+ per formula unit. At $x = 0, 0.01$, and 0.10 for monoclinic phase with space group C2/c, there is a detectable plateau $\sim 2.05 \text{ V}$ vs. Li^+/Li , however at onset of higher values of x i.e. from $x = 0.25$ the same plateau $\sim 2.05 \text{ V}$ vs. Li^+/Li disappeared further suggesting a change to C2/m phase in $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$, which is consistent with the XRD (Figure 7) results. It is noticeable here that with the increase of Ir in $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$, a sloppy region in the charge curve arises between $3.7 \text{ V} - 4.1 \text{ V}$ and $4.3 \text{ V} - 4.6 \text{ V}$, this is due to rhombohedral symmetry of $\text{Li}_{0.9}\text{IrO}_3/\text{Li}_{0.9}\text{RuO}_3$ phase.¹⁹ It is interesting to mention here that after 1st charge/discharge cycle of Li_2RuO_3 sample the V vs. Q profile has two distinct plateaus (2nd, 25th and 50th cycles). The two distinct plateaus of Li_2RuO_3 indicates the multiple phase process which occurs at 3.66 V and 3.44 V during charge and 3.43 V and 3.29 V during discharge which is similar to earlier reports.^{29,30} It is noticeable here that the plateau above 4 V region in charge profile disappear after 1st cycle. The nature of the charge and discharge profile for 2nd, 25th and 50th cycles are identical in nature, which suggests structural reorientation after irreversible removable of oxygen during the first charging process.

Though Ru and Ir system have distinct charge/discharge profiles, however, the formation of solid solution between Ru-Ir system can be concluded from the CV (Figure 10a) profile of $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$ cathode. When $x = 0$ and $x = 1$ the CV profile designated the characteristic profile of pristine Li_2RuO_3 and of Li_2IrO_3 , respectively. With the increase in Ir concentration, the anodic peak shifted toward higher potential and forms unique CV profile which is distinct from pristine Li_2RuO_3 , and Li_2IrO_3 samples. To confirm the current findings regarding the change in charge/discharge profile of $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$ cathode material, galvanostatic intermittent titration technique (GITT) was performed for the compositions at $x = 0, 0.5$, and 1 . GITT was performed by applying 10 mA g^{-1} current for 30 min followed by 30 min relaxation time. The GITT profile illustrated in Figure 10b again confirms the change of nature of plateau for Li_2RuO_3 after 1st cycle, whereas in $\text{Li}_2\text{Ru}_{0.5}\text{Ir}_{0.5}\text{O}_3$ composition the plateaus are neither of Ru nor of Ir system, but forming a unique plateau due to the formation of solid solution between Ru-Ir. Further, the chemical diffusion coefficient of lithium-ion for Li_2RuO_3 , $\text{Li}_2\text{Ru}_{0.5}\text{Ir}_{0.5}\text{O}_3$ and Li_2IrO_3 cathode material was calculated according to equation given below:³¹

$$D_{\text{Lithium}} = (4/\pi) \cdot (V_M/SF)^2 \cdot (i^0 \Delta E_s / (\delta E_s / \delta \sqrt{t}))^2$$

where $t \leq \tau$; V_M , S , F , and i^0 are the molar volume, surface area between electrode and electrolyte, Faradays constant and current applied. ΔE_s is change in the steady-state voltage obtained by subtracting the terminating voltage E_0 from the steady-state voltage E_s while $\delta E_s / \delta \sqrt{t}$ is the slope of short-time transient voltage change. The lithium diffusion co-efficient during first charge process of Li_2RuO_3 , $\text{Li}_2\text{Ru}_{0.5}\text{Ir}_{0.5}\text{O}_3$ and Li_2IrO_3 varies from 10^{-10} – $10^{-13} \text{ cm}^2 \text{ s}^{-1}$, 10^{-12} –

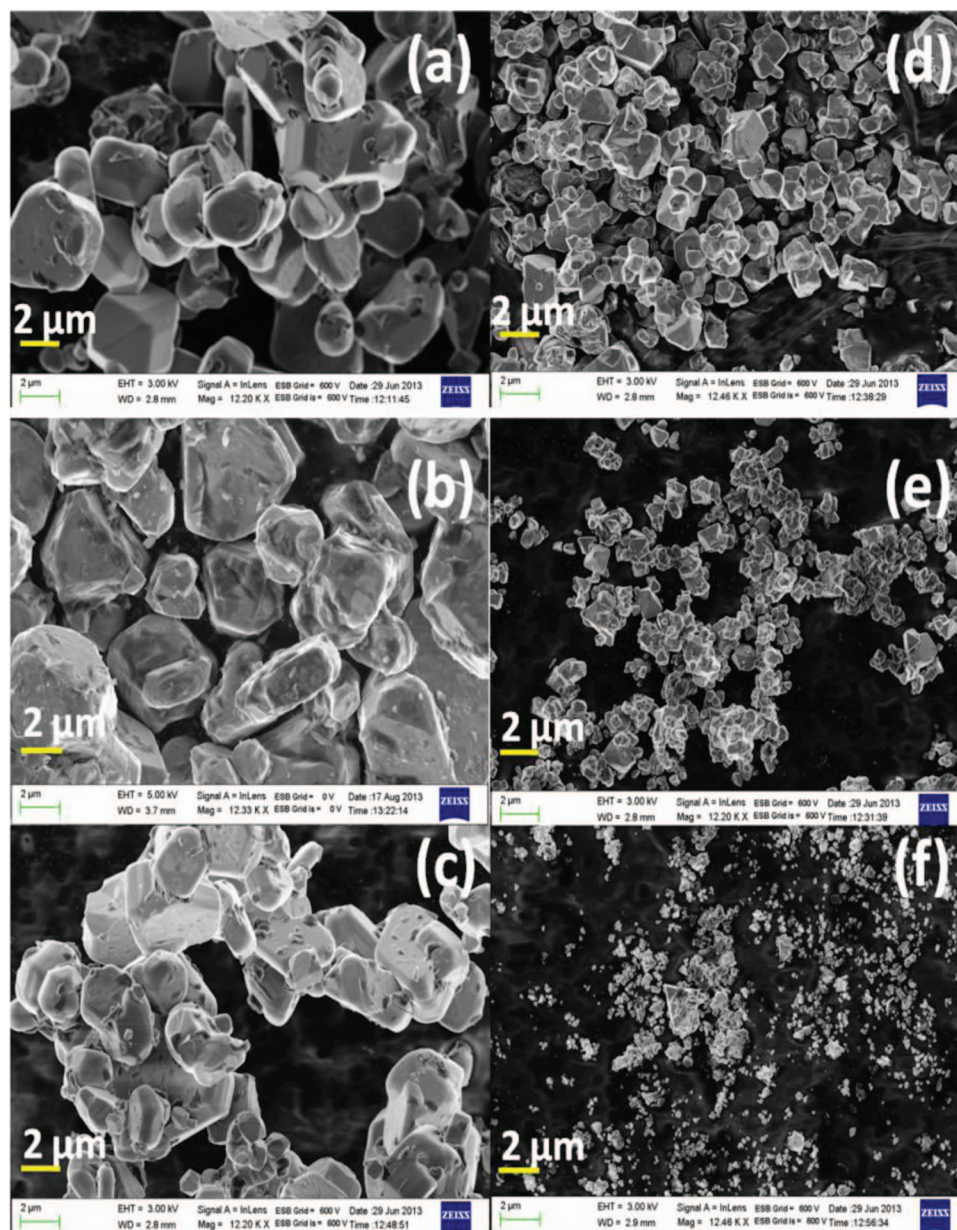


Figure 8. FEG-SEM of $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$ with varying composition “x” prepared by solid state reaction at 950°C at 10 h [a) $x = 0.01$, b) $x = 0.10$, c) $x = 0.25$, d) $x = 0.50$, e) $x = 0.75$, and f) $x = 1.0$].

$10^{-14} \text{ cm}^2 \text{ s}^{-1}$ and 10^{-14} – $10^{-15} \text{ cm}^2 \text{ s}^{-1}$, respectively; however the variation of diffusion co-efficient during first discharge was quite significant. In discharge process, diffusion co-efficient value varies from 10^{-8} – $10^{-12} \text{ cm}^2 \text{ s}^{-1}$, 10^{-11} – $10^{-13} \text{ cm}^2 \text{ s}^{-1}$ and 10^{-9} – $10^{-12} \text{ cm}^2 \text{ s}^{-1}$ for Li_2RuO_3 , $\text{Li}_2\text{Ru}_{0.5}\text{Ir}_{0.5}\text{O}_3$ and Li_2IrO_3 , respectively. After first charge/discharge process, structural rearrangement of $\text{Li}_2\text{Ru}_x\text{Ir}_x\text{O}_3$ takes place as evident from Figure 9, so; the diffusion co-efficient values in second charge process calculated by GITT varies significantly compared to first charge process which is in the range of 10^{-9} – $10^{-12} \text{ cm}^2 \text{ s}^{-1}$, 10^{-11} – $10^{-14} \text{ cm}^2 \text{ s}^{-1}$ and 10^{-9} – $10^{-13} \text{ cm}^2 \text{ s}^{-1}$ for Li_2RuO_3 , $\text{Li}_2\text{Ru}_{0.5}\text{Ir}_{0.5}\text{O}_3$ and Li_2IrO_3 , respectively. Further, during second discharge process variation in the value of diffusion co-efficient is comparable with that of first discharge process. The diffusion co-efficient of Li_2RuO_3 , $\text{Li}_2\text{Ru}_{0.5}\text{Ir}_{0.5}\text{O}_3$ and Li_2IrO_3 was estimated to be in the order of 10^{-9} – $10^{-12} \text{ cm}^2 \text{ s}^{-1}$, 10^{-11} – $10^{-13} \text{ cm}^2 \text{ s}^{-1}$ and 10^{-10} – $10^{-12} \text{ cm}^2 \text{ s}^{-1}$, respectively.

The de-lithiation process and charge compensation of $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$ electrode can be better understood by density of states (DOS) calculation for Li_2RuO_3 , and Li_2IrO_3 . A detailed DOS study has been carried out by Johannes et al.³² for Li_2RuO_3 and O’Malley et al.³³ for Li_2IrO_3 . To understand the lithium de-insertion process in closer angle, previous DOS study of Li_2RuO_3 and Li_2IrO_3 have been taken into account.^{32,33} Figure 11 shows the schematics of electronic band structure of Li_2RuO_3 , Li_2IrO_3 (from literature) and possible structure for $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$ (as schematic). As illustrated in the schematic, octahedral co-ordinate Ru^{4+} splits into t_{2g} (π^*) and e_g (σ^*) states where RuO_6 octahedra broaden the anti-bonding M-O levels into bands. Also, Li_2RuO_3 displays $2/3$ filled $\text{Ru}^{4+}(t_{2g})$ -band in which electrons are de-localized over Ru-O and Ru-Ru bonds, whereas; for Li_2IrO_3 $5/6$ filled $\text{Ir}^{4+}(t_{2g})$ -band electrons are delocalized over Ir-O and Ir-Ir bonds. Similar assumptions were made here for $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$ band structure shown in Figure 11. Considering at $x = 0.10$

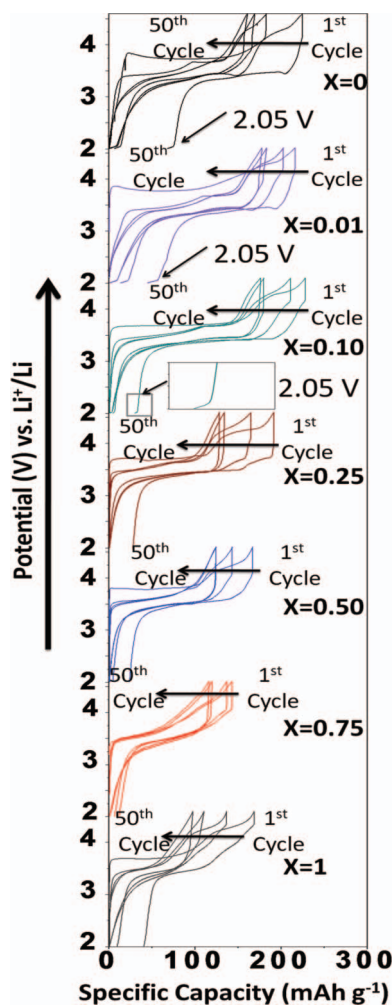


Figure 9. Galvanostatic charge-discharge profile of $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$ at 40 mA g^{-1} current rate (1st, 2nd, 25th and 50th cycle).

composition, i.e., $\text{Li}_2\text{Ru}_{0.90}\text{Ir}_{0.10}\text{O}_3$, Ru^{4+} is first to be oxidized into Ru^{5+} when Li^+ is removed with average potential $\sim 3.65 \text{ V}$, where t_{2g} -band of Ru^{5+} is merged with e_g band of O (2p)-band. Further, de-lithiation of $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$ will take place by oxidation of Ir^{4+} to $\text{Ir}^{5+} \sim 3.75 \text{ V}$ vs. Li^+/Li potential range. As further oxidation of Ru^{5+} , and Ir^{5+} is not possible, the de-lithiation of lithium-ion is supported by irreversible removable of oxygen $> 4.2 \text{ V}$ within $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$ system, was ascribed to loss of oxygen from the lattice. The capacity contribution due to loss of oxygen is shown in Figure 12a, as it is well illustrated that with the increase in Ir percentage in $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$, the evolution of oxygen decreases to certain extent. To explain the phase transformation and oxygen evolution from the host matrix, dq/dV plot against potential for $x = 0.5$ composition is drawn and shown in Figure 12b. It is evident from Figure 12b that de-insertion beyond 1 Li^+ is possible either creating oxygen vacancy or proton exchange. Further, extraction of Li^+ from Li_2RuO_3 occurs above 4.0 V ($4.1\text{--}4.3 \text{ V}$), which is ascribed to the irreversible loss of the oxygen from the lattice as commonly observed in the $\text{Li}_2\text{MnO}_3\text{--LiMO}_2$ system.²¹ As seen from potentiodynamic plot (Figure 12b), a unique peak between $\sim 3.79\text{--}3.9 \text{ V}$ in 1st cycle suggest that de-insertion of lithium occurring in single step, however; with increasing cycle number two distinct peaks $\sim 3.44\text{--}3.9 \text{ V}$ were observed which is consistent with CV and GITT experiments (Figure 10).

Figure 12a shows the capacity contribution in the first discharge cycle and oxygen evolution from the first charge process. It is evident from the Figure 9, a plateau is observed due to extraction of more than 1 Li^+ , above $> 4.0 \text{ V}$ within $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$ system, was ascribed to loss of oxygen from the lattice. The capacity contribution due to loss of oxygen is shown in Figure 12a, as it is well illustrated that with the increase in Ir percentage in $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$, the evolution of oxygen decreases to certain extent. To explain the phase transformation and oxygen evolution from the host matrix, dq/dV plot against potential for $x = 0.5$ composition is drawn and shown in Figure 12b. It is evident from Figure 12b that de-insertion beyond 1 Li^+ is possible either creating oxygen vacancy or proton exchange. Further, extraction of Li^+ from Li_2RuO_3 occurs above 4.0 V ($4.1\text{--}4.3 \text{ V}$), which is ascribed to the irreversible loss of the oxygen from the lattice as commonly observed in the $\text{Li}_2\text{MnO}_3\text{--LiMO}_2$ system.²¹ As seen from potentiodynamic plot (Figure 12b), a unique peak between $\sim 3.79\text{--}3.9 \text{ V}$ in 1st cycle suggest that de-insertion of lithium occurring in single step, however; with increasing cycle number two distinct peaks $\sim 3.44\text{--}3.9 \text{ V}$ were observed which is consistent with CV and GITT experiments (Figure 10).

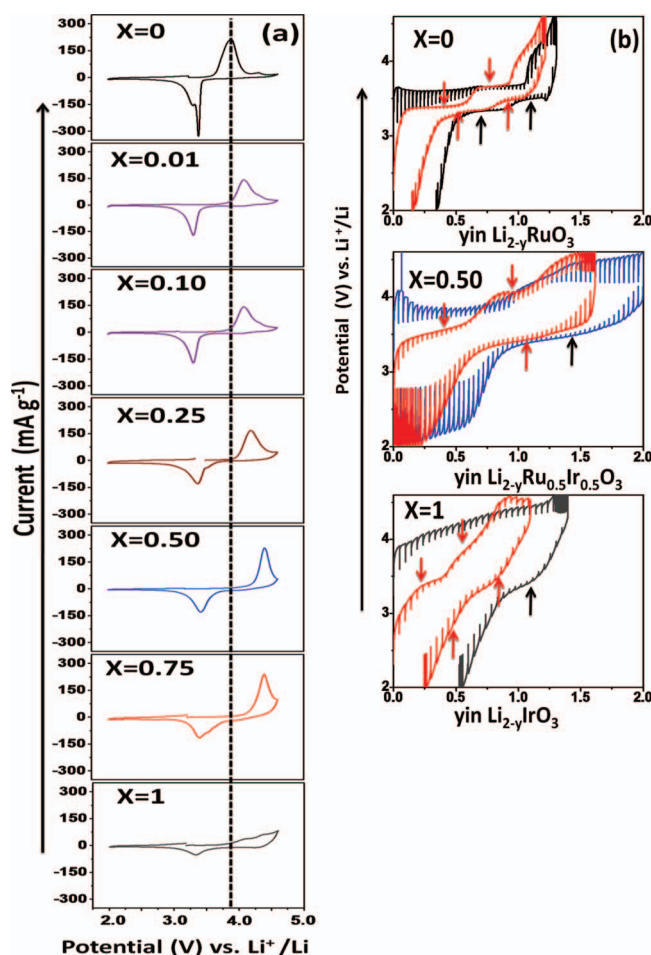


Figure 10. a) CV profile for 1st cycle of $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$ at 0.1 mV s^{-1} scan rate, and b) GITT for 1st and 2nd cycle of $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$ ($x = 0, 0.50$, and 1) at 10 mA g^{-1} current rate (red color profile for second cycle, black arrow for 1st cycle, and red arrow for 2nd cycle showing plateau region).

The splitting of single peak in to two distinct peaks suggest that the de-insertion of Li^+ after 1st cycle occurs in two steps. Further, the capacity contribution for $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$ ($x = 0.5$) between $4.1\text{--}4.3 \text{ V}$ during charging was estimated to be $\sim 31 \text{ mAh g}^{-1}$, which decreases

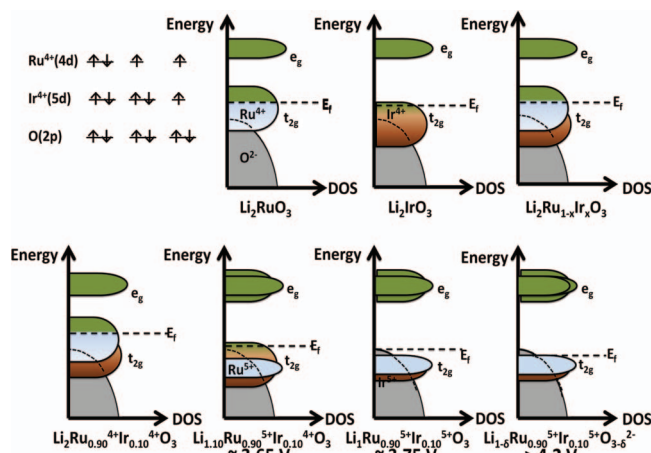


Figure 11. Schematic representation of the density of states of Li_2RuO_3 , Li_2IrO_3 (from literature)^{32,33} and $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$ in which Fermi level is marked as dotted line. The DOS of $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$ is an assumption case based on individual DOS of Li_2RuO_3 and Li_2IrO_3 and molecular orbital theory.

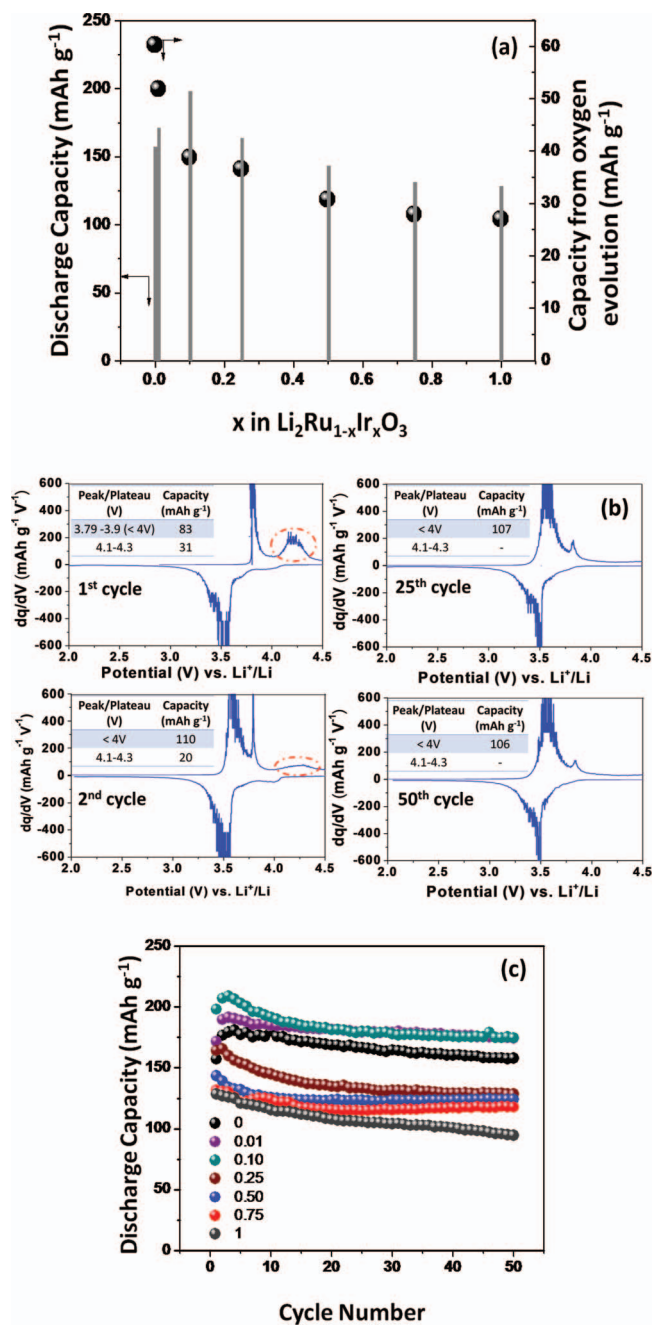


Figure 12. a) First discharge capacity for $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$ (bar graph) and capacity contribution from the evolution of oxygen from $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$ lattice during charge process (black dots), b) dq/dV plot for $\text{Li}_2\text{Ru}_{0.5}\text{Ir}_{0.5}\text{O}_3$ composition for 1st, 2nd, 25th and 50th cycle and c) Discharge curve against cycle number for $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$ with varying composition “ x ” at 40 mA g⁻¹ current rate.

after 1st cycle (shown in inset table of Figure 12b). It is interesting to mention here that with further increase in cycle number (25th and 50th cycle) no such peak ~4.1–4.3 V was observed which again suggests complete phase transformation of $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$ (where $x = 0.5$). As shown in Figure 12a, capacity contribution of Li_2RuO_3 is ~60 mAh g⁻¹ during 1st charge cycle due to oxygen evolution (plateau ~4.1–4.3 V) which is much higher compared to $\text{Li}_2\text{Ru}_{0.5}\text{Ir}_{0.5}\text{O}_3$ composition (~31 mAh g⁻¹) and decreases with cycle number. From the above discussion (Figure 12a and Figure 12b) we can conclude that with increase in the Ir concentration in $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$ composite, the capacity contribution from oxygen evolution minimized during cycling. $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$ cathode materials were subjected to continuous

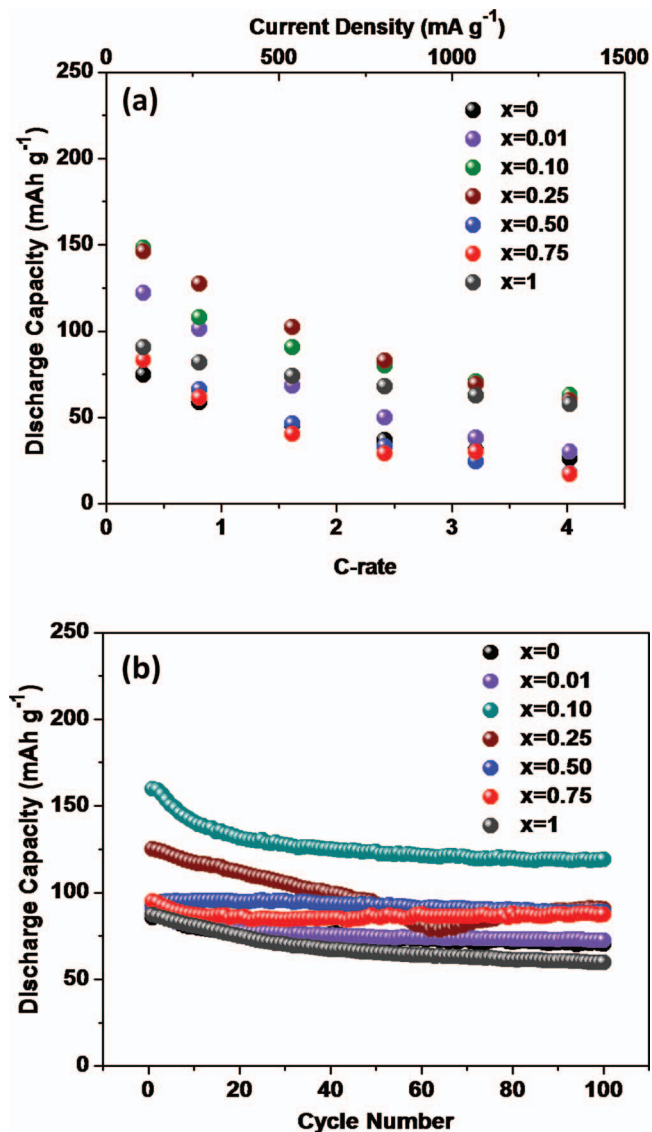


Figure 13. Discharge capacity for $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$ compositions a) at varying C-rate, and b) against cycle number at 105 mA g⁻¹ current rate after testing the cell at high current rate test.

charge-discharge process and Figure 12c shows the discharge profile as a function of cycle number. The initial discharge capacity for various compositions are 157.66 mAh g⁻¹, 171.75 mAh g⁻¹, 198.30 mAh g⁻¹, 164.31 mAh g⁻¹, 143.51 mAh g⁻¹, 131.58 mAh g⁻¹, and 128.54 mAh g⁻¹ for $x = 0, 0.01, 0.10, 0.25, 0.50, 0.75$, and 1.0, respectively at 40 mA g⁻¹. Cyclic stability of various compositions throughout 50 cycles is well illustrated from Figure 12c. The composition with highest cyclic stability was found to be at $x = 0.01$ and 0.10.

High current rate performances.— The robustness of present electrode material is tested at high current rate (Figure 13a). At 105 mA g⁻¹ current rate (equivalent to 0.33C-current rate, defining 1C; removal of complete Li⁺ in 1 h) the composition of $x = 0.1$ and $x = 0.25$ delivered discharge capacity of about ~150 mAh g⁻¹ at 150 mA g⁻¹ ~60 mAh g⁻¹ at 1322 mA g⁻¹ current rate (equivalent of 4C). After the completion of high rate test, the cell was again charged/discharged at 105 mA g⁻¹ current rate (Figure 13b) for 100 cycles. As seen from Figure 13b, $\text{Li}_2\text{Ru}_{0.90}\text{Ir}_{0.10}\text{O}_3$ delivers discharge capacity of 159 mAh g⁻¹ at 0.33C current rate (105 mA g⁻¹) and stabilized ~125 mAh g⁻¹ discharge capacity, whereas $\text{Li}_2\text{Ru}_{0.75}\text{Ir}_{0.25}\text{O}_3$ delivered initial capacity of 125 mAh g⁻¹.

Conclusion

As-synthesized layered Li_2RuO_3 , Li_2IrO_3 and $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$ materials have shown promising electrochemical properties. By analyzing their structural, physical and electrochemical properties that contribute to difference between the three compounds, we can design a suitable high potential cathode material by having a proper mixing of phases. The mechanism of lithium insertion and de-insertion is as complicated as that of Li_2MnO_3 - LiMnO_2 and we have also observed oxygen evolution at high potential above 4.2 V. But due to strong M-M bonding O_2 removal at high oxidation potential is somewhat restricted; at this stage we need more supporting study to confirm this hypothesis. From this study, few underlying properties of such compositions are observed like high voltage character due to high oxidation state of Ru and Ir. Secondly, two dimensional layered structure provides better lithium-ion diffusion and exhibit high power performance. Third point is strong Ru-Ru, Ir-Ir and/or Ru-Ir bonding which plays a crucial role in oxygen removal during de-lithiation process. Few observations like aggregation of particles decreases with the increase in Ir concentration in solid solution are not clearly understood. At the same time, $\text{Li}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_3$ material sustained high rate current test and delivers discharge capacity of 159 mAh g^{-1} at 105 mA g^{-1} . The phase transformations involved in the charge/discharge process have been identified and explained via ex-situ XRD, GITT and CV study at various stages of charge and discharge process. This phase transformation was well supported by the electrochemical charge/discharge study. Although, all the compositions displayed considerable capacity and cyclic stability, a remarkable capacity of $198.30 \text{ mAh g}^{-1}$ was observed for $x = 0.1$ composition with stable cyclic performance upto 50 cycles at 40 mA g^{-1} current rate.

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