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Anion intercalation into a graphite cathode from various sodium-based electrolyte mixtures for dual-ion battery applications

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ABSTRACT

Electrolyte plays a crucial role for dual-ion batteries by supplying the ions to be intercalated into electrodes. Yet, high operation potentials of such batteries limit the number of suitable electrolytes to be used since they have to be stable upon cycling. Here, sodium-based electrolytes were investigated by applying stability and cycling tests in order to observe their influences on anion intercalation behavior using graphitic cathodes. Intercalation of PF_6^- anions with organic carbonate solvents revealed relatively better discharge capacities compared to its anionic counterparts and 0.5 M $NaPF_6$/EC:EMC electrolyte was found to be the most promising mixture among them. PC solvent proved detrimental for anion intercalation, but FEC as an electrolyte additive in PC precluded undesired effects of PC and gave rise to reversible cycling. However, the ionic liquids based on $TFSI^-$ and FSI^- anions, mostly, yielded capacity fading under a charging end potential of 5.0 V vs. Na/Na^+, except the 0.7 M NaTFSI/Pip_{14}TFSI electrolyte, showing 98% coulombic efficiency over 200 cycles. During this work, electrochemical tests were conducted and evaluated to comprehend the impacts of electrolytes on the anion intercalation process. EC:EMC-based electrolyte was then used in our further research, where the compositional cathodic investigation was executed and the anion intercalation phenomenon was characterized.

1. Introduction

Graphite is an amphoteric material that can function as a host in both oxidative and reductive chemical intercalation reactions [1]. During electrochemical cycling with charge transfer interaction, insertion of species in between graphene layers forms graphite intercalation compounds (GICs) [2,3]. Today, for commercial lithium ion battery (LIB) applications, graphite comes to the fore as being the most commonly used anode material [4], while transition metal oxides having layered, spinel or olivine structures are used as cathode materials [5]. Utilization of graphite as both for anode and cathode electrodes was first reported by McCullough et al. [6] and the study of Carlin et al. [7] in 1994 showed the reversible anion intercalation by using ionic liquid (IL) electrolytes. Seel and Dahn particularly have leaned to this phenomenon in detail and provided exclusive studies [8,9] using liquid organic electrolytes reaching over 100 mAh/g discharge capacity with $LiPF_6$/EMS electrolyte. In another study with organic liquid electrolytes, Read et al. [10] have achieved a capacity of 82 mAh/g with significant reversibility by utilizing a $LiPF_6$/FEC-based electrolyte. Also, extensive researches in dual-ion systems have been conducted by Placke et al. [11–14] with the main focus on ionic liquid electrolytes, and they have attained comparatively higher discharge capacities with remarkable cycle life. Recently, dual-ion cells having Aluminum (Al) as both the anode and the current collector has drawn attention with their high energy density ($\sim$221 Wh kg^{-1} [15]), asserting a discharge capacity of 104 mAh/g with respectable cycling life and capacity retention [16,17] by employing Li-based electrolyte mixtures.

Dual-ion battery operation boils down to simultaneous cation and anion insertion into anode and cathode, respectively during charge operation. The reverse process happens upon discharge process by letting off the intercalated species into the electrolyte. In such systems, the electrolyte carries the utmost importance as the electrolyte salt supplies the ions (charge sources) and thereby determines the charge capacity of the cell [8,9]. Inherently, electrolyte concentration undergoes a change while charge and discharge processes are taking place. Also, the high working potentials of dual-ion cells provide an important advantage to the

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system, but bring the requirement to the electrolyte to be resistant against oxidation. However, not every electrolyte possesses high oxidative stability when they are exposed to high charging potentials, thence electrolyte might face with decomposition reactions which directly affects operational performance of the cell. In LIB anodes, solid electrolyte interphase (SEI) is known to be a stable passivating layer formed on the graphite surface by means of reductive decomposition of the electrolyte and it impedes further decomposition reactions to provide reversible Li^+ intercalation. A similar interphase layer can also emerge between cathode and electrolyte considering the instability of electrolyte components above certain applied potentials [18]. Thus, the selection of a good salt-solvent combination is the cornerstone for dual-ion batteries to ensure sufficient ionic conductivity and good chemical and electrochemical stability.

Operation and optimization of a dual-ion battery can only be understood by elucidating anion intercalation mechanism [8]. Many preceding studies, mentioned above, used Li-based electrolytes while studying the anion intercalation mechanism into graphite cathodes. However Na-based batteries as an alternative to that of Li-based ones, enable a cost advantage with Na element's higher abundance and availability, yet standard reduction potential of sodium shows 0.3 V lower potential compared to that of lithium's [19]. So far as we know, Na-based electrolytes for dual-ion cells have been used for the first time in our previous work [20] by the examination of PF_6^- and BF_4^- intercalation into a graphite cathode using organic carbonate solvents. Herewith, we enlarge the scope of Na-based electrolyte investigation for dual-ion battery applications by conducting electrochemical measurements to graphite cathode electrodes to determine the most promising electrolyte mixture which will then be used in our parallel study [21] where the best electrolyte-electrode combination is determined to discover the particle size effect, staging phenomenon and the structural changes occurring at the graphite cathode during charge/discharge processes for Na-based dual-ion cells. Various Na-based electrolytes were examined throughout this work in terms of their capacity and electrochemical stability in order to comprehend the anion intercalation process of different electrolyte mixtures.

2. Experimental Procedure

2.1. Electrolyte preparation

In order to prepare organic liquid electrolytes, sodium salts of 1 M $NaClO_4$ (Alfa Aesar, >98%), 0.5 M $NaPF_6$ (Alfa-Aesar, 99%), 1 M NaTFSI (Solvionic, 99.7%) and 1 M NaFSI (Solvionic, 99.5%) were dissolved in diverse organic solvents including, PC, EC, DEC, DMC, EMC, and FEC as an electrolyte additive. EC, EMC solvents were supplied by Merck, PC by BASF, and rest of the organic solvents were provided by Sigma-Aldrich. All solvent purities were 99% with a water content below 20 ppm. The salts were dried under 80 °C with low pressure (10^{-2} mbar) for 15 h before the electrolytes were prepared. Then, electrolyte preparation was made in an Argon filled glove box at room temperature (RT, 23 °C) with water and oxygen content being less than 1 ppm. Salt concentrations were determined by the consecutive addition of a 0.1 M salt equivalent into the solvent mixture, followed by 2 h mixing until the maximum possible concentrations were reached in order to supply the utmost ionically conductive platform to the cell as the electrolyte salt generates the source of charges to be stored in the electrodes.

For ionic liquid electrolyte preparation, NaTFSI and NaFSI electrolyte salts were dissolved in piperidinium- and pyrrolidinium-based ILs. Apart from $Pip_{13}FSI$ (Solvionic, 99.5%), any other tested ILs were supplied by Io-Li-Tec with the assay degree of 99%. Analogous steps to carbonate-based electrolytes were applied to complete the electrolyte preparation.

2.2. Graphite electrode fabrication

Synthetic graphite of KS6 (Imerys, Timcal, particle size – d90 = 6.5 μm, BET surface area = 26 m^2/g) was used during this work where the graphitic electrodes consisted of 90 wt% of graphite, 2 wt% of carbon black (Imerys, Timcal, Super C65) and 8 wt% of polyvinylidene fluoride (PVDF) binder (Solef 6020, Solvay). The powders were mixed in a planetary mixer (Thinky ARE-250 mixer) for 15 min at 230 rpm to obtain a homogeneously dispersed powder mixture. Then, a sufficient amount of N-methyl-2-pyrrolidone (NMP, Carl Roth ≥ 99.8%) was admixed to the powder to dissolve the binder and the mixture was stirred again at 2000 rpm for 30 s repeatedly until the slurry was homogenized. The slurry was coated on an aluminum (Al) foil by doctor blade technique with a gap thickness of 250 μm. The coated foil was then heated to 90 °C for 3 h in order to let the NMP evaporate. After the heating process, the electrode was calendered in order to get evenly distributed electrode thickness, and punched afterwards with a round shaped cutter with a diameter of 11 mm. Before placing the electrodes inside the glove box for cell assembly, the round shaped electrodes were dried at 100 °C below 10^{-2} mbar overnight in a vacuum chamber.

2.3. Cell assembly

Schematic representation of the laboratory test cell (glass cell in coin cell setup) is given in Fig. 1 below. The working electrode is separated from the sodium metal that serves as the counter and reference electrode by using two 12 mm glass fiber separators (Whatman, GF/A, thickness: 260 μm) in order to prevent the cell from short circuit. The separators in between the electrodes were drenched with 100 μl electrolyte and the electrodes were sandwiched between two stainless steel disks serving as current collectors. A metal spring was used on top of the metal disk to ensure a better contact between the electrodes and the electrolyte. Test cells were sealed and rested for 2 h to enable sufficient wetting before the electrochemical tests were performed.

2.4. Constant current constant voltage (CCCV) cycling test

Constant current constant voltage (CCCV) cycling tests were conducted to evaluate and compare cells containing different electrolyte mixtures in terms of their performances. Cycling tests were carried out by a CTS battery cell tester (Basytec). Many preceding studies postulated a specific discharge capacity of a dual-ion cell as 100 mAh/g [12,13,20]. Therefore, in order to perform CCCV tests at C/4 rate (considering a typical active material mass of 4.0 mg), constant charge/discharge current of 100 μA was usually used during cycling with the potential interval of 3.0 V to 5.0 V vs. Na/Na^+ (different limits in some experiments).

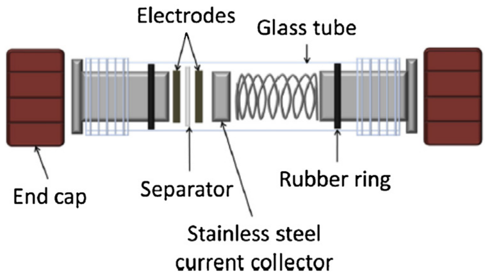

Fig. 1. Two electrode test cell setup configuration [17].