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# All Titanium Based Electrodes for Sodium-Ion Batteries

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Although Li ion batteries have conquered the portable electronics market and are the primary choice of EVs, lower cost sustainable alternative chemistries would be desirable for large scale grid storage. Within this scenario, an analogous technology based on sodium, which is inexpensive and abundant, could be a viable option [1]. In the quest for new materials to turn such a concept into a tangible reality, both high throughput computing [2], and analogy with the well known lithium ion battery chemistry [3]have proved to be a good option.

Whilst a variety of active sodium phases have been reported as possible cathodes, the choices on anodes are limited. Apart from Na-alloying anodes which are at their infancy, hard carbon is the one widely used to demonstrate the concept of Na-ion batteries [4, 5]. We have recently reported sodium insertion into $Na_2Ti_3O_7$ at 0.3 V with a capacity of 200 mAh/g [6]. Structural rearrangement is believed to be responsible for such a low voltage intercalation but also to result in limited capacity retention [7].

Alternatively aiming at stable structural framework based on $Ti^{3+}/Ti^{2+}$ redox couple, which is relatively uncommon but already reported for lithium insertion into $TiS_2$ [8], is a plausible strategy to attain low voltage sodium insertion anode. Within this context, NASICON $Na_3Ti_2(PO_4)_3$ appears to be an attractive option since its vanadium analogue has been reported to insert one mol of sodium ions concomitant to reduction from $V^{3+}$ to $V^{2+}$ [9]. Although oxidation of $Na_3Ti_2(PO_4)_3$ through $Ti^{4+}/Ti^{3+}$ couple has been widely reported [10], no attempt to insert sodium into this phase to attain such lower oxidation state for titanium had been reported. Figure 1 shows cycling of $Na_3Ti_2(PO_4)_3$ Vs. Na metal operating on both redox couples. Upon oxidation a plateau ~2.1 V is observed which corresponds to oxidation of Ti(III) to Ti(IV), while two plateaus are observed upon reduction. The first, at 0.7 V corresponds to irreversible reaction between carbon black and the electrolyte and the second at 0.4 V related to the reduction of Ti(III) to Ti (II). Taking advantage of such behavior we have successfully built symmetric cells (Figure 2) in which the active material of both cathode and anode was $Na_3Ti_2(PO_4)_3$ [11] .

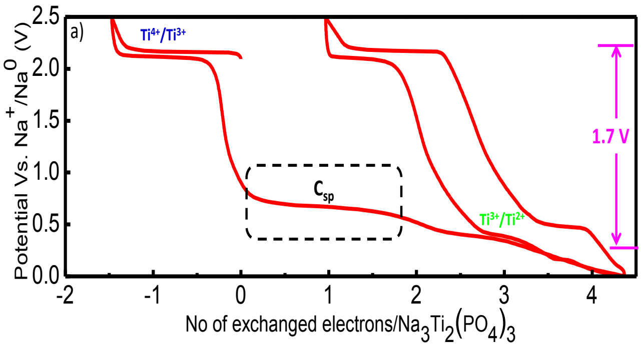

Figure 1: Galvanostatic cycling of $Na_3Ti_2(PO_4)_3$ Vs. Na between 2.5-0 V at C/25 for the first and second oxidation/reduction cycles using $NaClO_4$ in PC as electrolyte

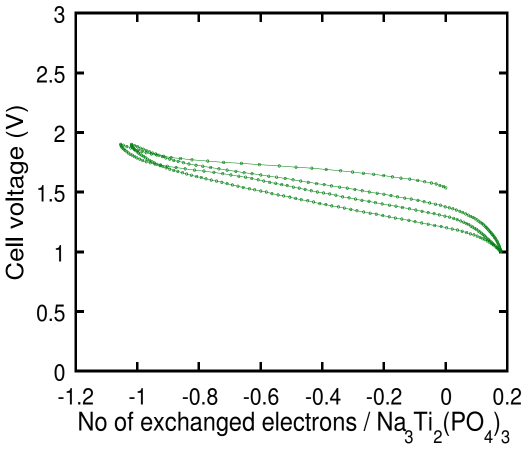

Figure 2: Potential versus capacity profile for symmetric $Na_3Ti_2(PO_4)_3||NaClO_4$ in $PC||Na_3Ti_2(PO_4)_3$ cells cycled at C/10 at room temperature.

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