Towards new ionic Li-ion rich conducting materials

Research’s progresses in rechargeable batteries are driven by ever increasing demands dictated by the energy transition. Rechargeable lithium ion batteries, because of their high energy density, have conquered most of today’s portable electronics. They are now penetrating the EV’s market and stand as a serious contender for grids applications provided that their safety is mastered. An elegant way to address safety is to move from non-aqueous liquid electrolytes to inorganic solid electrolytes. Research towards Li(Na)based ionic conducting membranes has been intense in the 1980’s, but rapidly falls into oblivion because of i) the lack of suitable high ionic conducting materials, ii) the weak rate and cycling capabilities of assembly batteries due to poor interfaces and iii) the high moisture sensitivity of sulfides which renders their manipulation difficult.

Thirty five years have passed and research in solid state batteries is getting back some momentum. This is driven by the foreseen interests of the automotive industry, namely TOYOTA. This renaissance has led to a revisit of the thio-LISICON solid solutions with composition Li$_4$Ge$_{1-x}$P$_x$S$_4$ ($x = 0.75$). Recently, Kanno has significantly improved the Li-ion conduction in these materials by moving towards the tetragonal solid solution with composition Li$_{11-x}$M$_{2x}$P$_{1+x}$S$_{12}$ ($M = Si, Ge, Sn$) which displays Li$^+$ ion conductivities on the order of $10^{-2}$ S cm$^{-1}$ at room temperature for Li$_{10}$GeP$_2$S$_{12}$ and even lower for Li$_{11}$Si$_2$PS$_{12}$. Taking a different approach, Holtzmann et al. reported nearly similar ionic conductivity in the layered sulfide phases Li$_{0.6}$[Li$_{0.2}$Sn$_{0.8}$S$_2$]. These findings provide ionic conductors with high ionic conductivity, but sulfides are materials difficult to handle/manipulate aside from forming easily interfaces. The aim of the PhD is therefore to move towards ionic oxides (rather than sulfides) and master the interfaces.

Interestingly, the lastly reported phases Li$_{0.6}$[Li$_{0.2}$Sn$_{0.8}$S$_2$] can simply be viewed as deviating from today’s Li-rich layered oxides, so called Li-rich NMC (ex: Li$_{1}$[Li$_{1/3}$Ru$_{2/3}$O$_2$]) that we are presently studying intensively as positive electrodes because of their staggering capacities. The difference simply resides in the facts that we are using i) O rather than S , ii) a redox active d-metal as opposed to a non-reductive one (Sn is 4d$^{10}$) and iii) a full Li layer rather than a deficient one. Within this context, the phases Li$_2$TiO$_3$, Li$_2$ZrO$_3$ will be used use as our playground to demonstrate the feasibility to inject high ionic conductivity within the layered oxides.


Background: This project will be carried out mainly at the Collège de France within the context of the RS2E with the benefits of having an easy access to state of the art characterization techniques, provided the student considers mobility as career enrichment. We are looking for a PhD candidate having a great education in materials science with a good handling of analytical techniques. The PhD candidate should be a highly motivated person, hard worker, with a pronounced interest for synthesis and experimental work. English mandatory.