# Solid-State NMR on the Family of Positive Electrode Materials Li<sub>2</sub>Ru<sub>1-y</sub>Sn<sub>y</sub>O<sub>3</sub> for Li-ion batteries

# Supplementary information

Elodie Salager,<sup>1,2\*</sup> Vincent Sarou-Kanian,<sup>1,2</sup> M. Sathiya,<sup>3,4,5</sup> Mingxue Tang<sup>1,2</sup>, Jean-Bernard Leriche,<sup>2,4</sup> Philippe Melin,<sup>1,2</sup> Zhongli Wang,<sup>1,2</sup> Hervé Vezin,<sup>6</sup> Catherine Bessada,<sup>1,2</sup> Michael Deschamps<sup>1,2</sup> and Jean-Marie Tarascon<sup>2,3,5</sup>

- 1. CNRS, CEMHTI (UPR3079), Université d'Orleans, 1D avenue de la recherche scientifique, 45071 Orléans Cedex 2, France
- 2. Réseau sur le Stockage Electrochimique de l'Energie (RS2E), CNRS FR3459, 33 rue Saint Leu, 80039 Amiens Cedex, France
- 3. Collège de France, CNRS FRE3357, 11 place Marcelin Berthelot, 75005 Paris, France
- 4. Laboratoire de Réactivité et de Chimie des Solides (UMR 7314), Université de Picardie Jules Verne, 33 rue Saint Leu, 80039 Amiens Cedex, France
- 5. Alistore European Research Institute, CNRS FR3104, 33 rue Saint Leu, 80039 Amiens Cedex, France

6. Université Lille Nord de France, CNRS UMR 8516-LASIR, Univ. Lille 1, F-59655 Villeneuve d'Ascq, France

1. Deconvolution of the spectra for Li<sub>2</sub>Ru<sub>1-y</sub>Sn<sub>y</sub>O<sub>3</sub>

All spectra were fitted using pure Gaussians, except in the case of Li<sub>2</sub>SnO<sub>3</sub>. The position, contribution to the total area and full width at half height (FWHH) in ppm are indicated in the tables.



Figure S<sub>1</sub>. Deconvolution of the spectra for the  $Li_2Ru_{1-y}Sn_yO_3$  family. For each spectrum, the experimental spectrum is shown in blue; the fit in dashed red. The main components are shown below the experimental spectrum and the fit. Parameters for the fit are given in the tables; FWHH is expressed in ppm and all peaks are Gaussian except for  $Li_2SnO_3$  for which the gausso-lorentzian ratio is given.

The spectra of  $Li_2RuO_3$ ,  $Li_2Ru_{0.75}Sn_{0.25}O_3$ ,  $Li_2Ru_{0.5}Sn_{0.5}O_3$  and  $Li_2Ru_{0.25}Sn_{0.75}O_3$  were acquired using a Hahnecho at 4.7 T with a spinning rate of 62.5 kHz.

To check for the effect of the quadrupolar interaction for the diamagnetic  $\text{Li}_2\text{SnO}_3$  sample, the spectrum was acquired at 17.6 T using a short single pulse (1 µs) with a spinning rate of 20 kHz. The TOP processing<sup>1,2</sup> was

applied in dmfit<sup>3</sup> to separate the spinning sidebands. Their position does not indicate any shift of the satellite transitions compared to the central transition, so the intensity contained in the spinning sidebands was folded back into the centerband to generate the corresponding "infinite spinning rate" spectrum. The fit contains two components at 0.8 ppm (72%) and -0.3 ppm (28%).

## 2. Fermi-contact shift contribution of 90° Ru-O-Li bonds and 180° Ru-O-Li bonds

We determine FC90 and FC180, the contributions of the 90° and 180° bonds, with the spectrum of  $Li_2Ru_{1/4}Sn_{3/4}O_3$ . It contains 4 main components at 0 ppm (19% of the signal), 4 ppm (19%), 9 ppm (23%) and 101 ppm (27%).

Assuming statistical distribution, we expect 3 predominant environments (<sup>1</sup>/<sub>4</sub> of the Ru substitute Sn): 1 Ru<sub>90</sub> (14%), 2 Ru<sub>90</sub> (15%), and 1 Ru<sub>90</sub>+1 Ru<sub>180</sub> (32%). The highly shifted peak (101 ppm, 27% of the signal) is assigned to Li experiencing 1 or 2 Ru<sub>90</sub>, but no Ru<sub>180</sub>. We observe a mixture of these two environments, accounting for the broadness of the peak. Note that each Ru<sub>90</sub> generates two 90°-bonds, resulting in 3 Ru<sub>90</sub>-O-Li bonds on average. FC90 is deduced from this assignment (101/3=33 ppm). Then the 9 ppm peak is assigned to the predominant configuration for Li in Li layers, corresponding to an environment of 1 Ru<sub>90</sub> and 1 Ru<sub>180</sub>, and the FC180 contribution is deduced (-56 ppm). The o ppm peak is assigned to Li surrounded by only Sn and Li atoms, both in Li layers and Sn/Ru layers. The 4 ppm peak cannot be explained by this simple model and we assume that it arises from distortions in the structure and/or a long-range effect of the Ru not taken into account here. Before studying the spectra of the other members of the family, we calculate the FC shifts for all possible Li environments, using the FC90 and FC180 values just determined.

#### 3. Calculation of FC shifts for various Sn/Ru substitutions

We predict the shifts from the configuration of the Li using *FC*<sub>90</sub> and *FC*<sub>180</sub>. Table S<sub>1</sub> describes all the possible FC shifts for Sn/Ru substitution, including those corresponding to defects, ie Li atoms replaced by Ru. Note that one Ru<sub>90</sub> contributes to two 90° bonds. The greyed column with no Ru<sub>180</sub> corresponds to Li environments in Sn/Ru layers ( $n_{90}$ =0 for Li<sub>2</sub>SnO<sub>3</sub>,  $n_{90}$ =12 for Li<sub>2</sub>RuO<sub>3</sub>), and the hatched area corresponds to the Li in Li layers ( $n_{180}$ =4 and  $n_{90}$ =8 in Li<sub>2</sub>RuO<sub>3</sub>) expected for Ru/Sn substitutions. The rest of the table describes defects that would involve Li substitution by Ru.

$n_{90} \setminus n_{180}$	0	1	2	3	4	5	6
o Ru	0	-56	-112	-168	-224	-280	-336
2 (1Ru)	66	10	-46	-102	-158	-214	-270
4 (2Ru)	132	76	20	-36	-92	-148	-204
6 (3Ru)	198	142	86	30	-26	-82	-138
8 (4Ru)	264	208	152	96	40	-16	-72
10	330	274	218	162	106	50	-6
12	396	340	284	228	172	116	60
14	462	406	350	294	238	182	126
16	528	472	416	360	304	248	192
18	594	538	482	426	370	314	258
20	660	604	548	492	436	380	324
22	726	670	614	558	502	446	390
24	792	736	680	624	568	512	456

Table S1. Expected FC shifts for various Sn/Ru substitutions.

 $n_{180}$  is the number of  $180^{\circ}$  bonds containing Ru and  $n_{90}$  is the number of  $90^{\circ}$  bonds containing Ru. <sup>†</sup>In Li<sub>2</sub>RuO<sub>3</sub>,  $n_{90}=12$  (6 Ru<sub>90</sub>),  $n_{180}=0$  for the Li in Ru layers and  $n_{90}=8$ ,  $n_{180}=4$  (4 Ru<sub>90</sub>, 4 Ru<sub>180</sub>) for Li in the Li layers.

#### 4. Li<sub>2</sub>Ru<sub>1/2</sub>Sn<sub>1/2</sub>O<sub>3</sub>, Li<sub>2</sub>Ru<sub>3/4</sub>Sn<sub>1/4</sub>O<sub>3</sub> and Li<sub>2</sub>RuO<sub>3</sub> spectra and expected FC shifts

With higher amounts of Ru, the chemical disorder is increasing. The Li atoms experience a wider distribution of Ru environments and the peaks are much broader. Assuming a purely random substitution for  $\text{Li}_2\text{Ru}_{1/2}\text{Sn}_{1/2}\text{O}_3$ , we expect a main peak for Li in the Ru layers at 198 ppm (3 Ru<sub>90</sub>) and a peak at 20 ppm for Li in Li layers (2 Ru<sub>90</sub> + 2 Ru<sub>180</sub>). Experimentally, we need four major components at 11 ppm (19%), 28 ppm (24%),

81 ppm (18%) and 141 ppm (23%) to describe the spectrum. The tail towards higher shifts is very broad and many decompositions are possible. We chose to use only one Gaussian peak with a very large width. The deconvolution gives a maximum at 141 ppm but the large width at half-height (from 50 ppm to 232 ppm) indicates that it is the result of a superposition of many environments, including the expected 198 ppm for a perfectly random substitution for Li in Ru layers. Turning to lower shifts in this spectrum, we also observe a large variety of shifts indicating that the substitution is influenced by the Ru already in place. A Ru-Ru interaction and a preference for dimerization most probably direct the subsequent substitutions. Indeed we do not get the environment expected for random substitution, but instead we have a Ru-rich environment with 2 more Ru (30 ppm,  $3 \text{ Ru}_{90} + 3 \text{ Ru}_{180}$ ) and a Ru-poor environment with two Ru missing (10 ppm,  $1 \text{ Ru}_{90} + 1 \text{ Ru}_{180}$ , with one Ru<sub>180</sub> missing, and  $3 \text{ Ru}_{90} + 2 \text{ Ru}_{180}$ , with one extra Ru<sub>90</sub>.

Li<sub>2</sub>Ru<sub>3/4</sub>Sn<sub>1/4</sub>O<sub>3</sub> is the most interesting of the family as it displays the highest reversible capacity. Unfortunately, the <sup>7</sup>Li spectrum is the broadest and the smoothest of the whole family, accounting for the widest distribution of Ru environments. Here we expect 4.5 Ru<sub>90</sub> (264-330 ppm) for Li in Ru layers and 3 Ru<sub>90</sub> + 3 Ru<sub>180</sub> for Li in Li layers (30 ppm). A possible deconvolution is shown in Figure S1. We find 5 major environments: 23 ppm (18%), 50 ppm (22%), 79 ppm (28%), 191 ppm (12%) and 250 ppm (11%). The most shifted peak (250 ppm, half-height at 111 ppm and 389 ppm) can account for the Li in Ru layers in the expected environment (4-5  $Ru_{90}$ ). The 190 ppm peak (111 and 271 ppm at half-width) also arises from Li in Ru layers, but these are most probably surrounded by 3 Ru<sub>40</sub> (198 ppm) instead of 4 or 5. The components at lower shifts do not fit well with a perfect random substitution and indicate that preferential substitution is also at stake in this sample. We expect Li in Li layers at 30 ppm (3  $Ru_{so}$  + 3  $Ru_{18o}$ ). Instead, the 23 ppm (13 and 53 ppm at HH) peak corresponds to  $2 \operatorname{Ru}_{90} + 2 \operatorname{Ru}_{180}$  (20 ppm), the 50 ppm (19-81 ppm at HH) peak to  $4 \operatorname{Ru}_{90} + 4 \operatorname{Ru}_{180}$ (48 ppm) and the 79 ppm (25 to 133 ppm at HH) peak to  $2 Ru_{90} + 1 Ru_{180}$  (76 ppm) and  $3 Ru_{90} + 2 Ru_{180}$ (86 ppm). It seems that environments with an even number of Ru are promoted, in agreement with the dimerization observed for Li<sub>2</sub>RuO<sub>2</sub>.<sup>4</sup> The remaining 10% of the signal are shared between pure Sn/Li environments (-o.8 ppm) and extremely Ru-rich regions (367-645 ppm at half-height), most probably issued from Li-substitution by Ru.

Finally, we study the end-member  $Li_2RuO_3$ .  $Li_2RuO_3$  was reported as either metallic (from photoelectron spectroscopy<sup>5</sup>) or semi-conductor with a tiny bandgap (53 meV<sup>6</sup>). We observe a series of peaks that indicate localized unpaired electrons rather than metallicity. The Li site in the LiRu<sub>2</sub> layers experiences 6 Ru<sub>90</sub>, so we expect a FC shift of 396 ppm. We get instead two peaks at high shift (208 and 405 ppm), accounting for 21.3% of the signal. Note that the peaks are broad so they cover a range of environments. The maximum however indicates the most probable environment. The peak centered at 208 ppm corresponds to less Ru<sub>90</sub> than expected ( $3Ru_{90}$  or  $4Ru_{90}+1Ru_{180}$ ), while the other peak is centered in a region of higher amounts of Ru<sub>90</sub> (6 Ru<sub>90</sub> or  $7Ru_{90}+1Ru_{180}$ ). We also find this trend for Li in Li layers. In the crystal structure, the Li sites in the Li layers are surrounded by  $4 Ru_{90} + 4 Ru_{180}$ , so one peak is expected at 40 ppm that would account for 75% of the signal. Three major components are found at lower shifts instead. The 40 ppm shift, in agreement with the X-ray structure, accounts for 36% of the signal only. The component at 29 ppm (11%) is narrow and we can easily assign it to Ru-deficient environments ( $3 Ru_{90} + 3 Ru_{180}$ ). The 75 ppm peak is much broader (it spans - 14 ppm;+134 ppm at half height) and it covers a broad range of potential environments. Its maximum is closest to the ( $2 Ru_{90} + 1 Ru_{180}$ ) environment.

As a conclusion, we clearly detect here a preferential organization of the Ru in the materials. Note that the FC shift probes the local environment of the lithium atoms and that these Ru-rich and Ru-poor environments might be clustered or distributed throughout the material. These observations are however in good agreement with reports of Ru dimerization in this material.<sup>4</sup>

### 3. <sup>119</sup>Sn NMR of the Li<sub>2</sub>Ru<sub>y</sub>Sn<sub>1-y</sub>O<sub>3</sub> family

<sup>19</sup>Sn has a low natural abundance of 8.6%. Several days of acquisition are therefore necessary to obtain a reasonable signal-to-noise ratio.

Two main peaks are obtained for the whole series, independently of the Ru-Sn substitution ratio. The least shifted peak has a longer relaxation time. Its shift is similar to the shifts in the  $Li_2SnO_3$  spectrum and does not change with the Ru-Sn substitution ratio, so it is assigned to Sn surrounded by Sn only. The other broad peak relaxes faster and is assigned to Sn surrounded by one, two or three  $Ru_{90}$ . The width of that peak increases with increasing Ru substitution as expected for a higher population of the Ru-rich (three  $Ru_{90}$ ) environments. The intensities do not match the statistical distribution, in good agreement with the <sup>7</sup>Li observations of a preferential substitution. Note that the <sup>119</sup>Sn chemical shift range is extremely wide (-2000;+1000) so part of the shift observed here might be embedded in the chemical shift, in addition to the paramagnetic shift. Further work is necessary to identify in a non-ambiguous way the <sup>119</sup>Sn NMR signals.



Figure S2. <sup>119</sup>Sn NMR signals for the  $Li_2Ru_{1-y}Sn_yO_3$  family. Acquisition times are indicated next to each spectrum.

# 4. Evolution of the NMR spectra upon charging of Li<sub>2</sub>RuO<sub>3</sub>



Figure S<sub>3</sub>. Spectra of a  $Li_2RuO_3$  electrode upon charging. At 4 V, a large shift and broad peak is observed at 106 ppm. The 4.6 V electrode does not go back to lower shifts for the pure Ru-end member of the family.

## 5. Video

Video showing the evolution of the  ${}^{7}Li$  spectrum of the  $Li_{2}Ru_{0.75}Sn_{0.25}O_{3}/Li$  cell during cycling.

### References

(1) Blümich, B.; Blümler, P.; Jansen, J. Solid State Nucl. Magn. Reson. 1992, 1, 111–113.

(2) Massiot, D.; Hiet, J.; Pellerin, N.; Fayon, F.; Deschamps, M.; Steuernagel, S.; Grandinetti, P. J. J. Magn. Reson. **2006**, 181, 310–315.

- (3) Massiot, D.; Fayon, F.; Capron, M.; King, I.; Le Calvé, S.; Alonso, B.; Durand, J.-O.; Bujoli, B.; Gan, Z.; Hoatson, G. *Magn. Reson. Chem.* **2002**, *40*, 70–76.
- (4) Miura, Y.; Yasui, Y.; Sato, M.; Igawa, N.; Kakurai, K. J. Phys. Soc. Jpn. 2007, 76, 033705.
- (5) James, A.; Goodenough, J. J. Solid State Chem. 1988, 74, 287–294.
- (6) Kobayashi, H.; Kanno, R.; Kawamoto, Y.; Tabuchi, M.; Nakamura, O.; Takano, M. Solid State Ion. **1995**, 82, 25–31.