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High Power Na-Ion Capacitor with TiS_2 as Insertion Host

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Abstract

High power capability of the hybrid charge storage device Na-ion capacitor (NIC) is fabricated using battery type TiS_2 as an insertion host with the double layer forming activated carbon (AC) as supercapacitor component. Earlier, it is presumed that Na/ TiS_2 system is considered as impractical energy storage system. TiS_2 single crystals are synthesized and exhibit the reversible insertion of ~ 0.62 mol. Na. AC/ TiS_2 assembly is delivering the maximum energy density of ~ 38 Wh kg^{-1} . One of the important aspects of this NIC is high power capability, which outperformed its analogue Li-ion capacitor fabricated under similar circumstances.

Keywords: Sodium-ion capacitor; Lithium-ion capacitor; energy density; intercalation; two dimensional

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Research activities on energy storage systems remain a hot topic of research for the past four decades since the commercialization of Li-batteries in the early 1970's with TiS_2 as intercalation host [1-5]. In parallel, Na-battery research activities are also accelerated, but unfortunately, Na-intercalation into TiS_2 was found difficult and hence research activities are limited. Also, the size of cation plays a vital role in the charge storage process which triggers the unprecedented activities on the development of the Li-based systems and successful commercialization in the later period. Further, the shifting from Li to Na increases the Coulombic interaction between Na-Na which handicaps the active material choice and slow-down the research activities on Na-based systems[6]. Of late, scarcity of the Li-deposits on the crust warned us to develop the alternate, competitive, and cost-effective systems for multifarious applications. Dominancy of the Li-ion battery (LIB) as a power source in most of the electronic gadgets are witnessed from the consumption and emergence of new manufacturing companies. Besides the extensive use in electronic devices, an attempt has also been made to deploy them to drive hybrid electric and electric vehicles (HEV and EV). However, the poor power capability is one of the main hurdles to drive EV and HEV for LIBs, which can be efficiency improved by integrating with supercapacitor called Li-ion capacitor. This hybrid configuration comprises the combined features of both LIB and supercapacitor. Clearly, such configuration exhibits high energy *via* redox reaction offered by battery component and power density by supercapacitor electrode *via* physisorption process. In this regard, developing Na-ion capacitor (NIC) is one of the important and timely approaches to tackle all the aforesaid issues [7-9].

As mentioned, battery type electrode undergoes the Faradaic process whereas supercapacitor component, preferably high surface area activated carbon (AC) involves a physisorption process at the electrode-electrolyte interface in a non-Faradaic way. Developing carbonaceous counterparts certainly boost the power capability of the system, but the improvement in the energy density would be marginal. However, dramatic improvement is required to employ as a power source to drive zero emission transportations, but it is possible only

with the exploration of battery type electrode. Unlike Li-ion capacitors, the insertion type material choices are very limited for NIC [7, 10]. Till date, hard carbons, $\text{NaTi}_2(\text{PO}_4)_3$, $\text{Na}_3\text{V}_2(\text{PO}_4)_3$, $\text{Na}_2\text{Ti}_3\text{O}_7$, and V_2O_5 have been studied as a negative electrode and described extensively in our review [7]. Amongst, hard carbon offers high energy density, but requires additional pre-sodiation step [11]. According to Newman and Klemann [12], Na- TiS_2 is an impractical energy storage system, but we are interested in this particular system owing to the unique structural prospect with weak van der Waal's spacing for the reversible insertion of the Na-ions [2-5, 13-16]. In this regard, we made an interesting attempt to synthesize utmost purity single crystals by chemical vapor transport (CVT) and eventually employed as a negative electrode for sustained Na-storage in half-cell configuration. This interesting Na-storage behavior logically thinks us to fabricate the hybrid energy storage system with AC counter electrode.

TiS_2 single crystals were prepared by the conventional CVT reported by us recently [14, 15]. All the electrochemical studies were performed using the standard CR 2016 coin-cell assembly in the two-electrode set-up. Composite electrodes like TiS_2 and AC (Kuraray, Japan) were prepared with 10 mg of accurately weighed active material, an equal amount (1.5 mg) of Super P and teflonized acetylene black-2 using ethanol over 16 mm dia. stainless steel mesh (Goodfellow, UK) current collector for both electrodes. Metallic Na was used as a reference-cum-counter electrode in half-cell assembly and separated by Whatman paper (Cat. No. 1825-047). 1M NaClO_4 in ethylene carbonate: propylene carbonate (1:1 vol.%) was used as the electrolyte. Prior to the fabrication of NIC, the mass loading was adjusted by keeping the aforesaid electrode formulation. Solartron 1470E electrochemical workstation was used to record the a.c. impedance spectroscopy (EIS) at different intervals. Electrochemical charge-discharge studies were conducted using Arbin BT 2000 at 25 °C.

Micrometer to millimeter sized crystalline flakes of TiS_2 was acquired from CVT. A simulated structure of an ICSD file (52195) was generated with the help of VESTA 3.3 program

and is shown in Figure 1a-b, which depicts the top (Figure 1a) and side view (Figure 1b) of the layered morphology of the pristine compound. Semi-quantitative analysis to ascertain the stoichiometric constitution of the synthesized compound is obtained *via* SEM/EDAX. The elemental concentration shown in Figure 1c reveals a near-perfect stoichiometric ratio (Ti:S :: 1:2) along with a micrograph showing the layered flakes of TiS₂. The powder XRD pattern confirms the formation of a highly crystalline TiS₂ phase on account of the sharp high-intensity diffraction peaks (Figure 1d). The observed reflections are indexed with P-3m1 space group. Further, SAED data was collected through TEM, and the pattern was indexed accordingly to reveal the trigonal arrangement of the atoms in the TiS₂ single crystal (Figure 1e-f).

Na-insertion properties of TiS₂ are evaluated in half-cell assembly between 1.05-2.6 V *vs.* Na at a current density of 100 mA g⁻¹ and given in Figure 2a-b. Apparently, a clear Na-insertion/extraction process is evidenced from charge-discharge studies. Theoretically, the insertion of one mol. Na is possible (239 mAh g⁻¹), but practically insertion of 0.73 mol. Na only feasible. Interestingly, Na-insertion characteristics are much better than Newman and Klemann report [12] since they suggested that “Na-TiS₂ is an impractical energy storage system”. To the best of our knowledge, no reports available on the Na-intercalation properties into TiS₂ after the aforesaid report. Sun *et al.*[17] also concluded that the Na/TiS₂ is impractical system towards Na-ion battery perspective. However, unusual electrochemical activity (*i.e.* pseudocapacitive storage) of TiS₂ nanoplates are reported by Liu *et al.*[18]. Usually, the TiS₂ is a well-known perfect insertion host, not only for Li and Na-ions but also for bivalent ion like Mg²⁺[19]. Upon the perfect topotactic intercalation process, a very prominent and high intense cyclic voltammograms are observed, but it is absent in the report of Li-ion insertion into TiS₂ by Liu *et al.*[18]. Clearly, there is no such characteristics plateau's/prominent peaks observed *i.e.* surface only involves the charge-storage process rather than bulk [20]. This high-end Na-insertion property could be achieved by possibly tailoring the synthesis procedure *i.e.* synthesizing utmost pure single crystals. Such single crystals displayed excellent Na-intercalation properties which are paralleled by differential capacity

profiles compared to the other synthetic protocols reported elsewhere. It is well established that Na-ion diffusion kinetics are weaker than Li-ions, which eventually results in less reversibility upon cycling [14]. As a consequence, 0.62 mol. Na only reversed during the charging process which corresponds to the ~85% reversibility in the first cycle. However, in the second cycle onwards, the efficiency is drastically improved (~85 to 97%) with a marginal decline in the capacity (~148 to ~140 mAh g⁻¹). Thereafter, very stable cycling profiles are observed with retention of ~85% after 50 cycles.

This notable performance logically alerts us to fabricate the practical device to demonstrate the suitability to be used as an intercalation host. In this line, non-aqueous NIC is fabricated with commercial AC. Pairing with high surface area AC is a tricky process since charge carriers are accumulated on the surface to form a double layer across the electrode-electrolyte interface in a non-Faradaic fashion. Mass loading between the electrodes plays a vital role to achieve higher values. Therefore, prior to the fabrication, the mass loading has been adjusted. Accordingly, Na/AC cell was assembled and tested at a current density of 100 mA g⁻¹ between 2.7-4.2 V *vs.* Na (Figure 2c) and delivered a reversible capacity of ~57 mAh g⁻¹ (corresponds to the capacitance of ~137 F g⁻¹). Based on the electrochemical performance of both materials, the mass ratio between TiS₂ to AC is fixed at 1:3.05 (5 mg: 15.25 mg).

Then NIC was subjected to various electrochemical studies and given in Figure 3. Based on the Na-intercalation potential, the testing window potential has been limited to 2.6 V and the applied current densities are based on the total mass loading of the active material (20.25 mg). In general, increasing current density leads to the decrease in discharge time which is reflected in this case well. This is mainly because of the partial utilization of the active material at higher rates. Upon charge process, the Na⁺ ions are intercalated into TiS₂ lattice, whereas ClO₄⁻ ions are accumulated over the surface of the AC across the electrode-electrolyte interface to form the double layer. This reaction is reversed during the discharge process. To estimate the calendar life

of this interesting configuration, the cycling studies were conducted at a rate of 1 A g⁻¹ and given in Figure 3b along with the Columbic efficiency. If we restrict the potential application of this configuration (at 80%), the cell can able to sustain up to 3600 cycles. However, surface modification with carbonaceous materials over TiS₂ may increase the lifetime. The decrease in the Na-ion kinetics is clearly revealed by EIS measurements at different intervals (Figure 3c). Interestingly, the Coloumbic efficiency of the cell is found over 99.5% which clearly suggests the excellent reversibility.

Energy and power densities are very crucial for each and every secondary energy storage systems. Total mass loading of the active materials is considered for the calculation of the energy and power densities by using standard procedures (Figure 3d). Thus, the energy and power density values were calculated using the following relation, $P = \frac{i(A) \times V}{m(mg) \times 10^{-6}}$ and $E = \frac{P \times \Delta t}{3600}$ where i is applied current in A, the Δt is discharge time in s, m is total weight the of active materials (TiS₂ and AC) in mg (20.25 mg), and V is the working potential of the cell *i.e.* taken at the intersection point of charge-discharge curve at each current rate. Accordingly, the AC/TiS₂ cell delivered a maximum energy density of ~38 Wh kg⁻¹ and the energy density started declining with increasing current rate. The observed values are comparable and even better than the lower potential insertion type anode, Na₃Ti₂O₇ [21-23] and other systems too [7]. Importantly, this specific AC/TiS₂ configuration delivered an excellent performance at higher rates which is similar to that of AC/NaTi₂(PO₄)-rGO system reported by us [8]. This high current performance of NIC is not only limited to other Na-ion intercalating materials, also with Li-ion capacitor as well (Figure 3d). Currently, we are in the process of making the composites, preferably with graphene nanosheets. In addition to the energy and power densities, enhancement in the cycling profile could also be expected.

We successfully demonstrated the suitability of using such 2D TiS₂ as intercalation type anode in Na-ion capacitor configuration with non-Faradaic type AC electrode by adjusting the

mass loading between the electrodes. The AC/TiS₂ configuration registered the energy density of ~38 Wh kg⁻¹ with a possible lifetime up to 3600 cycles (estimated at 80% DOD). Interestingly, this NIC displayed excellent performance at higher rates which opens up for further exploration of intercalation type negative electrodes for NIC's. First, we proved that the Na-intercalation process into the highly crystalline TiS₂ with high reversibility of over 0.6 mol. Na. Also, good stability during the electrochemical cycling is worth mentioning.

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Figure 1. Material characterization of TiS_2 : Simulated crystal structure of TiS_2 : (a) top-view, and (b) side view, (c) semi-quantitative analysis of as-grown TiS_2 crystallites, (d) Powder XRD pattern of as-grown TiS_2 compound indexed with standard ICSD file no. 52195 (the peak marked with * is from the aluminium sample holder), (e) Transmission electron microscopy image, and (f) corresponding select area electron diffraction pattern (SAED) pattern of an ultra-sonicated TiS_2 sample diluted in an ethanol solvent.

Figure 2. Na-storage properties of the TiS_2 prepared by CVT in half-cell configuration (Na/TiS_2): (a) typical charge-discharge curves recorded at 100 mA g^{-1} , and (b) Plot for capacity *vs.* cycle number. Inset: Differential capacity profiles of first two charge-discharge cycles, (c) typical charge-discharge curves of Li/AC , and (d) Plot for capacitance *vs.* cycle number

Figure 3. Electrochemical performance of AC/TiS₂ based NIC (a) typical charge-discharge curves recorded at various current densities, and (b) Cycling profile of AC/TiS₂ based NIC along with Coloumbic efficiency recorded at the current density of 1 A g⁻¹, (c) Ragone plot of AC/TiS₂ based NIC and LIC [14], and (d) Electrochemical impedance spectra of AC/TiS₂ based NIC at various intervals.