



Sodium-Based vs. Lithium-Based Dual-Ion Cells: Electrochemical Study of Anion Intercalation/De-Intercalation into/from Graphite and Metal Plating/Dissolution Behavior



Paul Meister^a, Olga Fromm^a, Sergej Rothermel^a, Johannes Kasnatscheew^a,
Martin Winter^{a,b,*}, Tobias Placke^{a,*}

^a University of Münster, MEET Battery Research Center, Institute of Physical Chemistry, Corrensstr. 46, 48149 Münster, Germany

^b Helmholtz Institute Münster, IEK-12, Forschungszentrum Jülich GmbH, Corrensstraße 46, 48149 Münster, Germany

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ABSTRACT

Energy storage systems utilizing a simultaneous intercalation of anions into a graphite host structure at the positive electrode and intercalation/insertion/reduction or deposition of cations at the negative electrode during charge, were introduced under the term dual-ion cells, recently. In this work, the electrochemical intercalation of TFSI⁻ anions into graphite has been studied in sodium-based dual-ion cells (SDICs) at different upper cut-off potentials varying between 4.5 V and 4.7 V vs. Na/Na⁺. Electrochemical characteristics of SDICs, including the reversible capacity, Coulombic efficiency, energy efficiency and onset potentials for anion intercalation, were evaluated in comparison to the lithium-based dual-ion cells (LDICs). A stable charge/discharge cycling performance over 500 cycles has been found for SDICs providing a specific capacity of $\approx 32 \text{ mAh g}^{-1}$ and a Coulombic efficiency exceeding 99% at an upper cut-off potential of 4.7 V vs. Na/Na⁺ at the graphite cathode. By the addition of the electrolyte additive ethylene sulfite (ES), an increase of the reversible capacity to $\approx 46 \text{ mAh g}^{-1}$ was achieved. Furthermore, possible reasons for the overall inferior cycling performance in terms of capacity for SDICs as compared to LDICs such as an increased overpotential for plating/stripping of Na⁺ ions as compared to Li⁺ ions are discussed. In this respect, we also found that the addition of ethylene sulfite particularly decreases the overpotentials for the metal plating process, which at least partially explains the enhanced reversible capacity in LDICs and SDICs by using ES as electrolyte additive.

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1. Introduction

In order to counterbalance the fluctuating energy generation by renewable energy sources, such as solar or wind power, appropriate electrochemical stationary energy storage systems are urgently needed. In contrast to storage systems for automotive applications, where a high energy density and power density are key parameters, the requirements for stationary batteries differ significantly. The most important parameters for stationary energy storage are a high safety, low costs, a long cycle and a long calendar life of the respective storage technology. [1,2] Beside lithium ion batteries (LIBs), various potential technologies have been proposed

for this application including e.g. sodium and sodium ion batteries (SIBs) [1,3], dual-ion or dual-graphite batteries [4–9] and redox flow batteries [10,11].

The dual-ion technology might be a promising option owing to the usage of low cost and non-toxic graphite as active material for the cathode, which can be furthermore easily processed using aqueous electrode coating technologies. [4,5] More recently, also the use of alternative cathode materials showing reversible anion-storage properties, such as metal organic frameworks or redox-active organic molecules, has been reported. [12–14] Furthermore, the application of electrolytes based on ionic liquids (ILs) is beneficial with regard to the safety of the cells, as ILs are non-flammable and possess a negligible vapor pressure. [4] In contrast to lithium ion or sodium ion batteries, where the alkali cations are shuttled between the positive and negative electrode during cycling, a different storage mechanism is present in the case of dual-ion cells. Upon charge the Li⁺ or Na⁺ cations are intercalated/

* Corresponding authors at: University of Münster, MEET Battery Research Center, Institute of Physical Chemistry, Corrensstr. 46, 48149 Münster, Germany.

E-mail addresses: martin.winter@uni-muenster.de, m.winter@fz-juelich.de (M. Winter), tobias.placke@uni-muenster.de (T. Placke).

inserted/reduced or deposited into/on the negative electrode and the anions are simultaneously intercalated into the positive graphite-based electrode. Upon discharge, the ions are released back into the electrolyte. Consequently, a continuous change of the salt concentration within the electrolyte takes place with ongoing cycling. [15]

Placke et al. were the first to present lithium-based dual-ion cells with a high Coulombic efficiency (exceeding 99%) and a stable capacity retention for several hundreds of cycles. [4,5,15,16] In their works, an ionic liquid-based electrolyte comprising of lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) in *N*-butyl-*N*-methylpyrrolidinium TFSI (Pyr₁₄TFSI) was applied, which shows an extraordinary high anodic stability. [17] Even though different electrolyte solvents, salts and mixtures were investigated for this storage system in the past, including carbonates [18,19], fluorinated carbonates [7], sulfones [20] and nitromethane [21,22], as well as different anions such as bis(fluorosulfonyl) imide (FSI) [17,23], fluorosulfonyl-(trifluoromethanesulfonyl) imide (FTFSI⁻) [24,25], tetrafluoroborate (BF₄⁻) [26] or hexafluorophosphate (PF₆⁻) [9], none of them could provide a comparable performance in terms of stability and reversibility.

Within the recent years, the research interest in sodium ion batteries (SIBs) has significantly increased, which is reflected by the rising number of publications. [27,28] In addition, there are also few publications on sodium-based dual-ion batteries [29,30]. In the context of a growing demand for LIBs, mainly concerns about the availability and the price of lithium [3,31] have prompted the quest for alternative rechargeable batteries. These systems should be based on abundant raw materials and provide low costs, a high safety as well as a stable long-term cycling behavior. [1] Against this background, SIBs were proposed as appropriate replacement for LIBs, in particular for stationary energy storage, as sodium sources are readily available, hence, leading to lower costs as compared to their lithium counterparts. [32] Further cost reductions compared to LIBs can be realized by the use of aluminum as current collector for the negative electrode due to the fact that sodium does not alloy with Al. [33] All these cost considerations do only regard the material costs, but not the running costs of the battery system, which to a large fraction are determined by the energy efficiency, which is particularly high for lithium ion battery insertion materials. [34,35]

In this work, we studied the electrochemical performance of a dual-ion cell based on a sodium ion-conducting ionic liquid electrolyte and a sodium metal anode with particular focus on the intercalation behavior of TFSI⁻ anions into the graphite positive electrode as well as on the plating/dissolution behavior of the sodium metal anode. Besides constant current charge/discharge studies at different upper cut-off potentials, the influence of the electrolyte additive ethylene sulfite (ES) [36], which already showed a beneficial effect with regard to the reversible capacity of lithium-based dual-ion cells (LDICs) [6,37], has been evaluated for sodium-based dual-ion cells (SDICs). By means of differential capacity plots, the intercalation and de-intercalation behavior was studied in detail and compared to the results of LDICs. As the anion uptake/release into/from the graphitic host structure is directly connected and dependent on the plating/stripping behavior of the electrolyte cations onto/from the metal anode, the deposition/dissolution of Li⁺ and Na⁺ ions has been studied in LDICs and SDICs, respectively.

2. Experimental

2.1. Electrode and electrolyte preparation

Electrode tapes for the positive electrode were composed of 90 wt.% KS6L graphite (*Imerys*), 5 wt.% conductive carbon black agent

C-nergyTM Super C65 (*Imerys*) and 5 wt.% sodium carboxymethyl-cellulose (Na-CMC) as binder (*Walogel CRT 2000 PPA 12, Dow Wolff Cellulosics*). The preparation of the electrode was conducted as reported in reference [24]. The average mass loading of the electrodes accounted for 2.5 mg cm⁻².

A mixture of 0.3 M sodium bis(trifluoromethanesulfonyl) imide (NaTFSI, purity: 99.5%, *Solvionic*) in the ionic liquid *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl) imide (Pyr₁₄TFSI, purity: 99.9%, *Solvionic*) was used as electrolyte in the case of SDICs. For the LDICs a mixture of 1 M LiTFSI (purity: 99.95%, 3 M) in Pyr₁₄TFSI was utilized. Prior to use, the ionic liquid as well as the conductive salts were dried at 110 °C applying an ultra-high vacuum procedure (< 1·10⁻⁵ Pa). The water contents of the dried ionic liquid were < 10 ppm as determined by Karl-Fischer titration. In addition, 2 wt.% of ethylene sulfite (ES, purity: 98%, *Sigma Aldrich*) were used as electrolyte additive and compared to those electrolytes without addition of any additive.

2.2. Electrochemical characterization

All electrochemical investigations were performed in lab-scale Swagelok type T-cells with a three-electrode set-up. Sodium metal sticks (purity: 99.8%, *Acros Organics*) or high-purity metallic lithium foil (*Rockwood Lithium*) were used for the negative and reference electrodes in SDICs and LDICs, respectively. A glass microfiber filter (*Whatman*, grade GF/D) was used as separator which was soaked with 120 μL of the corresponding electrolyte. After cell assembly, a rest step of 24 hours was conducted to ensure a sufficient wetting of the graphite electrode by the viscous ionic liquid-based electrolytes. A *Maccor 4000* battery test system and an environmental chamber adjusted to 20 °C were used to perform the galvanostatic charge/discharge investigations. Charging and discharging was performed using a constant current of 50 mA g⁻¹, as determined from the mass of the positive graphite electrode. Assuming a theoretical capacity of 100 mAh g⁻¹ for the positive electrode, a specific current of 50 mA g⁻¹ would be equal to a C-rate of 0.5.

In this work, two different cell set-ups were used, further abbreviated as set-up A and set-up B (see *supplementary data*, Fig. S1). In set-up A, the graphite cathode potential during charge/discharge of the cell is controlled via the reference electrode. The cut-off potentials for the charge process (TFSI⁻ intercalation/Li⁺ deposition) and discharge process (TFSI⁻ de-intercalation/Li⁺ stripping) of LDICs were set to 5.0 V and 3.4 V vs. Li/Li⁺, respectively (set-up A). The lower cut-off potential of the Na-based dual-ion cells was fixed to 3.0 V vs. Na/Na⁺, while the upper cut-off potential was varied between 4.5 V and 4.7 V vs. Na/Na⁺ (set-up A). In order to take into account the potential difference of the redox couple Li/Li⁺ and Na/Na⁺ of approximately 0.3 V, the results of the SDICs at an upper charging end potential of 4.7 V vs. Na/Na⁺ were compared with the corresponding results of the LDICs at an upper charging end potential of 5.0 V vs. Li/Li⁺.

In contrast, in set-up B, the cell voltage was controlled during charge/discharge, so that both the anode and cathode potentials are variable (see *supplementary data*, Fig. S1). In this set-up, the influence of overpotentials from the plating/stripping processes at the lithium or sodium metal anode will be studied. For comparison reasons, the cell voltage range of the LDICs was set to 3.4 V and 5.0 V, while the cell voltage range of the SDICs was set to 3.0 V and 4.7 V. For the recording of the plating/stripping overpotentials of the respective cations onto/from the anode vs. the reference electrode, additional auxiliary cables were used during the constant current cycling procedures.

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