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ABSTRACTS

09.25 am

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Compatibility studies of Huckel salt-based electrolytes with new sodium electrode materials

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This work is a part of a larger studies concerned the Hucckel type salts in application in lithium and sodium electrolytes. It consists the preparation and testing of the properties of (half)cells containing 4,5-dicyano-2-(trifluoromethyl) imidazolate sodium salt (NaTDI). This structure is more electrochemically and thermally stable than similar structures in which carbon atoms are used to bond. This change results in greater resistance to oxidation and reduced formation of ionic pairs. In the studied cells compatibility was tested mainly against the active material NaNi0,6Mn0,6Co0,6O2 (NaNMC 622). The material NaNMC 622 was chosen because of good predicted electrochemical properties, which are caused by simultaneous occurrence of manganese, nickel and cobalt in the transition metal layer. The obtained cells were characterized by electrochemical impendance spectroscopy and galvanostatic cycling. Measurements obtained by impedance spectroscopy confirmed the possibility of obtaining a system containing NaNMC 622 as an electrode and an electrolyte containing NaTDI salt. Electrolyte and electrolyte resistance was determined by electrochemical impedance spectroscopy.

09.50 am

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Polyanionic materials at the positive of Na-ion batteries

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Polyanionic materials are intensively studied as promising positive electrode materials for Na-ion batteries thanks to their high stability and the fast ionic mobility within their structural framework.[1] Among those polyanionic materials, Na3V2(PO4)2F3 and Na3(VO)2(PO4)2F are the two most attractive ones due to their high voltage for two Na+ ions extraction and their high theoretical energy densities: 500 mAh.g-1 and 495 mAh.g-1, respectively. These two compositions are indeed the two end members of a family of compounds described with the general formula Na3V2(PO4)2F3-yOy where 0 ≤ y ≤ 2.
Optimized carbon-coated Na3V2(PO4)2F3 showed exceptional rate and electrochemical cycling capabilities, more than 4000 times at 1 C rate, as demonstrated by performance of the first hard carbon//Na3V2(PO4)2F3 18650 prototypes of 75 Wh kg−1 prepared by our partner CEA.[2] These attractive results, among others, participate to a renewed interest in the field of Na-ion batteries considering vanadium fluorophosphates at the positive electrode.

The optimization of their electrochemical performance requires the control of the carbon coating, [2] and the careful tuning of the oxygen and thus vanadyle-type defects' concentration through a deep understanding and control of the reaction synthesis. Indeed, the competition between the ionic V3+−F bond and the covalent V4+=O bond has a major effect on the structure of the pristine materials, and then on the phase diagram and redox mechanisms involved upon their cycling in batteries.[3-4] The influence of the anionic and cationic substitution will be illustrated for series of phases Na3V2xMx(PO4)2F3-yOy (M= transition metal) combining mainly Synchrotron X-ray diffraction and spectroscopic studies.[3-7]

Acknowledgements

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10.15 am

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Negative electrodes for Na-ion batteries based on alloys and beyond

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Recent research on Na-ion systems has been focused on the development of negative electrode materials, firstly based on the insertion of Na into hard carbon structures able to develop a capacity as high as ~300 mAh/g, but limited volumetric energy density. The large ionic radius of Na^+ with respect to Li^+ leads to a higher volume expansion upon cycling, which is expected to strongly affect insertion as well as alloying or conversion reactions. Despite this issue, p-block element-based electrodes have shown to be viable alternatives to hard carbon, providing very interesting performance with reversible capacities largely exceeding 400 mAh/g. We have investigated several phases containing X = Si, P, Sb, Pb and/or Sn,[1-4] or MX_n [5-6] phases (M transition metal) as negative electrode materials for Na batteries. The thorough investigation of both mechanism and performance of this family of materials will be highlighted. In particular, the good electrochemical performance of such materials is surprising if one considers the huge volume expansion expected from the electrochemical alloying with Na (from 200 to 400 %). To address this issue, a recent approach involving the preparation of lamellar p-bloc element phases such as siloxenes has shown interesting electrochemical properties.[8]

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10.40 am

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The sodiation-desodiation mechanism of Sb-based electrode materials revealed by operando spectroscopy assisted by chemometric data analysis

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In the search for efficient electrode materials for Na-ion batteries, *p*-block elements were found to be viable alternatives to hard carbon, showing interesting performance with reversible capacities exceeding 400 mAh/g.[1] In particular, Sb showed a specific affinity for Na, exhibiting excellent cycling stability even in the simplest form of bulk Sb.[2] Yet, the reason of this affinity is not thoroughly understood. Indeed, while the electrochemical signature suggests the formation of several possible intermediates, only Na_3Sb is detected by X-ray diffraction at the end of sodiation, all intermediates being amorphous. Only a recent study of the mechanism by Pair Distribution Function analysis revealed possible short-range structures for the intermediates formed while cycling pure Sb.[3] The same is observed for other Sb-based materials such as $FeSb_2$ and SnSb.[4,5]
With the goal of better understanding this specific affinity of Na for Sb, a thorough study of the electrochemical reaction of Sb, $FeSb_2$ and SnSb with Na was undertaken using operando X-ray absorption spectroscopy (XAS),[6-8] coupled to ^{57}Fe Mössbauer spectroscopy in the case of $FeSb_2$. The whole sets of spectra were analysed using multivariate chemometric tools (Principal Component Analysis and Multivariate Curve Resolution). The results of this analysis show that it is intrinsically impossible to prove by XAS the existence of some of the intermediates proposed in the case of pure Sb. On the contrary, in the case of SnSb, the possibility of studying simultaneously the absorption edges of Sn and Sb was essential to clarify the sodiation mechanism, which goes through a two-step process clearly distinct from the lithiation of SnSb.

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11.05 am

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Layered transition metal oxides as electrodes materials used in Sodium-ion batteries.

$Na_2Ti_3O_7$ is a promising anode material for Na-ion batteries due to its layered structure with an open framework and low operating voltage.[1] However, its poor electronic conductivity and rapid capacity fading hinder its use in practical applications.[2] The introduction of oxygen vacancies as shallow surface states in metal oxides has shown to improve the charge transfer process and conductivity of materials for different applications such as metal-air batteries, lithium-ion batteries, fuel cells, dye-sensitized solar cells, etc.[3] In addition, the concentration of oxygen vacancies can be tuned and optimised depending on the type of treatment (doping, annealing under vacuum, H_2, N_2, chemical reduction, chemical oxidation, anodization annealing, among others).[4] Therefore, it is reasonable that the generation of oxygen vacancies on the surface of $Na_2Ti_3O_7$ might be a viable route for overcoming its low electrical conductivity and enhance the electrochemical performance. There have been only a few studies that explore the effect of oxygen non-stoichiometry and enhanced electrical conduction on the energy storage properties in $Na_2Ti_3O_7$.[5]

Here we describe an effective and simple method to create oxygen vacancies on the surface of an oxide is by mixing the as-synthesised compounds with urea and annealing the mixture in nitrogen atmosphere at 470 °C for 2 h.[3] This methodology has been successfully employed in tungsten trioxide (WO_3), investigated as a counter electrode (CE) for applications in dye-synthesized solar cells.[3] The use of urea might be an effective way to introduce oxygen vacancies on the surface of $Na_2Ti_3O_7$ upon annealing treatment in a N_2 atmosphere. On the other hand, this methodology is cost-effective and safer compared to the direct use of H_2 or a mixture of N_2/H_2.[6] This approach has shown improved electrochemical performance with respect to the pristine material due to the introduction of oxygen vacancies on the surface of $Na_2Ti_3O_7$. The electrons bonded to the removed oxygen in the structure are transferred to the empty 3d levels at the bottom of the conduction band belonging to the adjacent Ti atoms, resulting in the reduction of Ti^{4+} to Ti^{3+}. In addition, the reducing atmosphere created upon the decomposition of urea led to partial decomposition of $Na_2Ti_3O_7$ into $Na_2Ti_6O_{13}$. This composition is also widely investigated as an anode material for Na-ion batteries. A comprehensive study was carried out in order to examine the effect of generated defects and formation of $Na_2Ti_6O_{13}$ on the structure, chemistry and charge storage properties of $Na_2Ti_3O_7$. These included morphological and structural analysis (PXRD and SEM/EDS), spectroscopic analysis (Raman, XPS, EPR and NMR) in conjunction with electrochemical analysis.

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11.55 am

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Reliable electrochemical setup for Post Li battery testing

Various metals have been used as battery anodes in electrochemical cells ever since the birth of batteries with Volta's pile and in the first commercialized primary (Zn/MnO_2, Leclanché 1866) and secondary (Pb/acid, Planté 1859) batteries. Despite issues to develop viable and safe metal anodes, new material (cathode, anode, or electrolyte) testing commonly involves the use of an electrochemical setup called a half-cell in which metal counter and reference electrodes are used. While this protocol has proved to be reliable in Li based cells, the essential properties for the use of Na, Mg and Ca metal electrodes remain to be fully assessed. Here we first describe the different issues that become critical when moving away from Li. Workarounds are given, and a versatile setup is proposed to run reliable electrochemical tests for post-Li battery materials in general, in a broad range of electrolyte compositions [R. Dugas, J. Forero-Saboya, A. Ponrouch, *Chem. Mater.* 2019, 31, 8613−8628].

12.20 pm

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Towards stable interfacial reactions in sodium-ion batteries

Formation of a stable passivation layer known as the solid electrolyte interphase (SEI) on the negative electrode materials such as hard carbon is necessary to design kinetically stable sodium-ion batteries (SIBs).[1]

Though the concept of SEI formation and its characteristics in SIBs are largely similar to that for lithium-ion batteries, there exist differences between SEI in those battery systems, which influence the capacity loss and ageing mechanism.[2] Therefore, a detailed investigation on SEI formation and the electrolyte stability in SIBs is essential to broaden current knowledge. Compared to its Li-counterpart, SEI formed in Na$^+$based electrolyte systems is stated to be more soluble.[2,3] This is due the higher solubility of most sodium salts presents in SEI compared to their lithium counterparts (*e.g.* NaF *vs.* LiF).

Here, we shed light on SEI formation and dissolution in different Na$^+$based electrolyte systems. We have also studied a range of new electrolyte chemistries in full-cell sodium-ion batteries using hard carbon anodes and Prussian white cathodes. The electrochemical window and SEI stability over time is monitored using electrochemical techniques. Via synchrotron-based hard Xray photoelectron spectroscopy (HAXPES) measurements, composition and changes of the SEI over time are investigated.

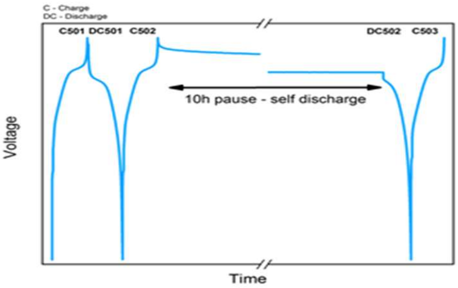

Figure 1. Extended relaxation/pause time in galvanostatic cycling of full-cell sodium-ion batteries based on hard carbon anode and Prussian White cathode.

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12.45 pm

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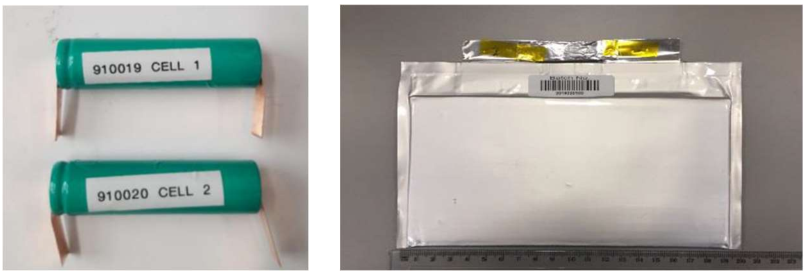
High Performance Na-ion Batteries: from Lab to Commercial Scale

Na-ion batteries represent an inexpensive alternative to their Li-ion counterparts, especially for large-format applications [1,2]. Faradion has identified a wide range of new Na-based active materials and electrolytes with low manufacturing costs, outstanding electrochemical properties and intrinsic safety [3]. The company has incorporated these materials into full-scale Na-ion cells to a point where performance is competitive with commercial Li-ion cells. These cells are manufactured on industry-standard Li-ion production lines using proven battery designs - see for example, Figure 1 [4]. Faradion has worked with its commercial partners to scale-up its Na-ion cell technology to the 40 Wh and 80 Wh commercial pouch cell level. These cells deliver a specific energy of over 150 Wh/kg and have been incorporated into a range of demonstrator applications, including residential, telecoms and automotive [5]. The technology roadmap indicates that a specific energy in excess of 190 Wh/kg will be accessible in the near future. Other key attributes such as low materials cost, long cycle life and excellent power and safety performance, indicate that Faradion's Na-ion technology will prove commercially successful.



Left panel: Faradion Na-ion 18650 cylindrical cells
Right panel: Faradion Na-ion 12 Ah pouch cell (physically shorted)

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2.10pm

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Green, low-cost and scalable synthesis of *Triphylite*-$NaFePO_4$ as positive electrode for sodium-ion batteries

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Triphylite-$NaFePO_4$ is one of the most attractive materials for sodium ion batteries, since its exhibits one of the highest reversible capacities reported up to date for a polyanionic Na-ion cathode material (154 mAh/g) sharing also the excellent properties of the analogous *triphylite*-$LiFePO_4$ used in commercial lithium-ion batteries: reaction within a narrow voltage range inside the voltage stability window of the electrolyte, good stability and good cyclability.[1,2]

In this work, *triphylite*-$NaFePO_4$ is synthesized from *triphylite*-$LiFePO_4$, by a low-cost, eco-friendly method, enabling the recovery and subsequent reuse of lithium, via the synthesis of Li_3PO_4, which may then be further transformed into a C/$LiFePO_4$ product with excellent electrochemical performance. The *triphylite*-$NaFePO_4$ delivered 132 mAh/g at C/10 with good capacity retention (~101 mAh/g with a 100 % of the coulombic efficiency after 200 cycles).[3]

The proposed approach maintains the excellent morphological and microstructural properties of the commercial parent *triphylite*-$LiFePO_4$, including particle size distribution (which is relevant for the processability of the final product), and is aimed to position *triphylite*-$NaFePO_4$ as a serious contender for real applications and future commercialization.

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2.35 pm

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3.00 pm

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Sodium Ion mobility in Disordered Perovskites and Implications for Battery Materials

The operation of a secondary sodium ion battery is predicated on facile and reversible migration of Na^+ through electrodes, electrolyte and across the interfaces between them. We are developing new complex oxide materials with crystal structures tailored to facilitate sodium movement and de-intercalation via redox processes. The examples of Na^+ conduction in '*beta alumina*' provides a classic example of Na^+ migration through a crystalline structure with significant disorder. We recently reported Na^+ conduction in a new perovskite prepared using microwave irradiation to drive the reaction to completion in only a few hours. The talk will show how the application of diffraction, muon relaxation measurements and impedance analysis can be used to build a picture of the behaviour of the Na^+ ion in this structure. The unusual observation of Na^+ on both the large and smaller interstices in the perovskite, and the ability to tune composition and redox behaviour in perovskites, suggest new target compositions and structures for new sodium battery materials.

3.25 pm

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Layered Sodium Manganese Oxides for Na-ion Batteries

The operation of a secondary sodium ion battery is predicated on facile and reversible migration of Na^+ through electrodes, electrolyte and across the interfaces between them. We are developing new complex oxide materials with crystal structures tailored to facilitate sodium movement and de-intercalation via redox processes. The examples of Na^+ conduction in '*beta alumina*' provides a classic example of Na^+ migration through a crystalline structure with significant disorder. We recently reported Na^+ conduction in a new perovskite prepared using microwave irradiation to drive the reaction to completion in only a few hours. The talk will show how the application of diffraction, muon relaxation measurements and impedance analysis can be used to build a picture of the behaviour of the Na^+ ion in this structure. The unusual observation of Na^+ on both the large and smaller interstices in the perovskite, and the ability to tune composition and redox behaviour in perovskites, suggest new target compositions and structures for new sodium battery materials.