Electrochimica Acta 211 (2016) 679–688

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

In-Situ Raman Study of the Intercalation of Bis(trifluoromethylsulfonyl) imid Ions into Graphite inside a Dual-Ion Cell

M. Balabajew*, H. Reinhardt, N. Bock, M. Duchardt, S. Kachel, N. Hampp, B. Roling

Department of Chemistry, University of Marburg, Hans-Meerwein-Strasse 4, D-35032 Marburg, Germany

ARTICLE INFO

Article history:
Received 22 April 2016
Received in revised form 31 May 2016
Accepted 17 June 2016
Available online 18 June 2016

Keywords:
in-situ Raman
dual-ion cell
anion intercalation
graphite intercalation compound

ABSTRACT

Anion intercalation into graphite is a central process for energy storage in dual-ion battery cells. Electrochemical investigations show a strong kinetic hindrance of the intercalation process in the first charging cycle and less kinetic hindrance in subsequent cycles. In order to obtain information about the structure and properties of the graphite electrode during cycling and about the origin of the kinetic hindrance, we carried out an in-situ Raman spectroscopy study during the first and second charging/discharging cycle of a dual-ion cell. This cell consisted of a metallic lithium anode, a graphite cathode and a $Pyr_{1,4}$TFSI/LiTFSI mixture as electrolyte. We show that the $TFSI^-$ anion intercalation is not fully reversible, implying that $TFSI^-$ anions remain inside the graphite matrix after completion of the first charging/discharging cycle. This is in contrast to the reversible intercalation/deintercalation of cations, like Li^+ ions. Remarkably, the $TFSI^-$ intercalation leads to enhanced Raman signals, also in stark contrast to Li^+ intercalation. We discuss the in-situ Raman spectra in terms of staging phenomena, mechanical strain formation, electronic charge densities, and defects. Furthermore, we show that intercalation-induced defects are self-healing over time. Our results suggest that there is an anti-correlation between the kinetic barrier for $TFSI^-$ intercalation in graphite and the number of defects.

1. Introduction

Nowadays, one of the major challenges in energy storage research is the development of secondary batteries with higher energy densities, higher power densities, longer life times, and reduced production costs. The most wide spread secondary batteries for many modern applications are lithium-ion batteries (LIBs). However, there are various alternative types of batteries, which are subject to intensive research, such as lithium-air batteries [1–4], lithium-sulfur batteries [5–7], sodium-ion batteries [8–11] and dual-ion cells [12–23]. Dual-ion cells make use of the intercalation of anions into graphite cathode. Major advantages of this type of cell are: (i) The cells are free of heavy metals and thus environment-friendly. (ii) They often exhibit a very long cycle life [14,15,18,19].

Ion intercalation into graphite is a phenomenon that has been used for decades in energy storage systems. The most prominent example is the electrochemical intercalation of Li^+ ions into graphite [24–30]. This process has been investigated by means of various characterization techniques, such as in-situ XRD [31,32], X-ray photoelectron spectroscopy [33], dilatometry [34–36], computational simulations [37–39], and in-situ Raman spectroscopy [40–42]. In comparison to this donor-type graphite intercalation compound (GIC), anion intercalation into graphite is much less widespread due to the absence of an important technological application of acceptor-type GICs. However, electrochemical intercalation of anions into graphite resulting in acceptor-type GICs has already been known since the 1930s [43]. It was also investigated with a view to potential applications in secondary batteries [21,22,44–46], but these systems were inferior to LIBs, in particular with regard to energy density [47]. However, recent work has demonstrated remarkable cycling stabilities of dual-ion cells with acceptor-type GICs [14,15,22]. In 2015, Lin et al. showed that secondary batteries based on anion intercalation can also show extraordinary high charging rates [19]. They developed an aluminum-ion battery which can be fully charged in less than one minute using intercalation of $AlCl_4^-$ into graphite [19]. In combination with the low cost of the electrode materials and the avoidance of heavy metals, batteries based on anion intercalation are promising candidates for stationary energy storage applications.

In this paper, we focus on a cell that was introduced by Placke et al. in 2012 [14,15]. This cell consists of a lithium metal anode and

---

* Corresponding author.
E-mail address: marco.balabajew@chemie.uni-marburg.de (M. Balabajew).

http://dx.doi.org/10.1016/j.electacta.2016.06.083
0013-4686/

a graphite cathode combined with a solution of lithium bis (trifluoromethanesulfonyl)imide (LiTFSI) in the room temperature ionic liquid (RTIL) 1-butyl-1-methylpyrrolidinium TFSI ($Pyr_{1,4}TFSI$) as electrolyte. During charging, lithium is plated on the metallic lithium electrode, while $TFSI^-$ anions are intercalated into graphite. This implies that the lithium salt LiTFSI is extracted from the electrolyte during charging and released back into the electrolyte during discharging. This leads to strong concentration changes and local concentration gradients during cycling [48]. During the first cycles, this system shows a significant irreversible capacity [14–16,49]. Placke et al. showed that these irreversible processes are not related to the formation of a solid electrolyte interphase (SEI) [16], which is commonly formed on graphite anodes in LIBs. In a recent paper, we demonstrated that the irreversible processes take place mainly at the graphite electrode [48]. However, further studies are needed to understand the exact origin of the irreversible processes.

In 2014, Placke et al. studied staging behavior during the electrochemical intercalation of $TFSI^-$ and other anions in dual-ion cells by means of in-situ powder x-ray diffraction (XRD) [23]. Staging of GICs is a well-known phenomenon first described by Rüdorff and Hofmann in 1938 [43]. The stage number indicates how many graphene layers are in between two intercalant layers (see Fig. 1). The XRD technique provides information about the staging mechanism and the amount of expansion of the graphite structure due to higher interlayer distances. Placke et al. investigated only a single charging/discharging cycle and did not analyze irreversible processes during this cycle. Huesker et al. investigated the same system by means of dilatometry [50]. They found that the expansion of the graphite matrix during charging is not completely reversible, but they did not give an explanation for this phenomenon.

Here we report on an in-situ Raman investigation of the intercalation of $TFSI^-$ into graphite. First studies on this field were carried out by Hardwick et al. [51]. However, they only investigated the first charging/discharging cycle with a focus on the unintentional intercalation of anions into conductive carbon inside high-voltage cathodes for lithium-ion batteries. Instead we focus on the intentional intercalation of $TFSI^-$ into graphite in dual-ion cells. We show that in the first charging/discharging cycle, the intercalation of $TFSI^-$ is not completely reversible, implying that a certain amount of $TFSI^-$ anions remain trapped in the graphite matrix during discharging. This is in contrast to Li^+ intercalation/deintercalation in graphite. We also find clear evidence for mechanical strain and changes in the electronic charge density induced by the anion intercalation. Finally, we show that during charging, lattice defects are formed, which do not disappear after discharging, but which can be healed by long rest times of the cell. There seems to be an anti-correlation between the number of these defects and the kinetic barrier height for anion intercalation.

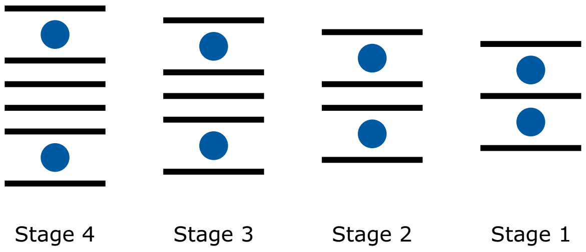

Fig. 1. Schematic illustration of different stages of GICs. The black lines represent graphene layers, while the blue dots represent intercalant layers (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

2. Experimental

2.1. Synthesis

Graphitic foam was synthesized similar to the route described by Chen et al. [52]. Nickel foam (Ni-4753, Recemat BV) acted as a template for chemical vapor deposition (CVD) of carbon. Rectangular blanks of 40 mm × 20 mm and 1.6 mm thickness were laser-cut from a nickel foam sheet and placed in a horizontal quartz tube furnace of 35 mm inner diameter and 500 mm length. The templates were heated to 1000 °C at a rate of 30 °C min^{-1} under forming gas (5% H_2/95% N_2) at a flow rate of 200 s.c.c.m. Carbon deposition on nickel was induced by adding 10 s.c.c.m CH_4 to the forming gas flow for a period of 7 minutes. Subsequently, the samples were cooled to room temperature at a rate of about 100 °C min^{-1}. As-prepared samples were drop-coated with a solution of 4 wt% polymethyl methacrylate (PMMA) in $CHCl_3$ and dried for 30 min at 180 °C in ambient air. PMMA-coated samples were immersed in HCl (3 mol/L) at 85 °C for 3 h in order to dissolve the nickel templates. Finally, the protective PMMA-coatings were removed by immersing the samples in acetone at 55 °C for 10 min.

2.2. Scanning Electron Microscopy

The nickel foam used as template for the graphitic foam and the graphitic foam itself were characterized by means of a JSM–7500 F (JEOL) scanning electron microscope (SEM). The SEM was operated at an accelerating voltage of 10.0 keV and at a working distance of 8.0 mm.

2.3. Electrochemical Measurements

For the electrochemical measurements, the synthesized graphitic foam was used as active cathode material. It was cut into 10 mm disks, dried at 80 °C for 24 h under a diffusion-pump vacuum. To contact the active material as working electrode, it was pressed onto an aluminum grid (EL-CELL GmbH). As an electrolyte, a solution of LiTFSI (Sigma-Aldrich, purity: 99.95%) in $Pyr_{1,4}TFSI$ with a molar ratio LiTFSI:$Pyr_{1,4}TFSI$ of 1:3.34 (1 mol/L) was used. The RTIL was synthesized and purified by Passerini et al. by means of a method described in [53,54] and was dried at a pressure of 10^{-6} mbar at 80 °C. The water content of the RTIL was less than 15 ppm as measured by Karl-Fischer titration (Mettler-Toledo, C20 Coulometric Karl-Fischer-Titrator). As anode and as reference electrode, high-purity lithium foil (Chemetall) was used. The electrodes were separated by a glass fiber separator (EL-CELL GmbH).

All electrochemical measurements were performed in a three-electrode setup within an ECC-Opto-Std Cell (EL-CELL GmbH) by means of an IviumStat Electrochemical Interface (Ivium Technologies). This cell allows for optical observation of the backside of the working electrode through an optical glass window of 0.3 mm thickness. The cells were assembled in an argon-filled glove box (UniLab, MBraun) and equilibrated for 24 h prior to further use. The cells had an open circuit potential (OCP) of approximately 3.0 V vs. Li^+/Li. Galvanostatic cycling was performed at room temperature (RT) with charging and discharging currents of 12.5 mA/g in a potential range from 3.4 V to 5.0 V vs. Li^+/Li.

2.4. In Situ Raman Measurements

The electrochemical cell used for the in-situ Raman measurements was assembled as described above. Raman spectra were recorded at OCP prior to cycling and at specific potentials during galvanostatic cycling with charging and discharging currents of