Synthesis, structure and electrochemical behaviour of new Ru-containing lithium-rich layered oxides

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ABSTRACT

Three new series of rocksalt related layered Li-rich oxides of formulas, $Li[Li_xM_{0.5 - x/2}Ru_{0.5 - x/2}]O_2$ (I) [for M = Co, Ni; x = 0.125, 0.25, 0.33], $Li[Li_xM_{1 - 2x}Ru_x]O_2$ (II) [for M = Co, Ni; x = 0.25] and $Li[Li_xM_{1 - 3x}Mn_xRu_x]O_2$ (III) [for M = Co, Ni; x = 0.25], have been synthesized, structurally characterized and their electrochemical behaviour investigated. Oxides of series I for M = Co; x = 0.125, 0.25 and 0.33 and for M = Ni; x = 0.33 adopt the $LiCoO_2$ (R-3m) structure. Oxides of series I for M = Ni; x = 0.125 and 0.25 form in the Li_2TiO_3 (C2/c) structure. Series II oxides for M = Co; x = 0.25 crystallize in the $LiCoO_2$ (R-3m) structure; for M = Ni; x = 0.25 form in the Li_2RuO_3 (C2/c) structure. Series III oxides for M = Co, Ni; x = 0.25 adopt the Li_2RuO_3 (C2/c) structure. Electrochemical studies indicate that the Co-containing oxides exhibit a higher initial discharge capacity [for e.g. ~180 mAh g^{-1} oxide of series I for M = Co, x = 0.33 (Li_4CoRuO_6)] as well as a higher reversible discharge capacity [~130 mAh g^{-1} for oxide of series I for M = Co, x = 0.33 (Li_4CoRuO_6)] compared to the corresponding Ni-analogs. Participation of oxide ions (higher oxidation state of Ru) in the redox process could explain the higher discharge capacity during the first cycle. Reduced capacity (capacity fade) during the subsequent cycles could arise from the oxygen evolution due to the redox process ($2O^{2-} \rightarrow 2O^- \rightarrow O_2$), which is not reversible. The present work shows that ruthenium incorporation in rocksalt layered oxides along with Co/Ni appears to give a beneficial effect in producing a higher discharge capacity. In addition, the compounds crystallizing with the $LiCoO_2$ related structure appears to give a better reversible capacity than the compounds crystallizing in the Li_2RuO_3 and Li_2TiO_3 structures.

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1. Introduction

Rechargeable Li-ion batteries have become ubiquitous for their many uses in portable electronic devices as well as in hybrid electric vehicles. Thus, there is considerable interest to search for newer and better electrode materials for advanced Li-ion batteries [1–3]. The rocksalt derived layered compound, $LiCoO_2$, along with many other substituents at the cobalt site has been the choice of materials for many commercial applications [4]. The low-cost along with good electrochemical performance and thermal stability make the $LiNi_{0.5}Mn_{0.5}O_2$ as an attractive candidate [5]. There have been many efforts in this direction by clever choice of redox equilibrium among the transition metals, which resulted in $Li(Ni_{1 - x - y}Co_xMn_y)O_2$, and holds much promise [6,7]. In recent years, there has been considerable interest to study lithium rich layered oxides such as Li_2MnO_3 [8–10]. By combining Li_2MnO_3 and $LiMO_2$ (M = Cr, Mn, Fe, Co and Ni) oxides, new cathode materials have been explored [11–14].

It is known that the redox potentials of Mn^{III}/Mn^{IV} and Ru^{IV}/Ru^{V} are comparable in oxides. There have been attempts towards exploring Li-rich Li_2RuO_3 along with other substituents for possible cathode materials [15,16]. We have been interested in investigating similar compounds containing ruthenium and explored $Li_3M_2RuO_6$ (M = Co, Ni) and Li_3MRuO_5 (M = Mn, Fe, Co and Ni) towards the electrochemical lithium insertion-deinsertion studies [17–19]. In continuation of the theme, we have now prepared new members with the general formulae, $Li[Li_xM_{0.5 - x/2}Ru_{0.5 - x/2}]O_2$ (I) [for M = Co, Ni; x = 0.125, 0.25, 0.33], $Li[Li_xM_{1 - 2x}Ru_x]O_2$ (II) [for M = Co, Ni; x = 0.25] and $Li[Li_xM_{1 - 3x}Mn_xRu_x]O_2$ (III) [for M = Co, Ni; x = 0.25]. Herein, we report the synthesis, structure and electrochemical characteristics of these materials.

2. Experimental

2.1. Synthesis

All oxides were synthesized by the conventional ceramic method. Oxides of series I and II were prepared by reacting stoichiometric mixtures of Li_2CO_3, $MC_2O_4 \cdot 2H_2O$ (M = Co and Ni) and RuO_2 (predried at 125 °C overnight) at progressively increasing temperatures from 810 °C to 975 °C with several intermittent grindings. Series III oxides did not result in a single phase product following the above mentioned

synthesis procedure. These oxides are prepared by a two step process. In the first step, Li_3RuO_4 precursor was synthesized by reacting stoichiometric quantities of Li_2CO_3 and RuO_2 [20]. The freshly prepared Li_3RuO_4 was reacted with $MC_2O_4 \cdot 2H_2O$ (M = Mn, Co and Ni) to obtain single phase products (see Table 1 for synthesis conditions). The cobalt containing oxides were obtained by quenching the compounds from the reaction temperature, while the nickel containing oxides were furnace-cooled to room temperature.

2.2. Structural characterization

Formation of single phase products was confirmed by powder X-ray diffraction (PXRD). PXRD patterns were recorded with a PANalytical X'Pert diffractometer operated at 45 kV and 30 mA using Ni-filtered Cu Kα radiation. For Rietveld refinement of the prepared compounds, the PXRD data were collected employing the same equipment in the 2θ range 5 to 90° with a step size of 0.02° and step duration of 50 s. Rietveld refinements of the structures were carried out employing GSAS program [21]. A sixth order Chebychev polynomial for the background, zero, LP factor, scale, pseudo-Voigt profile function (U, V, W and X), lattice parameters, atomic coordinates and B_{iso} (total 23 parameters) were refined. Thermal parameters were constrained to be the same for atoms occupying the same site. PXRD patterns were simulated using the program POWDERCELL [22].

2.3. X-ray photoelectron spectroscopy (XPS) characterization

XPS measurements of the pristine oxides were carried out with Kratos Axis Ultra DLD Spectrometer, using a focused monochromatised Al-Kα radiation (1486.708 eV). The pressure inside the chamber was kept around 5×10^{-9} mbar during the measurements. The peak positions of all the spectra were corrected to the C1s core level peak at 284.6 eV. Core peaks were analyzed using non-linear Shirley-type background. The positions of the peaks and the area under the curves were optimized by a weighted least-squares fitting method employing XPSpeak41 software.

2.4. Electrochemical characterization

Electrochemical characterization of all the oxides was carried out by galvanostatic method. The positive electrodes or working electrodes were prepared by mixing the active materials with conductive carbon (acetylene black) and a binder (polyvinylidene fluoride) in 70:20:10 weight ratio, respectively. N-methylpyrrolidine (NMP) solution was added to make homogeneous slurry of the mixture, which was coated on known weight of aluminium (Al) foils and dried at 100 °C under vacuum.

Swagelok-type cells were employed for the electrochemical characterization of these materials. In a typical set up, the material coated Al foil was used as the working electrode, lithium foil as both counter and reference electrode and 1 M $LiPF_6$ in ethylene carbonate and dimethyl carbonate (1:1 in volume ratio) as electrolyte. The two electrodes were separated by a separator (Whatman GF/D borosilicate glass fiber sheet) soaked with the electrolyte. The complete cell fabrication was carried out in Ar atmosphere inside a glove box, which contains less than 1 ppm of O_2 and H_2O.

The galvanostatic charge-discharge experiments were carried out using an electrochemical work station (Arbin cell test equipment) at 25 °C. The cells were cycled between 2.2 and 4.2 V versus Li/Li^+ and all capacities are reported in mAh/g with respect to the mass of the material.

3. Results and discussion

3.1. Structure

PXRD patterns of all the synthesized compounds indicate the formation of single phase materials having rocksalt related $LiCoO_2$ [23], Li_2RuO_3 [24], or Li_2TiO_3 structures [25]. PXRD patterns of representative members are shown in Fig. 1. Oxides of series I for M = Co; x = 0.125, 0.25 and 0.33 ($Li_9Co_{3.5}Ru_{3.5}O_{16}$, $Li_5Co_{1.5}Ru_{1.5}O_8$ and Li_4CoRuO_6) and for M = Ni; x = 0.33 (Li_4NiRuO_6) and oxide of series II for M = Co, x = 0.25 ($Li_5Co_2RuO_8$) crystallize in the $LiCoO_2$ structure [23]. Series I oxides for M = Ni; x = 0.125 and 0.25 ($Li_9Ni_{3.5}Ru_{3.5}O_{16}$ and $Li_5Ni_{1.5}Ru_{1.5}O_8$) adopt the Li_2TiO_3 structure [25]. Series II oxide for M = Ni, x = 0.25 ($Li_5Ni_2RuO_8$) and series III oxides for M = Co, Ni; x = 0.25 ($Li_5CoMnRuO_8$ and $Li_5NiMnRuO_8$) form in the Li_2RuO_3 related structure [24].

The structural refinement of the compounds, series I oxides for M = Co; x = 0.125, 0.25 and 0.33 ($Li_9Co_{3.5}Ru_{3.5}O_{16}$, $Li_5Co_{1.5}Ru_{1.5}O_8$ and Li_4CoRuO_6) and for M = Ni; x = 0.33 (Li_4NiRuO_6) and series II oxide for M = Co, x = 0.25 ($Li_5Co_2RuO_8$) was carried out based on $LiCoO_2$ structure having a rhombohedral R-3m symmetry [23]. The refinement results of the representative member, series I oxide for M = Co; x = 0.25 ($Li_5Co_{1.5}Ru_{1.5}O_8$) are given in Fig. 2 and Table 2. The refinement results for the series I oxides for M = Co; x = 0.125 and 0.33 ($Li_9Co_{3.5}Ru_{3.5}O_{16}$ and Li_4CoRuO_6) and for M = Ni; x = 0.33 (Li_4NiRuO_6) and series II oxide for M = Co, x = 0.25 ($Li_5Co_2RuO_8$), are given in Appendix (Fig. S1 and Tables S1–S4). The refinement of series I oxide for M = Co; x = 0.25, $Li_5Co_{1.5}Ru_{1.5}O_8$, indicated a near-ideal distribution of the various ions resulting in the formula, $[Li_{0.996}Co_{0.002}Ru_{0.002}]_{3a}[Li_{0.254}Co_{0.373}Ru_{0.373}]O_2$. If we ignore the small mixing of the atoms, the actual formula can be written as $Li[Li_{0.250}Co_{0.375}Ru_{0.375}]O_2$ in which Li occupy the 3a (0,0,0) position and Li, Co, Ru atoms occupy the 3b (0,0,0.5) position in the R-3m space group. This arrangements result in alternating sheets of $(Li/Co/Ru)O_6$ and LiO_6 octahedra along the cubic [111] direction (Fig.3). The average $(Li/Co/Ru)_{3b}$—O bond lengths (1.995 Å) were observed to be longer than the Co_{3b}—O bond length (1.921 Å) observed in $LiCoO_2$.

As mentioned above, series II oxide for M = Ni, x = 0.25 ($Li_5Ni_2RuO_8$) and series III oxides for M = Co; x = 0.25 ($Li_5CoMnRuO_8$) and for M = Ni; x = 0.25 ($Li_5NiMnRuO_8$) were refined in the Li_2RuO_3

Table 1

Final reaction conditions of the synthesis of oxides of series I: $Li[Li_xM_{0.5-x/2}Ru_{0.5-x/2}]O_2$ for M = Co, Ni; x = 0.125, 0.25, 0.33, oxides of series II: $Li[Li_xM_{1-2x}Ru_x]O_2$ for M = Co, Ni; x = 0.25, and oxides of series III: $Li[Li_xM_{1-3x}Mn_xRu_x]O_2$ for M = Co, Ni; x = 0.25.

Value of x	Formula equivalent to $LiCoO_2$	Compound	Starting materials	Final heating conditions (°C/h)
Series I x = 0.125	$Li[Li_{0.125}M_{0.4375}Ru_{0.4375}]O_2$	$Li_9Co_{3.5}Ru_{3.5}O_{16}$	$Li_2CO_3 + CoC_2O_4 \cdot 2H_2O + RuO_2$	850/12[a]
$Li[Li_xM_{0.5-x/2}Ru_{0.5-x/2}]O_2$		$Li_9Ni_{3.5}Ru_{3.5}O_{16}$	$Li_2CO_3 + NiC_2O_4 \cdot 2H_2O + RuO_2$	810/12
Series I x = 0.25	$Li[Li_{0.25}M_{0.375}Ru_{0.375}]O_2$	$Li_5Co_{1.5}Ru_{1.5}O_8$	$Li_2CO_3 + CoC_2O_4 \cdot 2H_2O + RuO_2$	925/12[a]
$Li[Li_xM_{0.5-x/2}Ru_{0.5-x/2}]O_2$		$Li_5Ni_{1.5}Ru_{1.5}O_8$	$Li_2CO_3 + NiC_2O_4 \cdot 2H_2O + RuO_2$	825/12
Series II x = 0.25	$Li[Li_{0.25}M_{0.5}Ru_{0.25}]O_2$	$Li_5Co_2RuO_8$	$Li_2CO_3 + CoC_2O_4 \cdot 2H_2O + RuO_2$	975/12[a]
$Li[Li_xM_{1-2x}Ru_x]O_2$		$Li_5Ni_2RuO_8$	$Li_2CO_3 + NiC_2O_4 \cdot 2H_2O + RuO_2$	810/12
Series III x = 0.25		$Li_5CoMnRuO_8$	$Li_3RuO_4 + CoC_2O_4 \cdot 2H_2O + MnC_2O_4 \cdot 2H_2O$	925/12[a]
$Li[Li_xM_{1-3x}Mn_xRu_x]O_2$	$Li[Li_{0.25}M_{0.25}Mn_{0.25}Ru_{0.25}]O_2$	$Li_5NiMnRuO_8$	$Li_3RuO_4 + NiC_2O_4 \cdot 2H_2O + MnC_2O_4 \cdot 2H_2O$	960/12
Series I x = 0.33	$Li[Li_{0.33}M_{0.34}Ru_{0.33}]O_2$	Li_4CoRuO_6	$Li_2CO_3 + CoC_2O_4 \cdot 2H_2O + RuO_2$	925/12[a]
$Li[Li_xM_{0.5-x/2}Ru_{0.5-x/2}]O_2$		Li_4NiRuO_6	$Li_2CO_3 + NiC_2O_4 \cdot 2H_2O + RuO_2$	810/12

[a] Quenched to room temperature.