Hydrogenated amorphous silicon thin film as electrode for lithium-ion batteries

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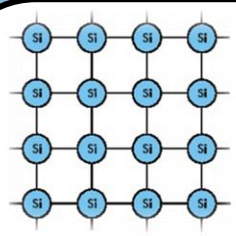
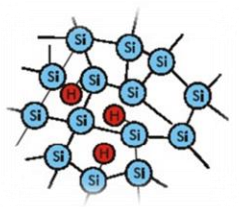
Abstract and objectives



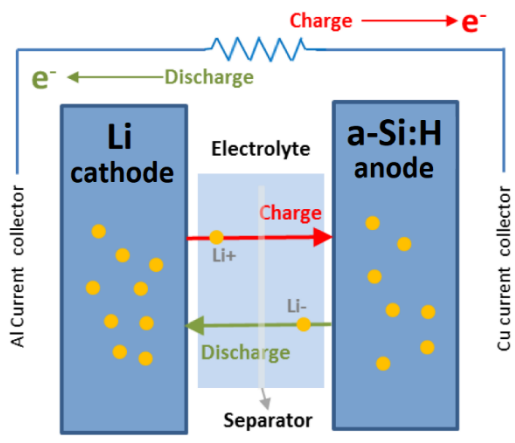
c-Si structure



a-Si:H structure

Traditionally, Lithium-ion batteries (LIBs) have incorporated **graphite** anodes, that has a maximum specific capacity of **372 mAh/g**, which is lower than demanded. By comparison, **crystalline silicon (c-Si)** has **4200 mAh/g** but due to the huge volumetric changes (greater than 300%) it exhibits during charge and discharge, **it degrades readily**. It is thought that the **amorphous nature of the hydrogenated amorphous silicon** (a-Si:H) and its high porosity **could avoid the enormous changes of volume during the lithiation** in order to increase the life of the LIBs.

The aim of this project is to study the influence of structural properties of anodes based on a-Si:H thin films on specific capacity and stability of LIBs. In particular, we have analyzed anodes of intrinsic and n-doped a-Si:H (with a higher electrical conductivity), grown by Plasma Assisted Chemical Vapour Deposition (PECVD), with different hydrogen contents in form of poli-hydrides (Si-H_x). [1]



LIB scheme

Experimental method

- **a-Si:H thin films growth**

The different a-Si:H electrodes were grown on a copper foil by PECVD [2], a technique that can control the hydrogen content and the amount phosphorus (the n-doping element) in the material.

Nº	[Si-H_x] (%)	Doped	Nº	[Si-H_x] (%)	Doped
1	0	No	5	6.3	Yes
2	2.4	No	6	9.4	Yes+
3	3.1	No	7	25.7	Yes
4	4.7	Yes			

Table 1: a-Si:H thin film depending on poli-hydrides content and doping

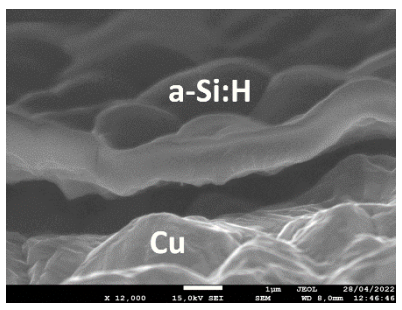


Image 1: Cross-sectional SEM image of the electrode

- **Batteries assembly**

Subsequently, the a-Si:H thin films have been incorporated as LIBs electrodes in a coin cell inside an argon glovebox (<1ppm O_2) to avoid Li oxidation.

- **Battery cycling**

To evaluate the electrochemical performance, the batteries were subjected to 200 charge/descharge cycles at a current density of 1000 mAg^{-1} using a potentiostat, at room temperature.

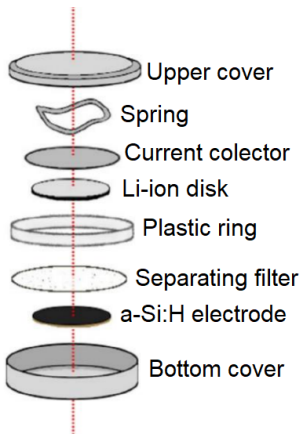


Image 2: Batteries elements in order of assembly

Conclusions

- Doped and intrinsic a-Si:H electrodes have presented initial specific capacity values between 2000 mAh/g and 3000 mAh/g, which gradually decays with cycle number.
- Battery stability decreases with increasing the poli-hydride concentration. It suggests limiting the poli-hydride presence in the a-Si:H anode for future research.
- Through the *Figure 3*, we have obtained a method that allows us to predict experimentally the stability of a-Si:H electrodes in Li ion batteries from its poli-hydride concentration [Si-H_x].
- We have not found a clear correlation between the a-Si:H conductivity and LIB stability. It could be due to the increase of poli-hydride content when phosphorus is incorporated in a-Si:H during PECVD thin film.
- The advantage of PECVD growth technique is that its deposition parameters can be varied, and the hydrogen concentration can be controlled. It will be studied in future works.

Results

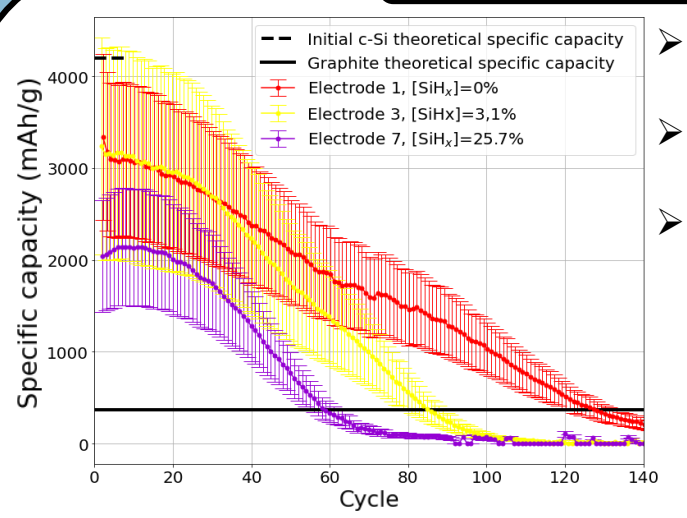


Figure 1: charge capacity curves of batteries with aSi-Hx electrodes #1, #3 (intrinsic a-Si:H) and #7 (doped a-Si:H)

- **Initial specific capacities** around **2000 $mAhg^{-1}$** and **3000 $mAhg^{-1}$**.
- **No improvements** are observed **for doped electrodes.**
- a-Si:H electrodes have a **higher specific capacity than graphite** for the first 60-120 cycles (in the worst- and best-case scenario).

Charge capacity curves cannot be conclusively compared because of the anode active masses standard deviation (~13%).

Therefore, to compare the battery stability properly, we have performed a **normalization** and a **linear fitting** of the charge capacity curves.

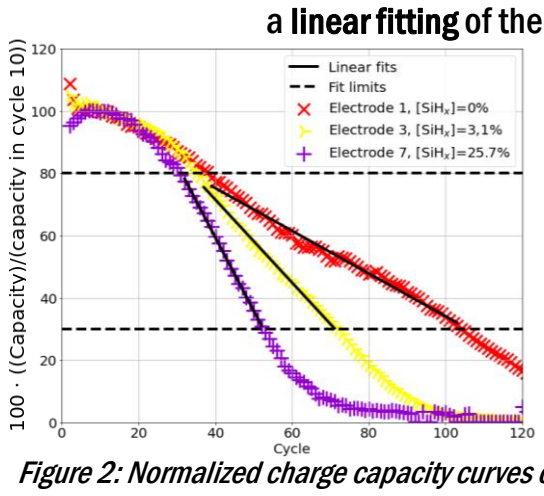


Figure 2: Normalized charge capacity curves of batteries a-Si:H electrodes #1, #3 and #7

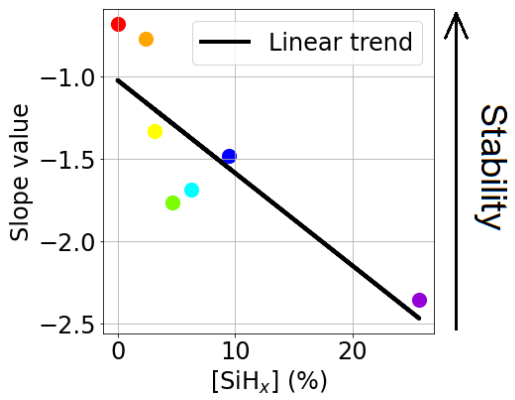


Figure 3; Linear fit slope value of each electrode versus its [Si-H_x]

- There is a **correlation between [Si-H_x] and the anodes instability.**

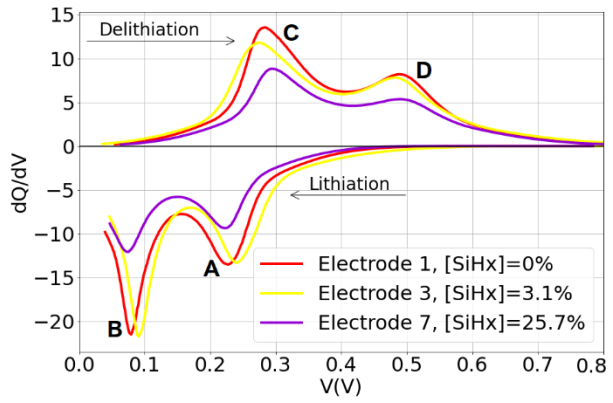


Figure 4: Differential capacity (dQ/dV) profiles

Phase transition

$$a\text{-}Si + xLi \underset{D}{\overset{A}{\rightleftharpoons}} a\text{-}Li_xSi$$

$$a\text{-}Li_xSi + yLi \underset{C}{\overset{B}{\rightleftharpoons}} a\text{-}Li_{x+y}Si$$

$$x \approx 2.5 \qquad x + y = 3.75 \; [3]$$

- **Two reversible phase transitions** are distinguished.

References

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Funding: This research has been funded by the Spanish of Ministry of Economy and Competitiveness under projects SCALED (PID2019-109215RB-C42, NanoCat-Com (PID2021-124667OB-I00) and STORIES (LC-GD-9-1-2020-European Research Infrastructures capacities and services to address European Green Deal).