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Short communication

Studying the electrochemical response to emulated photovoltaic electrochemical constrains of Li-ion electrode materials at the lab-scale

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ABSTRACT

As part of a research project on new lithium-ion secondary cells to store energy from renewable power sources, this work reports on the development of a new methodology for a laboratory-scale study of electrode materials for these cells under the specific constraints of photovoltaic charging. A first example is that of a cell containing the spinel anode $Li_4Ti_5O_{12}$, charging under different solar irradiation regimes. This material is well suited to applications under discontinuous charge/discharge conditions. At the end of the test, after about 250 cycles, the two cells tested provide the same capacity and energetic efficiency of about 2.2 mAh and 90%, respectively.

1. Introduction

Electrochemical energy storage systems are currently the subject of a large number of studies because of their potential application in many different domains, such as portable electronics, transportation and renewable energy. The latter field of application is particularly challenging, since a characteristic issue of renewable energy sources such as photovoltaic and wind energy resources is their discontinuous availability. Therefore, their viable large-scale development depends on the parallel development of an intelligent storage system, able to give back the energy when required by the consumer and/or the electrical network and to combine it with the electricity delivered by the network. In the case of photovoltaic systems (as well as those using wind, though at a different scale), the availability depends on both time and weather conditions: on a sunny day, for instance, solar irradiation is delivered with a sinusoidal-like profile, with a maximum at solar noon. For home applications, this maximum production does not usually correspond to the maximum consumption, which is rather observed in the evening [1]. At the same time, the currently applied strategy of injecting the complete photovoltaic energy production in the network hampers further spread of this renewable energy, because its time-dependent energy production profile does not follow the global consumption needs met by the network [1,2]. The development of efficient, reliable and long-lasting electrochemical storage systems is thus necessary to allow a viable rise of renewable power sources.

Li-ion cells are among the possible storage technologies that can be combined to photovoltaic energy production. In spite of their important cost compared to other technologies (e.g., lead-acid or Na–S cells), they provide several advantages:

- Superior energetic efficiency coupled to extremely stable and long lifetimes.
- Reliable and predictable performance, with almost no maintenance compared, for instance, to lead-acid cells.
- Possibility, in some cases, to stand deep discharges without influencing the cycling stability and global performance.
- Higher energy density compared to all other commonly used technologies.

Taking into account that a decrease in the cost of Li-ion secondary cells has recently occurred (−75% in the last four years) in the fields of application where this technology is widely employed (e.g., portable systems), together with the fact that they mostly employ environment-friendly materials, the Li-ion technology might become a valid alternative to other storage technologies.

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For this reason, real-scale tests are currently made worldwide by different industrial organizations, looking for the best combination of electrode materials and cell configuration (electrode formulation, electrolyte development, cell structure, etc.) specific to this application. Several cycling test procedures are available, and the major question is which one to choose depending on the application for which the cell is intended. In the case of Li-ion cells for photovoltaic applications, tests are currently conducted following different European and/or national standard procedures previously developed for other cell technologies [3]. However, these procedures might not be well-adapted to testing of Li-ion systems in general, and more specifically of Li-ion systems employed in photovoltaic energy storage. Moreover, these tests are not performed together with the detailed physico-chemical characterisation necessary to understand the intrinsic behaviour and the limitation processes of cell materials submitted to the intermittent cycling solicitations of photovoltaic systems.

To extend the application of typical tools employed for thorough characterisation of Li-ion cells and their cycling performance to photovoltaic energy storage, we present here a new concept of investigation allowing the study at a laboratory scale of electrode materials using photovoltaic energy charging. A first example of the application of this new concept to the study of $Li_4Ti_5O_{12}$, a well-known emerging negative electrode material for Li-ion cells, is presented.

The latter was selected as the anode, based on its safe operating voltage, low cost and non-toxicity [4–7].

2. Materials synthesis, electrode preparation and cell assembly

$Li_4Ti_5O_{12}$ was synthesised using a ceramic method. Stoichiometric amounts of TiO_2 (UMICORE, 45% anatase, 55% rutile, grain size ~20 μm) and Li_2CO_3 (UMICORE, grain size ~40 μm) were intimately mixed with cellulose (Sigmacell, type 20) using a planetary ball mill, and then heated at 800 °C for 60 min in air flow.

At the end of the synthesis, the sample was rapidly cooled to room temperature, and ground to fine powder. The samples were characterised by X-ray diffraction (XRD) with a Philips diffractometer using Cu K_α radiation.

The electrodes were prepared by homogeneously spreading a mixture of 91% $Li_4Ti_5O_{12}$, 5% black carbon, 4% polymeric binder (CMC) suspended in water on a copper foil using a Doctor Blade deposition method. The size of the electrode in the coin-type cell was 2 cm^2. After drying in air, the electrodes were cut and dried at 100 °C in vacuum in a Büchi glass oven.

Lithium half coin-type cells were assembled with $Li_4Ti_5O_{12}$ as working electrode and Li metal foil (Aldrich) as counter electrode. Sheets of Celgard membranes, used as a separator, were soaked with a 1 M $LiPF_6$ electrolyte solution in a mixture ethylene carbonate (EC), propylene carbonate (PC) and dimethyl carbonate (DMC) (EC:PC:DMC = 1:1:3) containing 1% of vinylene carbonate (VC). Electrochemical discharge/charge curves were recorded on a multichannel VMP system under galvanostatic conditions at various rates.

3. Development of a test bench simulating photovoltaic power sources

One of the principal innovations of this study is the development of a pilot conditioning system allowing the injection of realistic solar irradiation profiles into cells of very different capacities, from the small ones of the coin-type cells usually assembled in research laboratories for the studies of electrode materials to the commercial real-size cells.

The pilot test bench operates as resumed in Fig. 1; the current input to the cell is chosen from a database of real solar irradiation profiles. The profiles are conditioned taking into account the size and the theoretical capacity of the cell by a computer-controlled electronic system, and were introduced into the cell. Its state-of-charge was constantly monitored, and at end of charge, controlled discharge regimes and relaxation times could be applied after desired periods of time to complete the electrochemical cycle. It is worth noting that these regimes were completely flexible and adaptable not only to a very large range of cell sizes and capacities, but also to different system configurations (e.g., with or without connection to the distribution grid, etc.)

Cycling data such as capacity retention and efficiency, defined as the ratio between the energy returned during the discharge and the energy previously charged into the cell, were returned during discharge where capacity was evaluated as a function of cycle number, allowing a continuous monitoring of the cell performance. These data can then be used to perform complete evaluations of the effective costs of specific Li-ion technologies in view of their use as electrochemical storage devices of the photovoltaic energy, and to compare it to other taking energy storage technologies.

4. Application to the study of $Li_4Ti_5O_{12}$ as an anode material for Li-ion cells

The first test of this conditioning system has been performed using half-cells of $Li_4Ti_5O_{12}$ vs. Li metal, which were kept in the laboratory without specifically conditioning their temperature. This type of system was set up for probing the intrinsic cycling behaviour of both negative and positive electrode materials.

$Li_4Ti_5O_{12}$ is a well-known and largely studied negative electrode material for Li-ion cells [8–10]. It can react with up to three Li per unit formula via an insertion mechanism leading to the reduction of three Ti(IV) atoms out of five (corresponding to a theoretical capacity of 175 mAh g^{-1}). The insertion mechanism corresponds to a reversible spinel to NaCl structural type "easy" phase transition going along with a very limited volumetric expansion, making it a very stable and easy cyclable material, and thus a good candidate material for applications involving very irregular cycling regimes [11,12].

Two test cells with $Li_4Ti_5O_{12}$ against Li metal were submitted to the two basic cycling profiles shown in Fig. 2. The first profile representing a 24 h cycle operated in full sun days (Fig. 2(a)): the solar irradiation follows a sinusoidal-like curve from the morning to the evening (dotted line). When the cell is full charged, i.e., when a target charging potential is reached, charging was stopped (continuous line) and the cell was left on open circuit until 6 pm, when the cell was discharged to a threshold value. The second was similar to the first one, and simulated partially cloudy days (Fig. 2(b)). Several temporary decreases of the charge current deviating from the sinusoidal sunny curve simulate the shading of the sunlight by the passage of clouds in front of the sun.

The observed voltage-time profiles of $Li_4Ti_5O_{12}$ are similar in both cases and evolve consistently with the well-known insertion mechanism of this material: during discharge, the voltage quickly drops to below 1.6 V and decreases steadily to a flat operating voltage of about 1.50–1.55 V. Reversible capacities of 170 mAh g^{-1} were obtained using the aforementioned cycling conditions.

The cycling capacity and the efficiency during the first 250 cycles for the two $Li_4Ti_5O_{12}$/Li cells are shown in Fig. 3. The first cell (Cell 1) was operated for 110 days in the full sun profile, whereas the second test cell (Cell 2) was simultaneously operated in the cloudy profile. During the first 50 cycles (not shown in Fig. 3 for the sake of clarity) virtually no difference was observed in the behaviour of the two cells: Starting from cycle 50, a slight decrease in capacity is