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Investigation of Polyanion Materials with Multiple Intercalation Cations: Na Ions in Na-Ion Full Cell

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Sodium-ion (Na-ion) batteries offer the potential of combining intercalation chemistry such as that used in lithium-ion batteries with replacement of large amounts of lithium with lower cost and more abundant sodium. The differences between sodium and lithium, in particular the cation size, has led to many new materials being explored for Na-ion battery applications. During the study of multiple intercalation cations into the polyanion material $NaTi_2(PO_4)_3$ (NTP) as a candidate anode material, this study will report the electrochemical performance of coin cells containing NTP. In addition, the electrochemical performance of a candidate cathode material, $Na_3Ni_2SbO_6$ (NNS), will be reported with regards to sodium intercalation, and finally NTP/NNS full cells.

1. Introduction

As batteries move to larger scale applications, in particular grid applications, the need to keep material costs low becomes significant. Motivated by the pursuit of new materials for battery applications and the abundance and low price of sodium, a number of research groups have begun to pursue sodium-ion (Na-ion) batteries [1]. Relative to more established lithium-ion (Li-ion) battery materials, Na-ion materials have been less explored. The larger size of Na relative to Li often means that it is not necessarily straightforward to use a Li-ion battery material in a Na-ion system – thus both new anode and cathode materials will be needed for a commercially successful Na-ion battery.

Relative to Li-ion battery materials, Na-ion cathodes in many cases have lower potentials, thus finding Na-ion cathodes that can provide relatively high voltage which will be needed to compete with many existing commercial systems can be challenging. One Na-ion material that has shown promise is $Na_3Ni_2SbO_6$ (NNS) [2]. This material has a relatively high voltage, with almost all of the electrochemical capacity above 3.0 V (vs. Na/Na^+), including a plateau at ~3.1 V. Under some processing conditions, this material has even been reported as having good capacity retention at high C rates [2], even though the larger Na^+ ion generally makes achieving high rate capability more challenging with Na-ion materials relative to Li-ion materials.

The sodium super ion conductors (NASICON) class of materials have been reported in a number of studies in the battery literature [3], in particular because the high ionic conductivity of these solid-state materials makes them attractive as alkali-ion battery electrolytes [4]. In many cases; however, NASICON materials have also been reported as battery electrode active materials. While the particle size needs to be small and/or the particles must be carbon coated to make up for their intrinsically low electronic conductivity [5,6], these materials in particular have been reported to function as battery anodes. One example of a NASICON material that can be used as a Na-ion anode is $NaTi_2(PO_4)_3$ (NTP). This material has most of its capacity at ~2.0 V (vs. Na/Na^+), making it suitable as an anode material. Stable cycling of this material has previously been reported in the literature.

This paper will report electrochemical cycling of Na-ion half cells of Na/NNS and Na/NTP, as well as NTP/NNS full cells. Due to the Na^+ extraction from NNS and insertion from NTP on the first cycle, it was expected that these materials would make a suitable full cell paring. The capacity of NNS being >3.1 V coupled with the capacity of NTP being a ~2.0 V suggested that the full cell would have a cell voltage of~1.1 V.

2. Experimental

2.1 Materials Synthesis

For synthesis of NNS, stoichiometric amounts of Na_2CO_3 (Fisher), Sb_2O_3 (Acros), and NiO (Fisher) were roller milled dry with 1 cm diameter zirconia beads to form a well-mixed powder. The mixture was then fired at 900 °C for 12 hours. The resulting materials was then reground with a mortar and pestle and fired for an additional 12 hours at 900 °C. The resulting material was then ground with a mortar and pestle to form a fine powder.

NTP was synthesized via solid state reaction with Na_2CO_3 (Fisher), TiO_2 (Anatase, Alfa Aesar), and $NH_4H_2PO_4$ (Fisher). These precursor powders were mixed stoichiometrically and dry milled on a roller with 1 cm diameter zirconia beads. The precursors were fired at 300 °C for 2.5 hours in air for degassing. The degassed precursors were then ground again in a mortar and pestle and fired at 950 °C for 10 hours. The resulting materials was reground with a mortar and pestle and fired again at 950 °C for 10 hours. All firings were conducted in the lab atmosphere.

2.2 Electrochemical Characterization and Cell Fabrication

Active materials were ball milled with a 6.5:1 (by mass) active material:carbon ratio using 3 mm diameter zirconia beads in a Fritsch planetary mill. Milling was performed at 300 RPM for 7.5 hours. Electrode slurries were comprised of the milled carbon/active material mixture, additional carbon black, and polyvinylidene difluoride (PVDF) binder with extra n-methylpyrrolidone (NMP, Fisher) added to reduce the slurry viscosity to the desired consistency. The final compositions of the resulting electrode slurries were 65 wt% active material, 20 wt% carbon black, and 15 wt% PVDF. Slurries were blended in a slurry mixer (Thinky). The same electrode composition was used for both NNS and NTP.

The electrode slurries were coated onto 20 μm thick aluminum foil using a doctor blade with a blade height set at 200 μm. After drawing out the electrodes with the doctor blade, the films were dried in an oven overnight at 70 °C and then dried in a vacuum oven at 70 °C for a minimum of 4 hours. The thin film electrodes were then punched using a 9/16 inch diameter punch into disks, and these disks were used as the cathodes in 2032-type coin cells. Coin cells were assembled in an argon-filled glove box with H_2O and O_2 both < 1 ppm. For full cells, the NNS electrode was used as the cathode and the NTP electrode was used as the anode. For half cells, the NNS or NTP electrode was used as the cathode and the anode was a thin film of punched Na foil. The Na foil was produced by taking sodium cubes (Sigma) stored in oil, cutting off a thin piece of Na using a stainless steel razor blade in the glove box, rinsing the cut Na in hexane, allowing the rinsed Na to dry in the glove box, and then rolling the Na with a stainless steel cylinder by hand to draw out the metal into a thin film. The film was then punched with a 9/16 inch diameter punch into a disk and used as an anode.

The electrolyte used in all cells was prepared by first vacuum drying $NaPF_6$ (Sigma) overnight in a vacuum oven at 70 °C. The $NaPF_6$ was then transferred into the glove box and weighed out in sufficient quantity to produce 0.4 mol L^{-1} $NaPF_6$ dissolved in a blend of 30:70 (mass basis) ethylene carbonate:diethylcarbonate electrolyte. The electrolyte was impregnated within the composite electrode and polypropylene separator dropwise when assembling the cells in the glove box. The coin cells were then galvanostatically cycled on a MACCOR battery cycler. Cycling rates were based on the measured gravimetric capacities of each material at low rate (40 mAh g^{-1} for NNS and 150 mAh g^{-1} for NTP) and scaled appropriately for the actual loading of each material in the electrode and the desired C (e.g.; for 1C 40 mA g^{-1} NNS and 150 mA g^{-1} NTP). Full cells were all cathode limited, and thus the C rate for full cells was based on the cathode mass.

3. Results and Discussion

3.1 Na/NNS Half Cell Cycling

Na/NNS half cells were initially evaluated during charge/discharge at the relatively low rate of C/20, with the initial cycle starting on charge. A typical result for the first 2 cycles completed between 2.0-3.7 V (vs. Na/Na^+) can be found in Figure 1. Typical irreversible capacity loss on the first cycle was ~20%, which rapidly declined after the first cycle. The discharge capacity was typically 40 mAh g^{-1}. Almost all of the electrochemical capacity was above 3.0 V, with the majority of the discharge capacity being delivered at a plateau at 3.1 V.

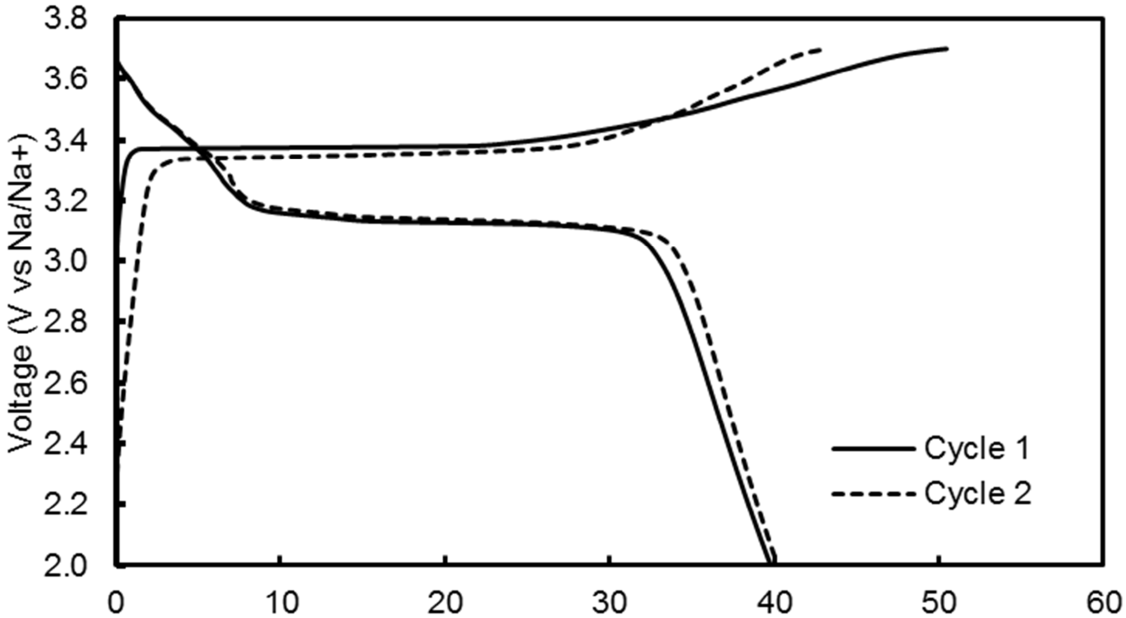

Figure 1. First (—) and second (- -) charge/discharge cycles of a $Na/Na_3Ni_2SbO_6$ half cell at a rate of C/20.

After confirming the voltage profile at low rate, Na/NNS cells were fabricated to evaluate the rate capability of the NNS material (Figure 2). For rate capability, the cells were charged and discharged at the same rate. The cells were cycled at the same rate for 5 cycles, and the rate was progressively increased from C/20 to 2C. The rate capability was very good, with >85% capacity retention at 2C relative to the initial capacity at C/20. We do note that the final 3 cycles at C/20 after cycling at 2C had slightly higher capacity than the initial cycles at C/20, indicating that the rate capability was likely slightly less due to additional capacity gained with cycling. This additional capacity was the result of an activation process in the cell that has not yet been full explored, but was consistently observed. It is also noted that the material was ball milled and there was significant excess of carbon black in the cathode, and thus at higher active material loadings the rate capability would likely be diminished relative to these results; however, the rate capability was encouraging, particularly for a Na-ion material.

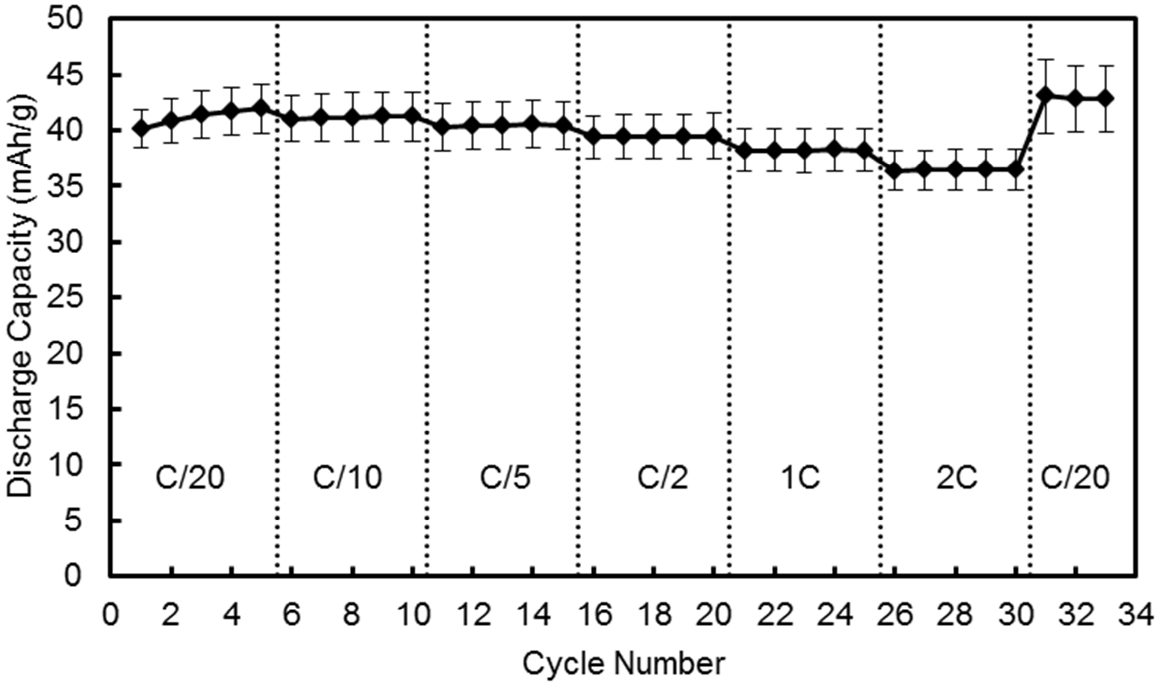

Figure 2. Discharge capacity (♦) of three Na/$Na_3Ni_2SbO_6$ half cells at rates of C/20, C/10, C/5, C/2, 1C, and 2C. Cells were charged and discharged at the same rate. Error bars represent the standard deviation of three cells.

3.2 Na/NTP Half Cell Cycling

Na/NTP half cells were first cycled at the rate of C/20, with the initial cycle starting on discharge. The charge/discharge voltage profiles for the first 2 cycles, completed with a voltage window of 1.0 to 3.4 V (vs. Na/Na^+) are shown in Figure 3. The starting reversible capacity was typically 150 mAh g^{-1}, and the majority of electrochemical capacity occurred at a plateau at 2.1 V.

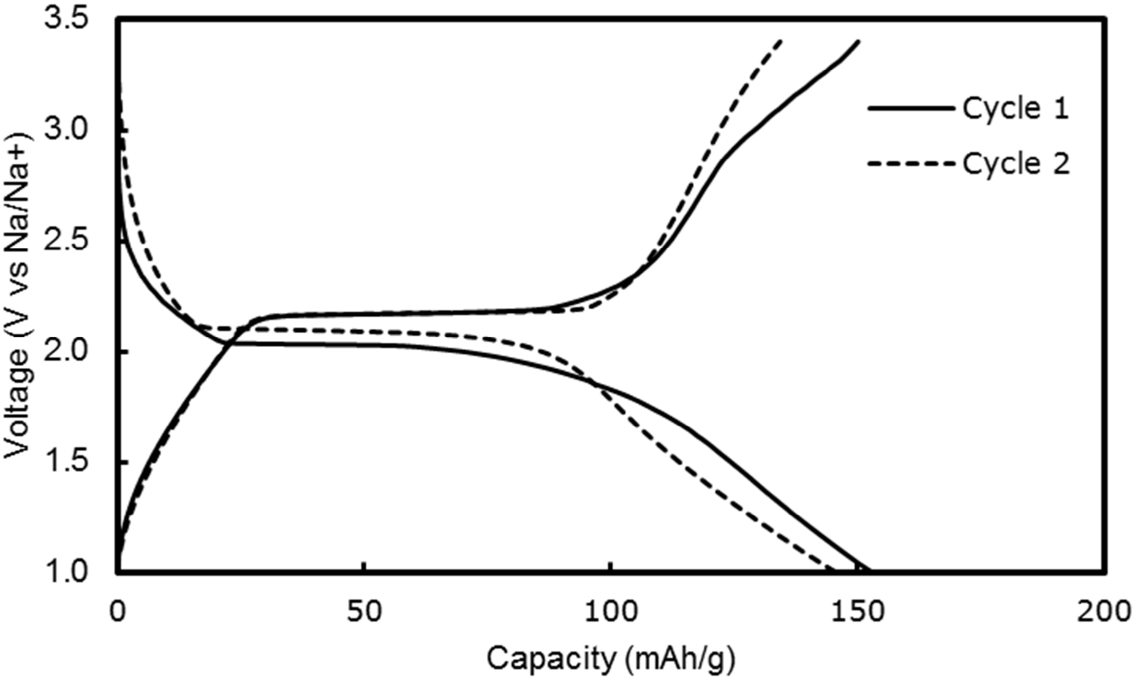

Figure 3. First (—) and second (- -) discharge/charge cycles at C/20 of a Na/$NaTi_2(PO_4)_3$ half cell.

Rate capability for Na/NTP cells can be found in Figure 4. Unlike the NNS electrodes, which gain capacity during the first few cycles, the NTP electrodes rapidly lost discharge capacity by dropping to 110 mAh g-1 over the first 5 cycles at C/20. The capacity stabilized on the fifth cycle; however, and any further reductions in discharge capacity were attributed to the reduction in discharge capacity due to increased cycling rate. This speculation was confirmed by the fact that the discharge capacity was consistent within each increased rate (C/10, C/5, C/2, and 1C) and that the capacity recovered on cycling at C/20 after completing the cycles at 1C. Rate capability for the NTP material was relatively low, with <20% of the capacity retained at 1C relative to the capacity at C/20. The NTP electrodes were ball milled and carbon coated using equivalent processes to the NNS electrodes, so the poor capacity retention likely reflects relatively larger particle sizes for the NTP material relative to the NNS material [7]. Given the more extensive firing procedure for the NTP, it would not be surprising if the material became highly sintered and had large particles – though analysis of particle morphology was not conducted for this study.

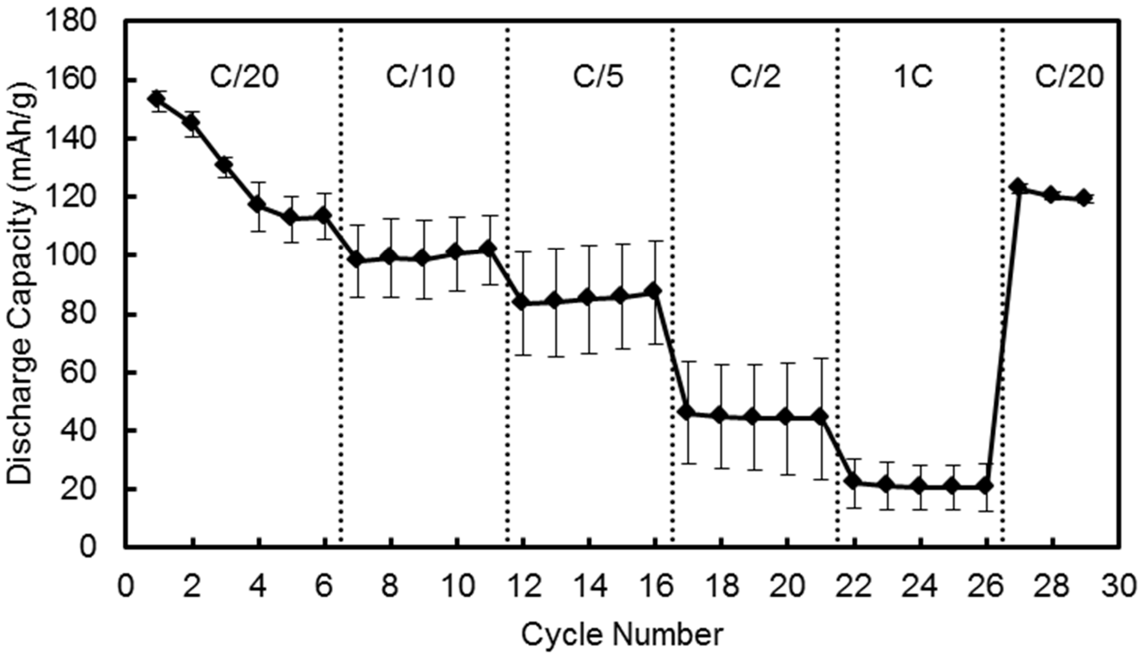

Figure 4. Average discharge capacity (♦) of three Na/$NaTi_2(PO_4)_3$ half cells at discharge/charge rates of C/20, C/10, C/5, C/2, and 1C. Error bars represent the standard deviation of the 3 cells.

3.3 NTP/NNS Full Cell Cycling

The final electrochemical evaluation was conducted using NTP/NNS full cells. These cells were extremely cathode limited, with a typical ratio of cathode:anode capacity of 3:1. All rates and capacities were scaled according to the mass of the cathode material. Figure 5 displays the charge/discharge curves at a rate of C/20 for a NTP/NNS cell cycled between .01-1.4 V (cell voltage). The cell had very high irreversible capacity on both of the first two cycles. The irreversible capacities of both the anode and cathode resulted in a particularly low coulombic efficiency when the two materials were combined. This was also evident in the rate capability evaluation (Figure 6), where the coulombic efficiency gradually improved but failed to reach 90% over the first 10 cycles, and only reached a maximum value at 90%. The capacity of the NTP/NNS full cell, even on just the basis of NNS loading, was very low. While the initial performance of this system is relatively modest, it does demonstrate stable cycling of a relatively new anode and cathode pair for a Na-ion full cell. Further improvements and optimization of the anode and cathode materials in isolation will likely result in substantial improvements in the full cell performance.

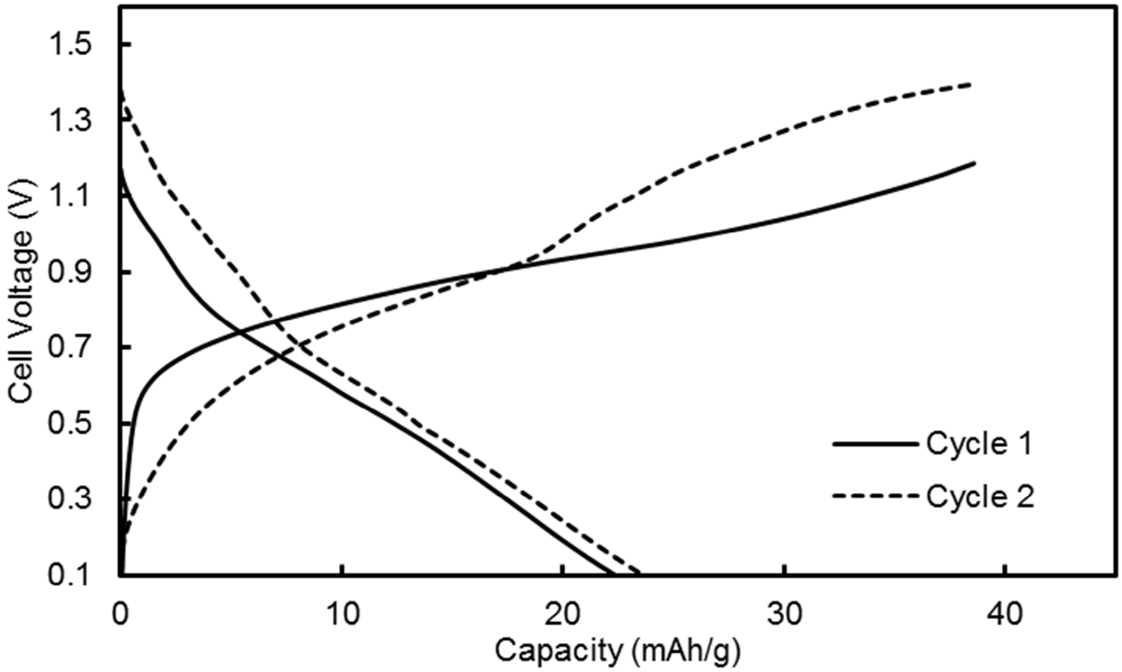

Figure 5. First (—) and second (- -) charge/discharge cycles of a $NaTi_2(PO_4)_3/Na_3Ni_2SbO_6$ full cell at a rate of C/20.

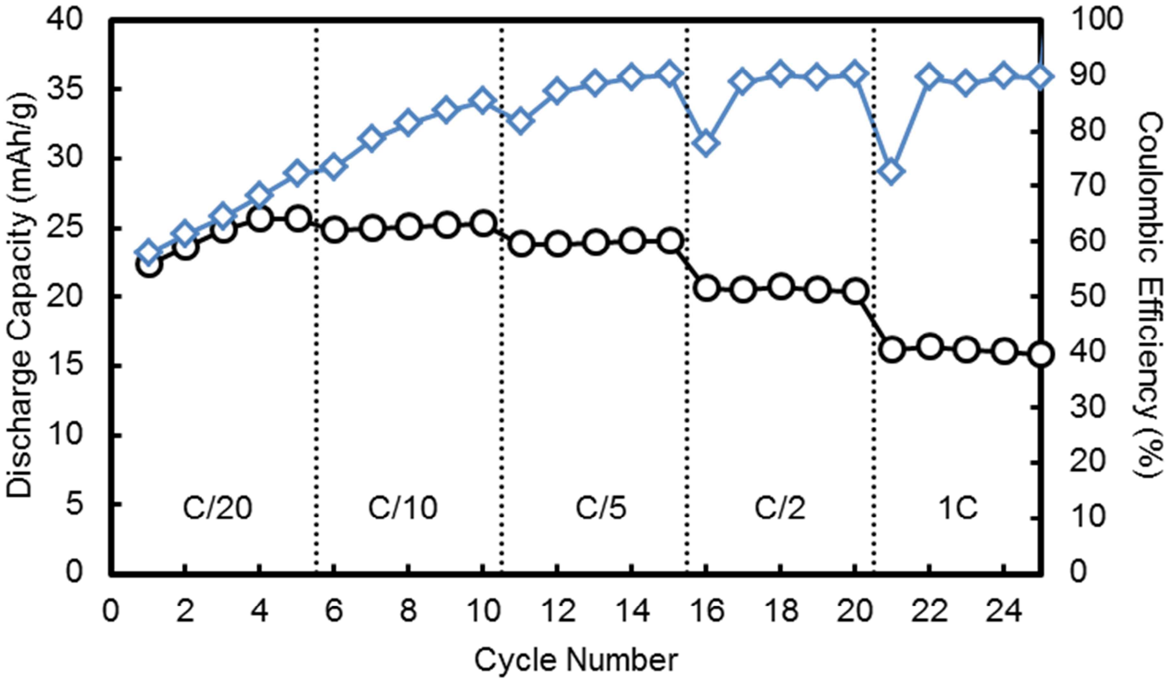

Figure 6. Discharge capacity (black circles) and coulombic efficiency (blue diamonds) of $NaTi_2(PO_4)_3/Na_3Ni_2SbO_6$ full cell at charge/discharge rates of C/20, C/10, C/5, C/2, and

1C. Five cycles were completed at each rate. C rate was based on the cathode loading and the cells were significantly cathode limited.

.4. Conclusion

A Na-ion anode and cathode material were synthesized and evaluated electrochemically in both half cells paired with sodium metal and full cells paired with each other. The NNS cathode material had good retention of discharge capacity at increasing rates; however, the overall gravimetric capacity started relatively low at ~40 mAh g^{-1}. The NTP anode had higher gravimetric capacity at ~150 mAh g^{-1}; however, the discharge capacity faded severely with the first few cycles and the rate capability was much less relative to the cathode material. Full cell cycling revealed relatively low coulombic efficiency, due to the combined independent contributions of coulombic efficiency losses from the anode and cathode. While the capacity and energy density of the full cell were modest, the full cell pairing does result in a stable Na-ion full cell battery for dozens of cycles.

Acknowledgements

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