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Reinstating lead for high-loaded efficient negative electrode for rechargeable sodium-ion battery



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HIGHLIGHTS

- Pb recycling is more than 99% which is one of the highest recycling rates.
- The cycling performances of the Pb/Na battery in diglyme/NaPF₆ are unexpected.
- High loaded Pb electrode showed sustainable capacity retention of 464 mA h/g.
- Preliminary tests in Pb//Na₃V₂(PO₄)₂F₃ full cells showed promising results.
- *In situ* XRD study shows a sodiation–desodiation process in four steps.

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ABSTRACT

Due to its weight and toxicity, Pb is usually not considered as possible anode for Li- and Na-ion (NIBs) batteries. Nevertheless the toxicity is related to specific applications and its recycling is more than 99% which is one of the highest recycling rates on the planet where no other power source is utilized in more applications with such sustainability. For this reason, we have investigated micrometric lead particles as electrode for NIBs in an ether-based electrolyte (1 M NaPF₆ in diglyme). The cyclability, coulombic efficiency and rate capability of lead were unexpected. A high loaded lead electrode with 98%wt of Pb and only 1% of carbon additive showed i) a capacity retention of 464 mA h/g after 50 cycles with only 1.5% of capacity loss, which represents a high volumetric capacity of 5289 mA h/cm³ due to the high density of Pb and ii) a very interesting capacity retention even at high current rate (1950 mA/g). *In situ* XRD study confirmed a sodiation–desodiation process in four steps. Preliminary tests in Pb//Na₃V₂(PO₄)₂F₃ full cells showed promising results demonstrating that Pb could be a practical candidate for future high energy density Na-ion batteries with an efficient sodiated or non sodiated positive electrode.

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1. Introduction

Over the last decade, electrochemical energy storage (EES) technologies based on batteries showed considerable promises as a result of many breakthroughs. Their appealing features include high round-trip efficiency, flexible power and energy to meet different grid functions, long cycle life and low maintenance [1]. Batteries, in particular, represent a sustainable energy storage technology for the integration of renewable resources that provide intermittent energy into the grid. Rechargeable Li-ion batteries (LIBs) have been widely used for various portable applications due to their high energy densities [2]. However, in view of the increasing demand for batteries

have raised questions as to whether the Li natural reserves will continue to meet industrial needs in a commercially viable manner. These concerns have led to an active search for alternatives to the Li-ion battery technologies. Among the alternatives that are being explored for this purpose, the Na-ion battery (NIB) is a prime candidate [3–10].

Since Na is electrochemically close to Li, efforts to identify suitable electrode materials for Na-ion batteries have mainly focused on materials structurally similar to those used in Li-ion battery electrodes [11]. However, the electrochemistry of sodium-based materials has a long history [12,13]. So far, many positive electrode materials have been proposed [9,14–24], whereas only few negative electrode materials have been investigated and to date even less candidates have practical application as anodes for Na ion batteries.

Graphite, which is the commercial negative electrode for Li-ion batteries, has firstly shown to be unusable for NIBs due to its inability to intercalate Na atoms [25–27]. However, recently, Kim

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et al. [28] and Jache et al. [29] showed that graphite can exhibit excellent Na-ion intercalation/deintercalation at low overpotentials with good cycle life by using ether-based electrolytes. Other carbon morphologies have been also proposed for sodium storage at the anode, mostly hard carbon that once heat treated to 1100 °C can exhibit a sodiation capacity of 300 mA h/g which is comparable to that of graphite in Li cells [25]. Nevertheless the high irreversible capacity is still a drawback.

Concerning the p-elements, recently, Sb-based materials have been considered as a promising candidate for sodium-ion batteries SIBs because of its high capacity, excellent cycle stability and rate performance when combined with conductive carbon materials [30–40]. On the other hand, for Sn which catalytically reacts with electrolyte, sodiation is difficult and limited [41]. This catalytic reaction can be avoided if a high current pulse is applied to the cell prior to cycling, which leads to the formation of a sodium-tin alloy on the surface of the electrode. Once this latter is formed, first sodiation can proceed easily. Lead has been forgotten in the last years due to its weight which obviously limit the specific capacity and due to its toxicity that is, however, related to specific applications. Moreover a recent study showed that the recycling rate of Pb is 99% (for the years 2009–2013) which is one of the highest recycling rates on the planet compared to tires, paper, aluminum canes and glass. This feature represents a serious advantage in terms of cost. In 1987, Jow et al. [42] were the first to study the sodiation of lead at room temperature. They suggested that NaPb₃, NaPb, Na₅Pb₂, and Na₁₅Pb₄ sequentially form as lead is sodiated, without, however, any evidence of their formation. The voltage curve of lead was found to closely match the equilibrium Na–Pb phase diagram [43]. The fully sodiated phase of lead, Na₁₅Pb₄, has a theoretical capacity of 485 mA h/g corresponding to a 365% of volume expansion. Impressive reversibility was demonstrated when a poly(p-phenylene)-based binder and limited voltage window were used, resulting in hundreds of cycles with little capacity fade. It should be noted that they used the highest sodiated Na–Pb phase as starting electrode material. Indeed they limited the overpotential observed in the case of Tin and the catalytic parasitic reactions. Twenty-three years later, Komaba et al. performed electrochemical tests on the Pb-poly(acrylic acid) composite electrode material where only one cycle was shown [21]. The obtained results were in good agreement with general knowledge that Pb electrode reversibly forms Na₁₅Pb₄ by electrochemical reduction [42]. Recently, Obrovac's group reported an *in situ* XRD study on lead electrode thin film in non-aqueous sodium cells. They showed that the electrochemical processes do not precisely follow the Na–Pb phase diagram during sodiation. No single phase regions were evidenced and Na₅Pb₂ was not formed as predicted by Jow et al. [42]. They suspected that this latter was not formed because of kinetic limitation. As lead was also found to catalytically react with electrolyte at the electrode surface, a high current pulse was necessary during the first 20 s, leading to the formation of Na–Pb phases on the lead surface and then only sodiation could proceed.

In this work, bare lead particles were used as electrode material vs Na. 1 M NaPF₆ in diglyme which has been newly reported as suitable electrolyte for the cycling of graphite. 2-Methoxyethyl ether (Diglyme, DG), a high molecular weight ether, is a stable and high-boiling solvent. It appears attractive as a solvent for dissolving lithium salts as it acts as a Lewis base toward the Li⁺ ion and is liquid in a large domain of temperatures (from –68–162 °C [44]). This latter has always been tested as co-solvent and never been used as solvent in batteries [45]. In a recent study on FeS₂ material, Wang et al. reported for the first time that by simple substitution of the commonly used carbonate-based electrolyte by an ether-based electrolyte significantly enhanced the cyclability of graphite and FeS₂ towards sodium storage [46]. Herein, we combined this electro-

Table 1
Different electrode formulations tested.

Electrode	%wt of active material	%wt of conductive additive	%wt of binder
A	70	18	12
B	90	5	5
C	95	2.5	2.5
D	98	1	1
E	98%	0	2
F	99	0.5	0.5

lyte formulation to an efficient and easy electrode preparation to enhance the electrochemical performance of bare lead.

To our best knowledge, this is the first time that a high loaded negative electrode for NIBs (about 98% of active material corresponding to 12 mg/cm²) is reported and gives so high performance. For this electrode, the formulation was done in the presence of 1% of carbon additive and 1% of binder (PVdF) in NMP. Unexpected electrochemical performance and rate capability with a high current density have been tested successfully vs Na with this micrometric lead particles based electrodes. Moreover a full cell Pb//Na₃V₂(PO₄)₂F₃ has been cycled showing excellent preliminary results.

2. Experimental details

2.1. Electrodes preparation and electrochemical characterizations

The electrochemical performance of micrometric lead particles as negative electrode materials were examined in standard coin cells assembled in an argon-filled glove box. The micrometric powder used in this study was provided by Sigma–Aldrich (99.95% purity, ~325 mesh), and has been used without any additional treatment. Electrode formulation was made using a mixture of carbon black and vapor ground carbon fibers (VGCF-H) as conductive additive, and Poly(vinylidene fluoride) (PVdF) (Solef 5130, Solvay) as binder, in 1-Methyl-2-pyrrolidinone (NMP, anhydrous, 99.5% sigma-aldrich). A slurry containing the active material (AM), the binder and the conductive additive (CA) (Table 1) was homogeneously mixed by a planetary ball-milling for 1 h, tape casted on a 150 μm thick copper foil, dried at room temperature for 12 h and finally at 120 °C under vacuum overnight. The final mass loading of active material on the electrode varied between 5 and 12 mg/cm² depending of the percentage of active material in the formulation.

The electrochemical performances of micrometric lead particles as negative electrode materials were examined in a standard coin cells assembled in an argon-filled glove box.

The electrochemical tests vs. Na were performed against a counter-electrode of pure sodium (from sigma Aldrich), using 1 M NaPF₆ in DG as electrolyte. Whatman glass-fiber was used as separator. All tests were carried out at room temperature (25 °C) using a multichannel VMP system under galvanostatic mode from 0 to 1.5 V vs Na⁺/Na at nC rate (i.e. n = 1, 1 Na in one hour). For *in-situ* X-ray diffraction (XRD) study, electrode was made as previously reported on an aluminum collector. The beryllium disk served as a window in the XRD cell for X-rays to pass, so that XRD patterns could be obtained from the working electrode as it was being cycled. *In situ* XRD cell was placed in an X'Pert Pro diffractometer with the Cu Kα radiation. The selected *in situ* XRD patterns at the end of each voltage plateau were refined with FULLPROF software [47]. The electrochemical measurements were controlled by a Mac pile system. The cell was cycled at a low rate of C/25 (reaction of one Na⁺ in 25 h), and the interval between two successive X-ray patterns corresponds to 0.04 inserted or de-inserted Na⁺.

A full cell was built with Na₃V₂(PO₄)₂F₃ (NVPF) as cathode material. An NVPF electrode was taken from a tape (90% in mass, 10.5 mg/cm²) coated on Al foil. Further parts of active material were

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