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# Hybrid all-solid-state thin film microsupercapacitor based on quasi amorphous ALD TiO<sub>2</sub> electrode.

Valentin Sallaz<sup>a\*</sup>, Sylvain Poulet<sup>b</sup>, Jouhaiz Rouchou<sup>b</sup>, Jean-Marc Boissel<sup>b</sup>, Isabelle Chevalier<sup>b</sup>, Frédéric Voiron<sup>a</sup>, Yann Lamy<sup>b</sup> and Sami Oukassi<sup>b\*</sup>

<sup>a</sup>*Murata Integrated Passive Solutions, 14000 Caen, France*

<sup>b</sup>*Univ. Grenoble Alpes, CEA LETI Minatec Campus, 38054 Grenoble, France*

\*Corresponding author

e-mail: [sami.oukassi@cea.fr](mailto:sami.oukassi@cea.fr) ; [valentin.sallaz@murata.com](mailto:valentin.sallaz@murata.com)

## Abstract

In this work, nanometric (6-21 nm thick) quasi amorphous  $\text{TiO}_2$  films have been elaborated and characterized in liquid and solid-state electrolyte (LiPON) half-cell architectures. For all considered configurations, the specific capacity extracted from cyclic voltammetry and galvanostatic cycling within [0.5-3V] potential range almost correspond to the theoretical value expected for the  $\text{Li}_{x=1}\text{TiO}_2$  phase at low current density. Interestingly,  $\text{TiO}_2$  films after LiPON deposition exhibited a constant initial amount of intercalated lithium ions independently of the different thicknesses and did not require a first activation process, in comparison to the liquid electrolyte configuration. Furthermore, the cooperative effects of high Li ion intercalation kinetics and low interfacial charge transfer resistance for 6nm  $\text{TiO}_2$  electrode lead to an outstanding specific capacity of  $2\text{mC}\cdot\text{cm}^{-2}$  at  $1\mu\text{A}\cdot\text{cm}^{-2}$ , and high rate performance with 60% capacity holding ratio at  $100\mu\text{A}\cdot\text{cm}^{-2}$ , thus highlighting the extrinsic pseudo-capacitive behavior of the sub 10nm electrodes.

A  $\text{Li}_x\text{TiO}_2$  6nm/LiPON 100nm/Pt hybrid microsupercapacitor has been successfully fabricated achieving an operating voltage window of 3V and a specific capacity of  $94\mu\text{F}\cdot\text{cm}^{-2}$  at  $50\text{mV}\cdot\text{s}^{-1}$ . In addition, the device also exhibited a 97% coulombic efficiency upon cycling for 10,000 continuous charge-discharge cycles. This work offers an approach to tune the Li ion storage properties of  $\text{TiO}_2$  by nano-engineering and gives insights into the enhancement of pseudocapacitance-assisted lithium-storage capacity.

Keywords: amorphous  $\text{TiO}_2$ ; asymmetric hybrid supercapacitor; thin film; all-solid-state; LiPON;

# 1. Introduction

In the perspective of a more connected and sustainable world, the extensive development of wireless sensor technologies or IoT requires always more miniaturized and on-chip integrated energy storage solutions [1]-[3]. If micro-batteries used to be one (if not the) essential element powering most of all electronic devices over the past decades [4], their limitation in terms of power density and lifespan have been the source of the emergence of high performance alternatives [5], [6]. In this regard, micro-supercapacitors (MSCs) appear as one of the most promising power sources to simultaneously meet high energy and power densities (compared to conventional dielectric capacitors and batteries respectively) and long term cycle life [7].

On-chip MSCs integration enables miniaturization and a fabrication complexity reduction of the whole system. Therefore, fabrication techniques like PVD, ALD or else must be compatible with semi-conductor and MEMS technology and the active materials - electrodes and the electrolyte - require high areal or volumetric performances. Lithium phosphorous oxinitride (LiPON), which is well known for its great advantages in terms of thermal and electrochemical stabilities [8], has recently been reported as promising thin solid ions conductor when integrated in 2D parallel plate on-chip electrical double layer microsupercapacitors (MSCs) [9]. The devices were obtained based on standard semi-conductor fabrication techniques and exhibited a power density of  $6.8 \mu\text{W}\cdot\text{cm}^{-2}$  and an energy density of  $68 \text{ nWh}\cdot\text{cm}^{-2}$  on more than 100.000 reversible cycles. As the authors mentioned however, the MSCs stacking was designed as a test vehicle, and improvements must be brought to boost the energy density.

Asymmetric Hybrid Microsupercapacitors (AsHMSCs) introduce a charge storage mechanism based on both electric double-layer phenomena and faradaic reaction, using respectively capacitive-type and insertion-type electrodes. Literature usually reports these insertion-type electrodes as either a battery-type electrode (e.g.  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  [10],  $\text{Ni}(\text{OH})_2$  [11]) or a pseudocapacitive material that store energy through fast reversible redox reaction (e.g. conductive polymers [12], metal-oxides [13], [14]...). This construction allows to increase the energy density (with both specific capacity and operating voltage), thus filling the gap between MSCs and microbatteries [15]. Within this context, the selection of electrode materials and their interaction at the electrolyte interface is a key issue to optimize the AsHMSC electrochemical performance.

$\text{TiO}_2$  as negative electrode material has arouse a great academic interest for sustainable Li-ions based MSCs. Abundant and stable,  $\text{TiO}_2$  film is easy to fabricate and the lithiation of  $\text{Li}_x\text{TiO}_2$  up to  $x = 1$  corresponds to a maximum theoretical capacity of  $336 \text{ mAh}\cdot\text{g}^{-1}$  [16]. Among all known  $\text{TiO}_2$  structures and polymorphs [17], [18], several including amorphous  $\text{TiO}_2$  phase was reported to demonstrate

pseudocapacitive properties [19], [20], such as a quasi linear potential variation with the state of charge (SoC) (within [0.5 - 2V] vs Li<sup>+</sup>/Li range) and fast rate capabilities, making it an interesting candidate for increasing the energy density of MSCs.

To study the benefits of amorphous TiO<sub>2</sub> electrode in a LiPON-based AsHMSC structure, an initial evaluation of nanometric TiO<sub>2</sub> was carried out in both liquid and solid-state electrolyte (LiPON) half-cell configurations. The impact of the solid LiPON/TiO<sub>2</sub> interface as well as the different Li ion intercalation kinetics of all TiO<sub>2</sub> thicknesses were evidenced, exhibiting the pseudocapacitive behavior of the sub 10nm electrodes. The integration of 6nm TiO<sub>2</sub> film within an all-solid-state Pt/TiO<sub>2</sub>/LiPON/Pt structure enabled to obtain a high specific capacitance of 95 μF.cm<sup>-2</sup> within a 3V voltage range obtained at 50 mV.s<sup>-1</sup>, and more than 10.000 successful continuous charge-discharge cycles. This work offers an approach to tune the Li ion storage properties of TiO<sub>2</sub> by nano-engineering and gives insights into the enhancement of pseudocapacitance ion-storage capacity.

## 2. Experimental

### 2.1. Materials

200mm Si wafers with  $\text{Si}_3\text{N}_4$  (160nm) and  $\text{SiO}_2$  (100nm) were used as substrate upon which were previously deposited and patterned Ti 50nm/Pt 250nm bilayer (Alcatel-600 tool). Pt electrode was used as bottom current collector known as a blocking electrode [9]. Thin  $\text{TiO}_2$  films were deposited by ALD (Cambridge-Savannag tool) using tetrakis dimethylamido titanium ( $\text{Ti}(\text{N}(\text{CH}_3)_2)_4$  or TDMAT) and water precursors at  $80^\circ\text{C}$ . Pulse and purges times used for depositions were respectively 450ms and 10s for TDMAT, 80ms and 15s for  $\text{H}_2\text{O}$  and sequences of 71, 142 and 284 cycles were performed to obtain 6, 11 and 21nm films respectively confirmed by spectroscopic ellipsometry (**Figure S1**).

On the first part of the study, half-cells were realized by depositing a 100nm LiPON film as solid-state electrolyte by rf-magnetron sputtering of  $\text{Li}_3\text{PO}_4\text{-Li}_2\text{O}$  (65% - 35% molar ratio) target under  $\text{N}_2$  reactive atmosphere (Endura PVD tool) and an evaporated Li electrode (1 $\mu\text{m}$ ) through shadow masks. For comparison, half-cells in liquid configuration were also assembled using Li foil (Rockwood Lithium GmbH, 135  $\mu\text{m}$  thickness) as reference and counter electrode, placed as close as possible to the working electrode. The electrolyte was a 1:1:3 mixture by volume of ethylene carbonate (EC), propylene carbonate (PC) and dimethyl carbonate (DMC) containing  $\text{LiPF}_6$  1M. The use of a polypropylen sheet and Celgard 2400 separator between both electrodes enabled to prevent from lithium dendrites formation upon cycling. An illustrated description is given in **Figure S2**.

On a second part, a Ti/Pt/ $\text{TiO}_2$ /LiPON/Pt stack was fabricated using a 250nm top Pt counter electrode to form the AsHMSC structure as shown in **Figure 1b**. The active area of the samples was comprised between 20 and 45  $\text{mm}^2$ .

### 2.2. Characterization methods

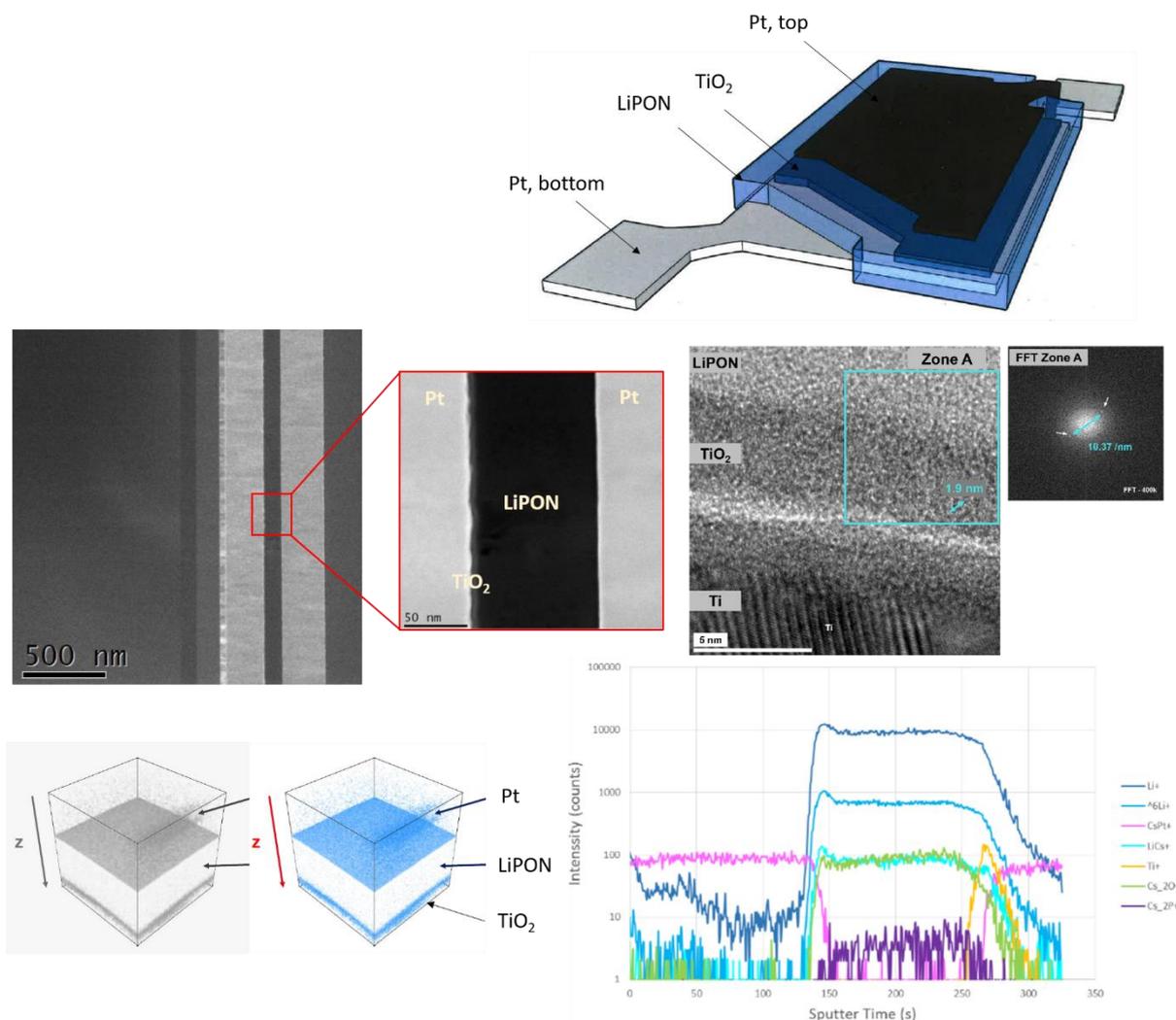
Cross sectional observations of the AsHMSC were carried out using a transmission electron microscope (TEM) coupled with focused ion beam (FIB) and the structure of  $\text{TiO}_2$  films was investigated by high resolution TEM (HR-TEM).

The chemistry of the AsHMSC structure was obtained with a time-of-flight scanning ion mass spectrometer (TOF-SIMS). The samples were profiled using a 2 keV  $\text{Cs}^+$  sputtering beam over rastered area of 150x150  $\mu\text{m}^2$  and a 25 keV  $\text{Bi}^{3+}$  analysis beam over analyzed area of 40x40  $\mu\text{m}^2$ , below  $-100^\circ\text{C}$  to immobilize Li ions. The elemental distribution of Li, P, O, N and Ti was visualized by  $^7\text{LiCs}^{2+}$ ,  $^{16}\text{Cs}^{2+}$ ,  $^{31}\text{PCs}^{2+}$ ,  $^{14}\text{NCs}^{2+}$  and  $^{22}\text{TiCs}^{2+}$  secondary ions.

Electrochemical Impedance Spectroscopy (EIS), cyclic voltammetry (CV) and galvanostatic charge and discharge (GCPL) experiments were conducted at room temperature using a VMP3 multipotentiostat (BioLogic) coupled with the EC-Lab software.

### 3. Results and discussion

#### 3.1. Characterization of TiO<sub>2</sub> electrode



**Figure 1.** (a) Schematic representation of fabricated AsHMSC. (b) Photo of the fabricated devices. (c) Cross sectional TEM observation of AsHMSC device. (d) HR-TEM images captured with magnification of 400k: nano crystallites around 2 nm in size have been found embedded inside TiO<sub>2</sub> amorphous matrix. (e) Depth profile analysis of AsHMSC stack. (f) 3D elemental mapping of Li and Ti elements enabled by TOF-SIMS.

A cross-sectional TEM image of the fabricated devices is shown in **Figure 1c**. Each layer appears continuous, homogeneous and presents smooth interfaces with no delamination or local blisters, which indicates good adhesion at the various interfaces. TiO<sub>2</sub> and LiPON films thicknesses are ~6nm and 110nm respectively and matches with the intended values.

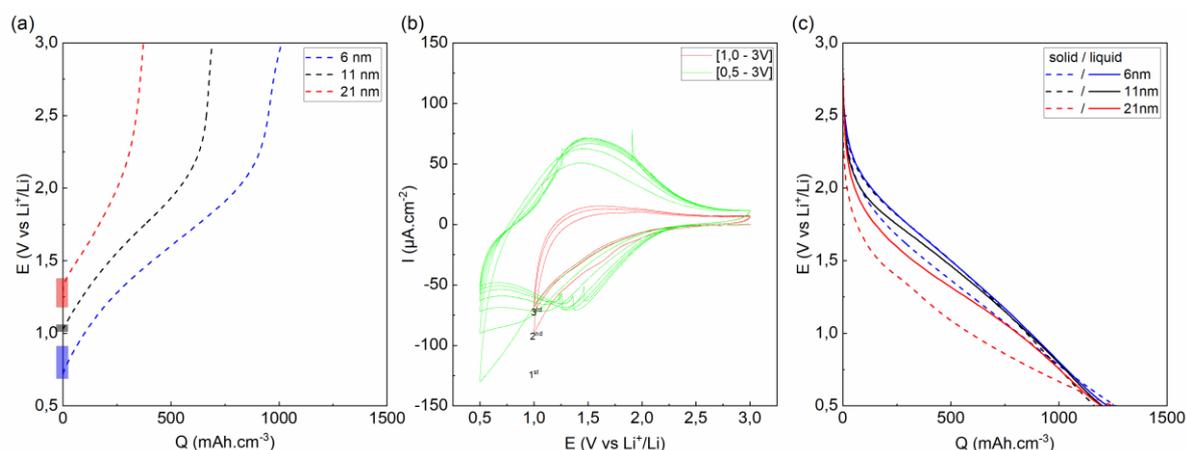
The 6nm-TiO<sub>2</sub> microstructure was characterized using high resolution transmission electron microscopy (HR-TEM). As seen in **Figure 1d**, the results confirmed that the synthesized film is mostly amorphous.

However, by doing local FFT in comparison with Si substrate reference (**Figure S3**), some spots are observed in the diffractogram (underlined by white arrows) and an interplanar spacing of lattice fringe of 0.207nm (i.e.  $d^* = 10.37\text{nm}^{-1}$  in the reciprocal space) is determined corresponding to the (210) crystal phase of rutile  $\text{TiO}_2$  [21]. Although rutile phase is generally obtained at very high temperature ( $> 800^\circ\text{C}$  [22]), the presence of nano-inclusions of rutile phase within as-formed ALD films has already been reported elsewhere depending on the nature of the substrate or the set of precursors used [23], [24].

TOF-SIMS analysis was performed next on the AsHMSC. A uniform distribution of Li, P, O and N elements is observed along LiPON film thickness (**Figure 1e**), and the 3D elemental mapping provided in **Figure 1f** reveals that Li element is notably present within  $\text{TiO}_2$  film (that will be discussed later).

Finally, the composition of the  $\text{TiO}_2$  film determined by XPS (**Figure S4**). Ti is essentially in the form of  $\text{Ti}^{4+}$  (97%) and we calculate an O/Ti ratio of 1.94 indicating an excellent stoichiometry of the as-deposited film. However, carbon and nitrogen contamination are present (1.3% and 1.0% respectively), likely originating from partially removed  $-\text{N}(\text{CH}_3)_2$  ligands due to low operating deposition temperature.

### 3.2. Electrochemical characterization of Pt/ $\text{TiO}_2$ electrode in liquid and solid-state half-cell: initial state of charge and activation process



**Figure 2.** (a) First charge curve for 6, 11 and 21nm  $\text{TiO}_2$  films in contact with LiPON. (b) First ten CV cycles within [1 - 3V] followed by ten cycles within [0.5 - 3V] for 21nm  $\text{TiO}_2$  in liquid half-cell. (c) Comparison of the 10<sup>th</sup> discharge curve in liquid and LiPON half-cell configuration for the three  $\text{TiO}_2$  thicknesses ( $I = 1 \mu\text{A}\cdot\text{cm}^{-2}$ ).

The following part will focus on the electrochemical behavior of single  $\text{TiO}_2$  electrodes implemented in half-cell configuration, using  $\text{LiPF}_6$  and LiPON as liquid and solid-state electrolyte respectively, and Li as reference electrode.

The Open Circuit Voltage (OCV) of both configuration was systematically measured before each electrical test in order to evaluate the potential initial Li intercalation "x" in  $\text{Li}_x\text{TiO}_2$ . Interestingly, we obtained 1.3V, 1V and 0.8V in average for 21, 11 and 6nm  $\text{TiO}_2$  films integrated with LiPON respectively, whereas the OCV was centered around 3V for all oxides thickness in liquid cell. These differences suggest that an initial amount of lithium was already inserted in the oxide layer in the presence of LiPON. Capacities of 345, 650 and 1010  $\text{mAh.cm}^{-3}$  can be extracted upon first charge step (**Figure 2a**) which lead to surface charge capacity of  $0.66 \mu\text{Ah.cm}^{-2}$  (=  $2.4 \text{ mC.cm}^{-2}$ ) in average and correspond to a state-of-charge (SoC) of 27, 51 and 79% for 21, 11 and 6nm electrodes respectively. These results demonstrate the existence of a surface pre-lithiation of bottom electrodes during LiPON deposition, under process that still needs to be understood (reducing environment, thermal diffusion, or other). This observation corroborates the previous result obtained by TOF-SIMS analysis in **Figure 1f**.

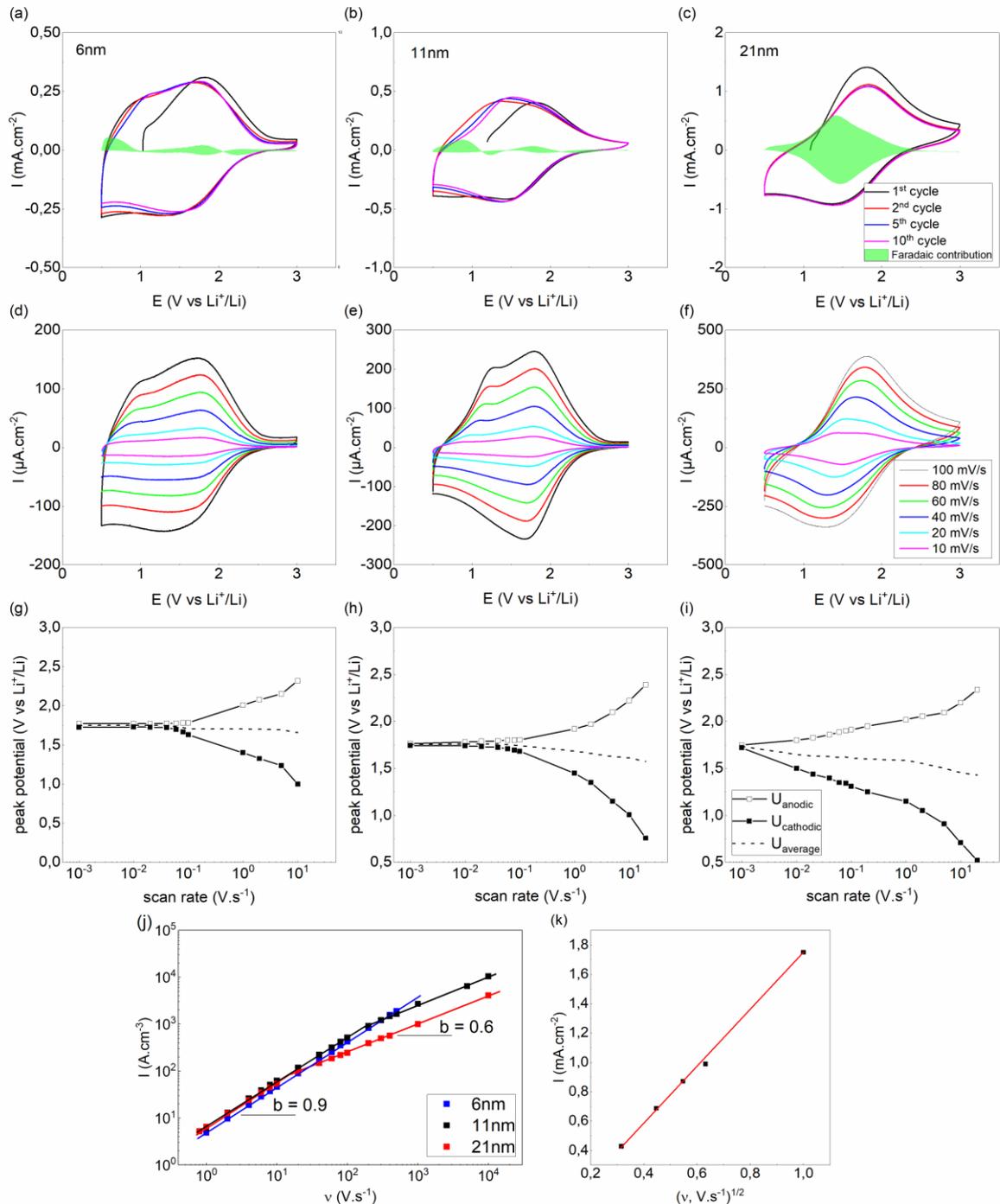
Focusing now on the first discharge step in liquid cell, it is interesting to observe through cyclic voltammetry measurements that no clear cathodic and anodic peaks appeared while cycling first within [1 - 3V] vs  $\text{Li}^+/\text{Li}$  range, without any impact of subsequent cycles on the CV shape (**Figure 2b**). Changes in the CV behavior only occurred when sweeping down to 0.5V with:

- (1) an (irreversible) increase of the cathodic current resulting in a discharge capacity of  $2250 \text{ mAh.cm}^{-3}$  (i.e. implying a Li fraction into  $\text{Li}_x\text{TiO}_2$  of  $x \sim 1.8$ ) (**Figure S5**).
- (2) the appearance of a broad oxidation peak between 1.2V and 1.8V and, inversely, a reduction peak at 1.5V vs  $\text{Li}^+/\text{Li}$ .

Such behavior has already been reported for ALD amorphous  $\text{TiO}_2$  cycled in liquid configuration as an "activation" process [25], [26]. Although the mechanism remains unclear, few works suggested that phase transition to cubic  $\text{Li}_2\text{Ti}_2\text{O}_4$  of a small fraction of amorphous  $\text{TiO}_2$  occurs during the first lithiation step [27]-[29]. Conversion reactions between Li-ions and micro-clusters or non-stoichiometric  $\text{TiO}_2$  spatially distributed within the whole films might also be considered in correlation with the first irreversible (volumetric) discharge capacity.

The potential discharge profiles of all configuration after 10 cycles of stabilization are given in **Figure 2c**. We observe that the curves are shifted towards lower potential values for  $\text{TiO}_2/\text{LiPON}$  interface or thicker  $\text{TiO}_2$  films, likely resulting from charge transfer mechanism or ohmic drop. In the present study, this does not seem to significantly impact the value of the discharge capacity at low rates ( $I = 1 \mu\text{A.cm}^{-2}$ ), which is extracted in average around  $1200 \text{ mAh.cm}^{-3}$  for all configurations. This fits with the  $\text{Li}_{0.95}\text{TiO}_2$  formula intended for amorphous phase and suggests here an almost complete transformation of  $\text{Ti}^{4+}$  into  $\text{Ti}^{3+}$ .

### 3.3. Charge storage phenomena and transport properties in TiO<sub>2</sub>



**Figure 3.** (a, b, c) 10<sup>th</sup> first CV cycles plotted at 200mV·s<sup>-1</sup> for 6nm, 11nm and 21nm TiO<sub>2</sub> films respectively including Faradaic contribution to overall signal. (d, e, f) CV plotted for scan rates between 10 and 100 mV·s<sup>-1</sup> for 6nm, 11 and 21nm films respectively. (g, h, i) Peaks potential shift as function of the scan rate for 6nm, 11 and 21nm films respectively. (j) Current oxidation peak density plotted as

function of the scan rates. (k) Oxidation peak  $I_{\text{peak}}$  vs  $\sqrt{v}$  for 21nm  $\text{TiO}_2$ .

Reversibility of Li-ion extraction in contact with LiPON upon first charge step is discussed based on CV measurements within [0.5 - 3V] range (**Figures 3a, b and c**). The main Li extraction potential is centered around 1.75V vs  $\text{Li}^+/\text{Li}$  with similar broad potential distributions as observed in liquid cell (see in **Figure S6a, b and c**). This feature is commonly accepted for amorphous  $\text{TiO}_2$  phase deposited by ALD which presents a high amount of defects and Li insertion/extraction sites at various redox potentials [30]. Identical current density levels are observed for both anodic and cathodic scans for each  $\text{TiO}_2$  thickness. No significant change appears between the first and subsequent cycles. Particularly, no electrical signature of the previously observed activation step is seen here, suggesting that LiPON deposition already enabled the  $\text{TiO}_2$  films activation. Similar experiments with scan rates varying from 10 to 100  $\text{mV}\cdot\text{s}^{-1}$  were carried out and presented in **Figures 3d, e and f**. A shift of main oxidation and reduction peaks towards higher and lower potential values respectively is observed when increasing both the scan rate and  $\text{TiO}_2$  film thickness (**Figures 3g, h and i**), which is usually related to overpotential caused by charge transfer or ohmic resistances of the electrolyte and/or electrodes. Besides, the average peak potential given by  $U_{\text{av}} = (U_{\text{anodic}} + U_{\text{cathodic}})/2$  also slightly decreases indicating a less favorable lithiation kinetics in comparison to delithiation. Experiments in liquid configuration (**Figure S6c, d and e**) exhibit similar CV shape, current levels and peak potential variations implying that LiPON does have an (significant) impact on the cell transport properties. It is also worth noticing the presence of a second redox peak at lower oxidation potential which participates to the overall capacity. This peak appears kinetically less favorable than the main reaction as more strongly subject to overpotential, up to the point that both peaks are almost combined for 21nm  $\text{TiO}_2$  film at high rate. A better observation of this peak is given in **Figure S7** for a scan rate of 1  $\text{mV}\cdot\text{s}^{-1}$ . However, no clue allowed us to determine at this time the nature of this reaction.

CV experiments also enables to observe the contribution of diffusion limited processes to overall capacity. **Figure 3j** presents plots of the peak current densities variation with the scan rate  $v$  from 1  $\text{mV}\cdot\text{s}^{-1}$  to 10  $\text{V}\cdot\text{s}^{-1}$  for the main anodic peak. The current density variation with  $v$  is commonly assumed to obey a power law and can be written as [31]:

$$I = a \cdot v^b \quad (3.1)$$

where  $a$  and  $b$  are adjustable coefficients. The exponent  $b$  is comprised between 0.5 and 1, which corresponds to semi-infinite diffusion process and an ideal capacitor behavior respectively. From the log-log plot, two regions can be observed depending on the  $\text{TiO}_2$  thickness: a low rate with  $b = 0.9$  corresponding to a surface limited storage mechanism and a diffusion limited charge at higher scan rates with  $b = 0.6$ . The volumetric current appears to be thickness independent but

the transition between the two regions varies while increasing the thickness: this substantiates the extrinsic pseudocapacitive behavior of amorphous TiO<sub>2</sub> [32], where lithium insertion/extraction is not kinetically limited by semi-infinite diffusion of Li-ions due to extremely small dimensions.

Accordingly, and focusing on the diffusion limited high scan rates region of 21nm TiO<sub>2</sub> films (i.e. between 100 mV.s<sup>-1</sup> and 1 V.s<sup>-1</sup>), the faradaic contribution is assumed to follow approximately the Randles-Sevcik equation [31]:

$$I_p \approx 268600 \cdot z^2 \cdot \sqrt{D_{Li}} \cdot C_{Li} \cdot \sqrt{v} \quad (3.2)$$

with  $I_p$  the peak current density (A.cm<sup>-2</sup>),  $z$  the valance of charge carrier (= +1 for Li-ions),  $D_{Li}$  the the apparent diffusion coefficient (cm<sup>2</sup>.s<sup>-1</sup>),  $v$  the scan rate (V.s<sup>-1</sup>) and  $C_{Li}$  the Li concentration into TiO<sub>2</sub>.

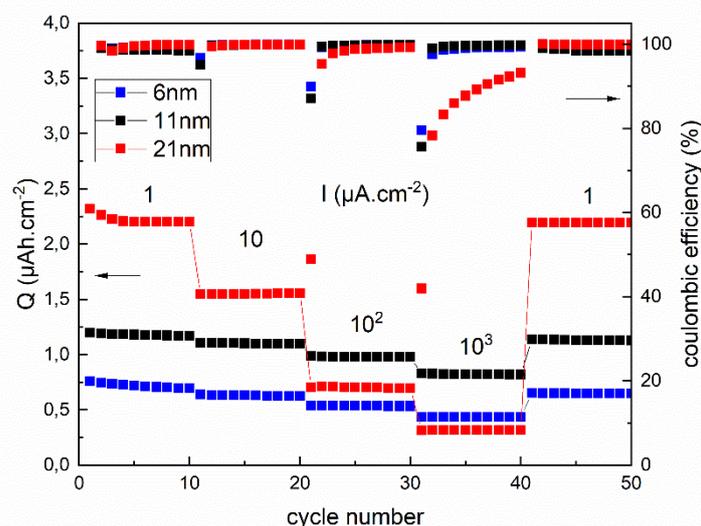
The Li concentration into TiO<sub>2</sub> is calculated from the maximum capacity obtained as 0.0464 mol.cm<sup>-3</sup>. The peak current densities extracted from CV measurements are plotted as function of square-root of the scan rate in **Figure 3k**. An almost linear variation with  $\sqrt{v}$  is observed, enabling the calculation of Li diffusion coefficient from the slope as  $2 \cdot 10^{-14}$  cm<sup>2</sup>.s<sup>-1</sup>  $\pm$  3%. This model does not consider any ohmic drop effects induced by the peak potential shift when increasing the scan rate, and thus ignores possible changes in Li-ions exchanged quantities ( $b = 0.6$  indicates a deviation from the Randles-Sevcik equation which could be explained by  $C_{Li+}$  variation with the scan rate). Notwithstanding, this result remains in the range of values previously reported in the literature for amorphous TiO<sub>2</sub> materials in liquid configuration [26], [32], [33], as solid-state configuration at this scale does not induce any further limitation related to diffusion in TiO<sub>2</sub> electrode.

For similar diffusion properties, the decrease of the TiO<sub>2</sub> thickness would enable a reduction of both Li diffusion path and electronic resistance improving the rate capability. Thus, by combining the high storage capacity of the amorphous phase and the pre-lithiation effect enabled by LiPON deposition, the 6nm-TiO<sub>2</sub> film meets the necessary requirements for pseudocapacitive electrode integrated in ASHMSC configuration.

### 3.4. Rate capability of a-TiO<sub>2</sub> electrode

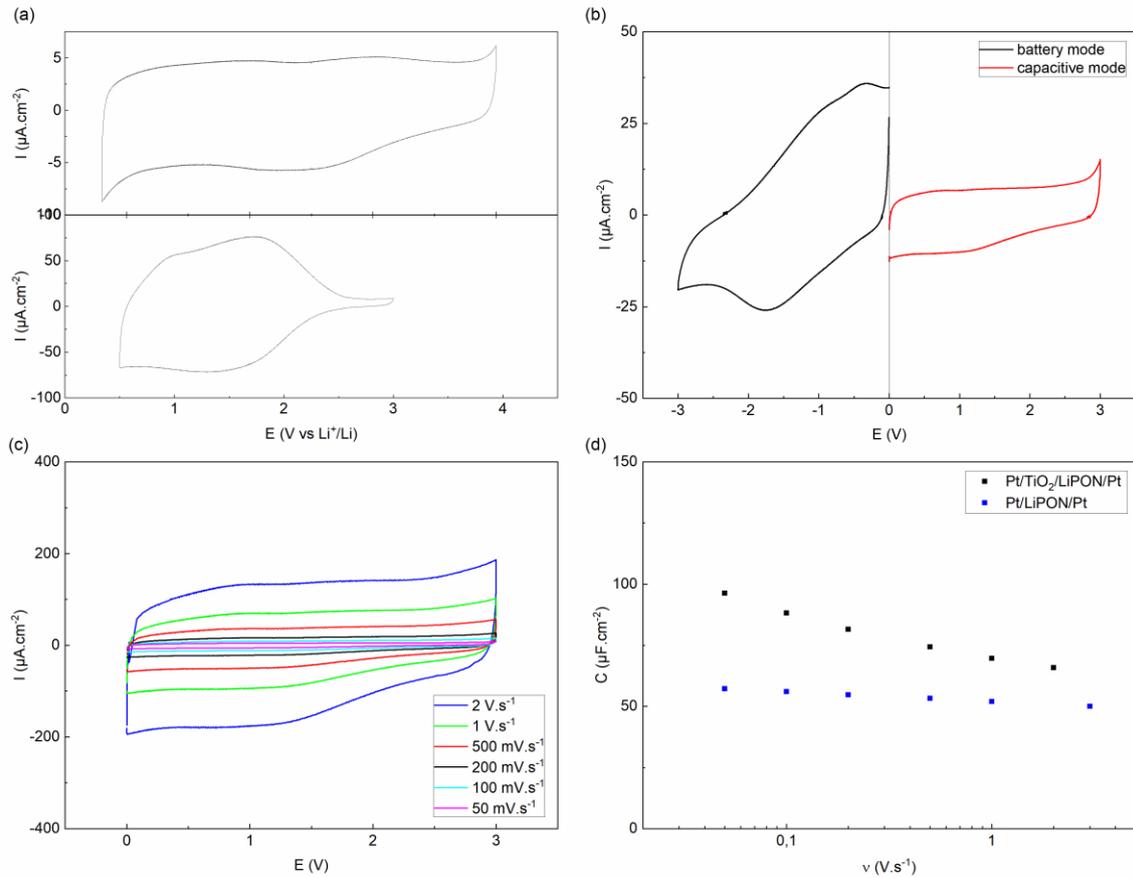
To investigate the Li ion diffusion properties into amorphous TiO<sub>2</sub> for different thicknesses, galvanostatic cycling was performed at a soft charge current density of 1  $\mu$ A.cm<sup>-2</sup> with various discharge current densities from 1 to 1000  $\mu$ A.cm<sup>-2</sup>. **Figure 4** depicts results of different rate performances of the 6, 11 and 21nm thin TiO<sub>2</sub> films. For 1  $\mu$ A.cm<sup>-2</sup> discharge current, the three films exhibit capacities of 0.7, 1.2 and

2.2  $\mu\text{Ah}\cdot\text{cm}^{-2}$  respectively, corresponding to the geometrical factor between the different thicknesses. By increasing the discharge rate, the gap between the three films is significantly reduced up to the point where the capacity of 21nm thin  $\text{TiO}_2$  becomes lower than 6nm  $\text{TiO}_2$  films. Specifically, the obtained capacity at discharge current density of  $1\text{ mA}\cdot\text{cm}^{-2}$  represents 62.5, 64.1 and 14.4% of the initial capacity (at  $1\text{ }\mu\text{A}\cdot\text{cm}^{-2}$ ), which confirms that the 21nm  $\text{TiO}_2$  film presents lower rate performance than the thinner films. As observed, the Coulombic efficiency is around 99.7% for 6nm and 11nm films indicating the excellent reversibility of Li-ions insertion and extraction. For 21nm films however, the efficiency decreases as the discharge current increases caused by the poor reaction kinetics. Last, one can observe that there is almost no variation in capacity when applying back low charge current density, substantiating that the use of alternate high and low rates (i) does not impact the reaction reversibility and (ii) that capacity decay is mostly related to kinetic limitations.



**Figure 4.** (a) Discharge capacity of 6, 11 and 21nm  $\text{TiO}_2$  films and (b) coulombic efficiency as function of the discharge rate.

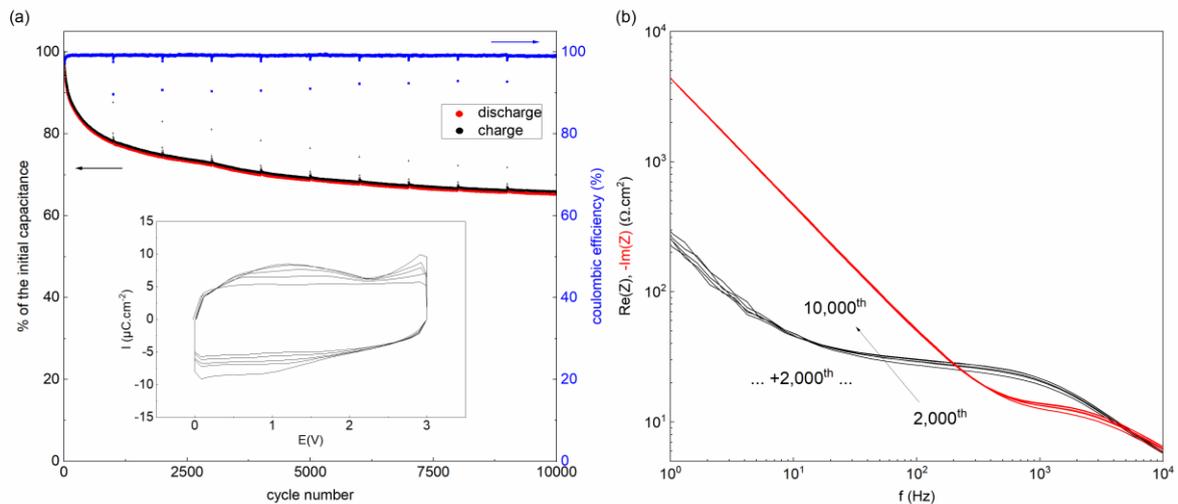
### 3.5. Towards high performance hybrid asymmetric MSC



**Figure 5.** (a) CV curves of Pt/LiPON/Li (top) and 6nm-TiO<sub>2</sub>/LiPON/Li (bottom) half-cells at 100 mV.s<sup>-1</sup>. (b) CV curves of Pt/LiPON/TiO<sub>2</sub> cell with positive (red curve) and negative bias (black curve) at 100 mV.s<sup>-1</sup>. (c) CV curves of AsHMSC plotted for scan rates between 50 mV.s<sup>-1</sup> and 2 V.s<sup>-1</sup>. (d) Extracted capacitance from CV curves plotted as function of the scan rate and compared with Pt/LiPON/Pt MSC.

The respective behaviors of 6nm-TiO<sub>2</sub> and Pt electrodes, recorded in half-cell solid configuration and presented in **Figure 5a**, enables to understand the overall behavior of the cell. The principle of AsHMSC is, by applied a positive bias at the Pt electrode, to make use of the double layer Pt/LiPON interface capacity within its whole stability range (i.e. 1V to 4V vs Li<sup>+</sup>/Li) while TiO<sub>2</sub> is operating around its broad lithiation peak. This behavior is thus obtained in **Figure 5b** (red curve) sharing with Pt/LiPON/Li half-cell (obtained in previous work) similar box like shape of the CV curve within [0 - 3V] voltage range and a capacitance around 90 μF.cm<sup>-2</sup> extracted for a scan rate of 100 mV.s<sup>-1</sup> [9]. Note that inversely by application of negative bias (**Figure 5b**, black curve), the device no longer acts as a capacitor but as a low performance "battery" implying Li-Pt alloying reactions on the Pt side (black curve). As seen in **Figure 5c**, the reversible CV shape remains almost unchanged when increasing the scan rate from 50 mV.s<sup>-1</sup> to 2 V.s<sup>-1</sup> and the different capacitances extracted from CV (plotted as function of the scan rate in **Figure 5d**) demonstrates well

the beneficial effect of adding an interfacial pseudocapacitive electrode to boost the capacitance density compared to Pt/LiPON/Pt MSCs. Nevertheless, a 28% decrease of the capacitance value is observed when increasing the cycling rate by 2 orders of magnitude, which can be explained by the impact of the high internal resistance related to amorphous  $\text{TiO}_2$  film (known as a bad electronic conductor with a band gap around 3.0 - 3.4 eV). The kinetic limitation would imply a shift of the Li insertion peak (on the negative electrode) from its thermodynamic value when cycled at high rate, and consequently an efficiency loss of the AsHMSC behavior. This observation is consistent with Conway's recommendation suggesting that AsHMSCs should not be cycled with speed rate exceeding 1C [15].



**Figure 6.** (a) Cycle life of AsHMSC over 10,000 cycles at  $10 \mu\text{A}\cdot\text{cm}^{-2}$  (Inset:  $dQ$  vs  $E$ ). (b) Evolution of the AsHMSC impedance spectra (real and imaginary parts) with cycling.

Finally, AsHMSC endurance was tested by applying a constant charge/discharge current of  $10 \mu\text{A}\cdot\text{cm}^{-2}$  between 0 and 3V (**Figure 6a**). The device exhibits a 97% coulombic efficiency even after cycling for 10,000 continuous charge-discharge cycles. An initial capacitance drop of  $\sim 18\%$  is observed however during the first five hundreds cycles followed by a smoother decay of  $2.10^{-3} \%$ /cycle in average for the following cycles. The derivative signal of the charge and discharge profiles (**Figure S8**) given in the inset is losing intensity in its entirety while cycling, however no second contribution to the impedance signal is seen (**Figure 6b**). This only comes with a very slight increase of the internal resistance of  $1.10^{-3} \%$ /cycle suggesting the  $\text{TiO}_2$  film remains stable over cycling, and thus that the capacitance loss would be more related to an increase of the overpotential on the  $\text{TiO}_2$  side during lithiation (previously observed as less favorable than delithiation).

## 4. Conclusion

In this work, we have introduced a thin pseudocapacitive electrode to enhance the electrochemical performance of Pt/LiPON/Pt MSC described in previous work. Amorphous  $\text{TiO}_2$  films, tested in liquid and solid-state (using LiPON) half-cell configurations, provides similar results in terms of storage capacity, typically 95% of the theoretical capacity. Interestingly,  $\text{TiO}_2$  films after LiPON deposition exhibits an initial amount of lithium almost constant for all considered thickness and do not require a first activation process, contrary to the liquid configuration. The broad potential distribution in addition to excellent rate capability properties for ultrathin films highlighted the extrinsic pseudocapacitive behavior of amorphous  $\text{TiO}_2$  material.

A thin 6nm- $\text{TiO}_2$  films has been implemented in AsHMSC configuration as insertion electrode facing a Pt electrode that sustains a double layer type storage mechanism. The device exhibits capacitance value of around  $94 \mu\text{F}\cdot\text{cm}^{-1}$  at  $50 \text{ mV}\cdot\text{s}^{-2}$  which is about twice higher than Pt/LiPON/Pt MSC and a good endurance of 10.000 cycles as expected for such configuration. However, this comes with a high and fast decrease of capacitance upon cycling, as well as moderate rate properties that seems to originate from an increase of the overpotential during the lithiation step particularly.

Although we succeeded to design high performance AsHMSC, improvements are still necessary to increase the cycling stability and the cycling rate. The development of ALD layers for electrodes and the electrolyte (sub 50nm) would enable a decrease of the internal resistance by decreasing significantly the whole stack thickness, and certainly a better control of the pre-lithiation by introducing lithiated precursors during the  $\text{TiO}_2$  ALD deposition.

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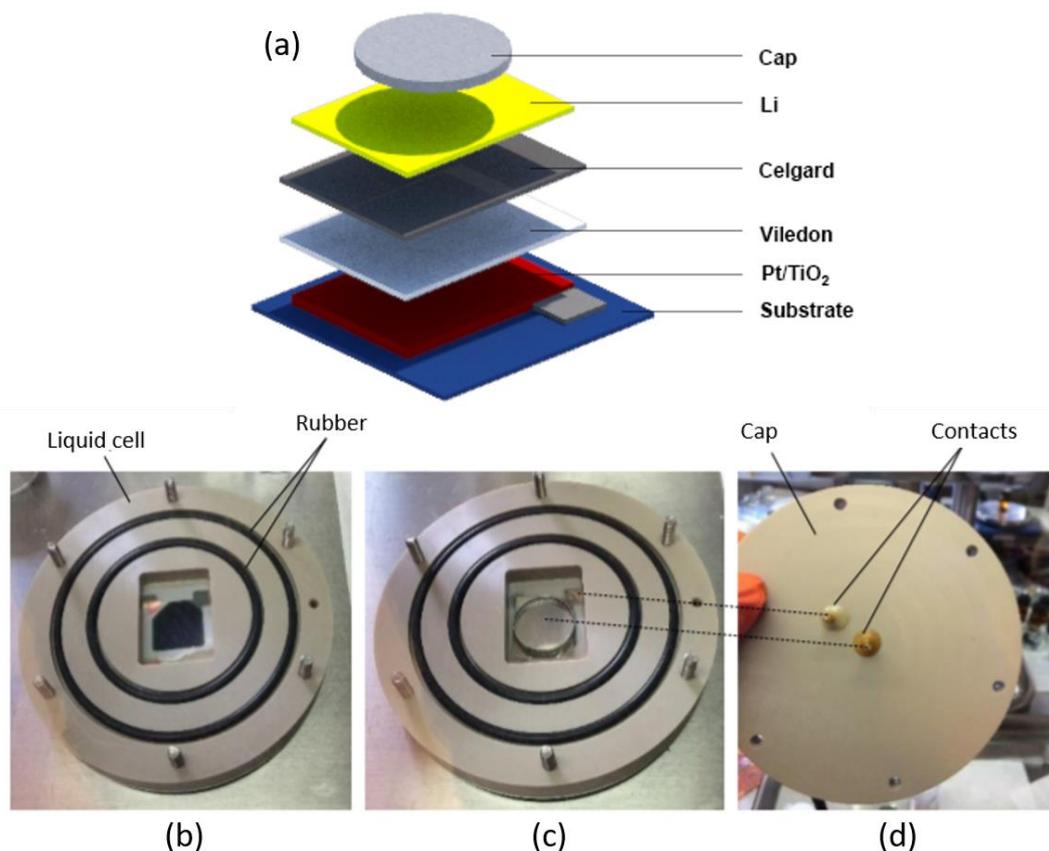
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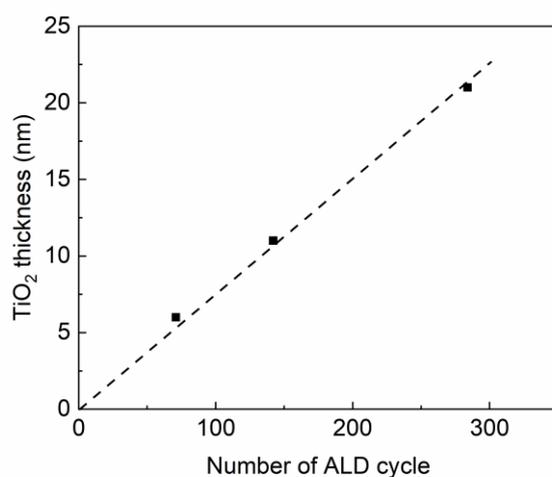
## Conflicts of interest

There are no conflicts to declare.

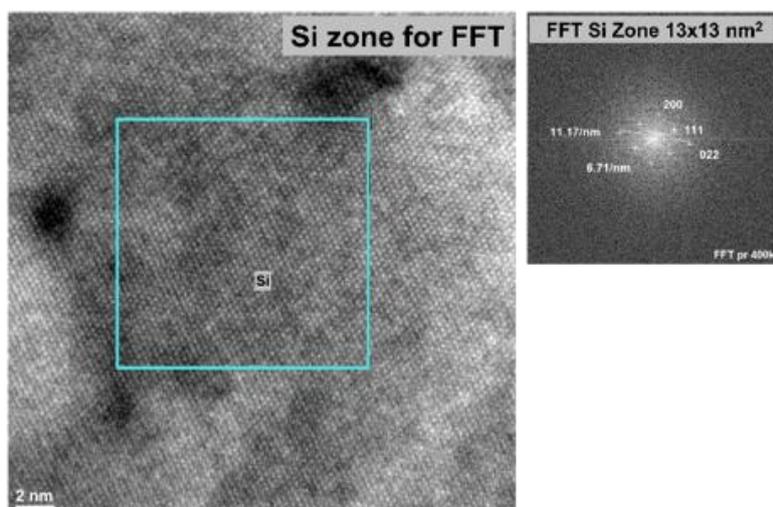
## Supplementary Information



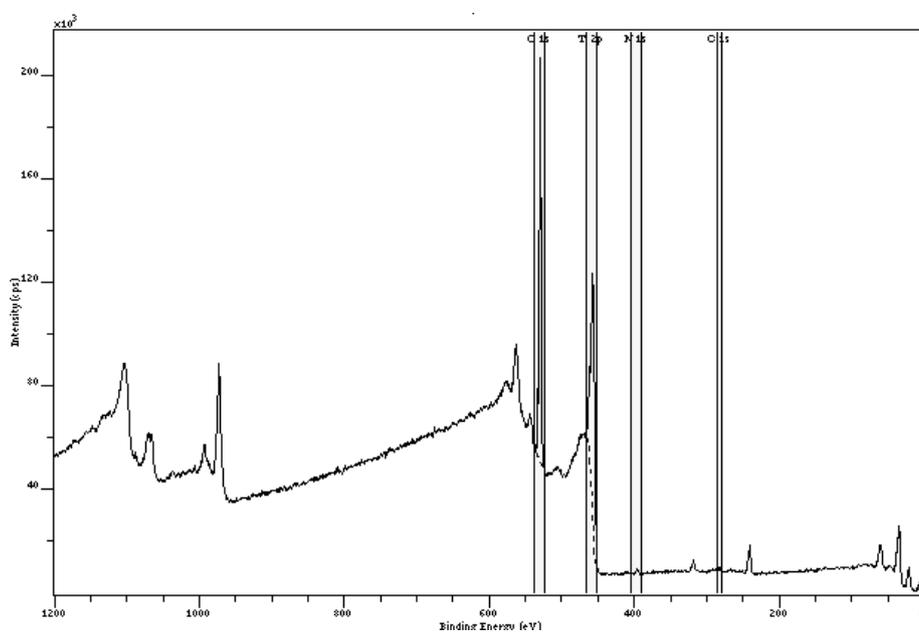
**Figure S1:** Photos of liquid cell assembly: (a) stack, (b) substrate laid into the cell, (c) separators, Li foil and metal cap placed onto the substrate, (d) cover with positive and negative contacts.



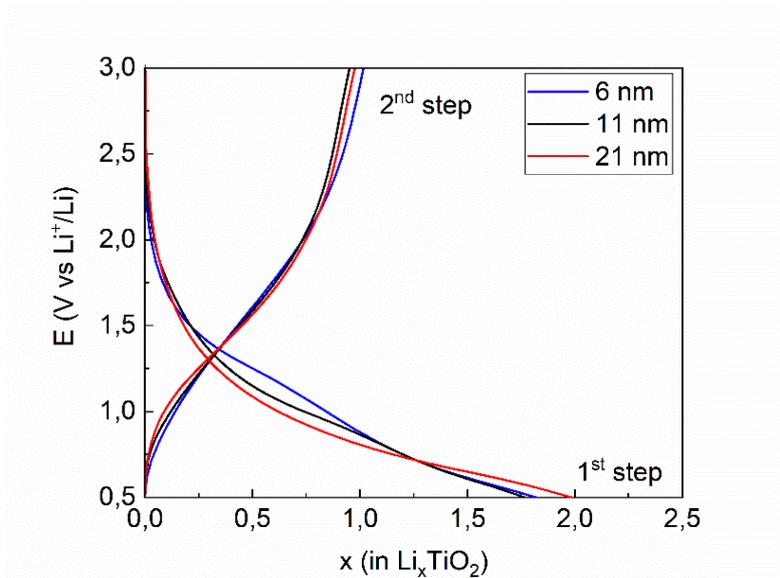
**Figure S2.** Growth of ALD TiO<sub>2</sub> films; thickness is obtained by SE.



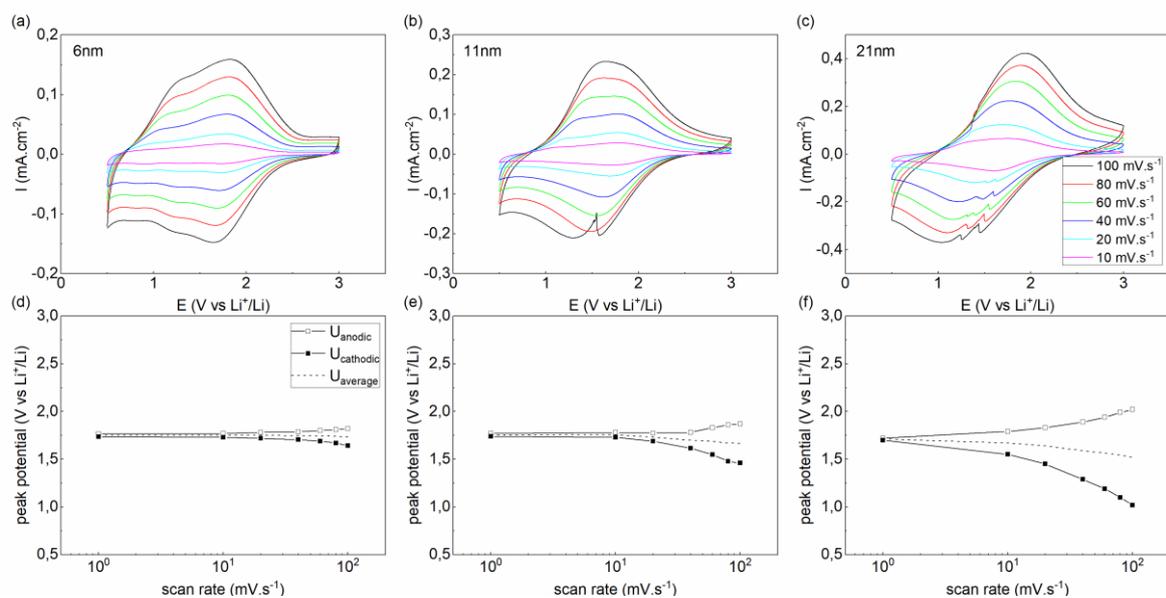
**Figure S3.** HR-TEM reference image of Si substrate captured with magnification of 400k.



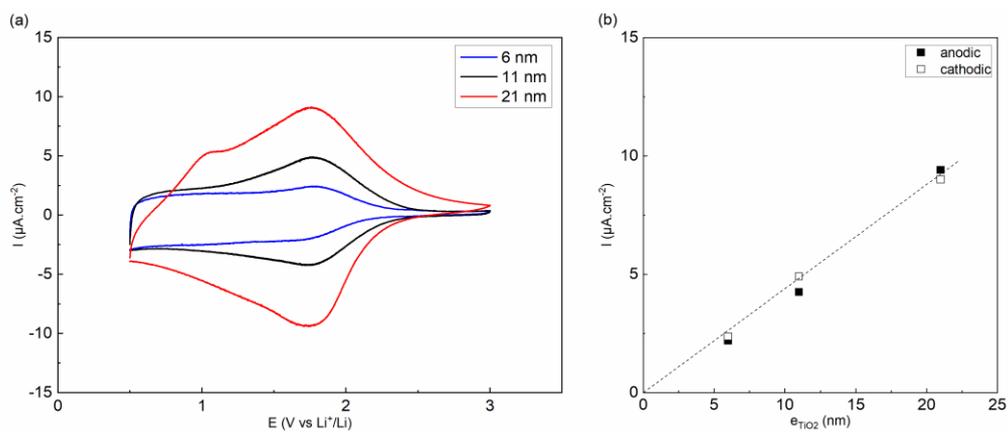
**Figure S4:** XPS survey spectra of TiO<sub>2</sub> film.



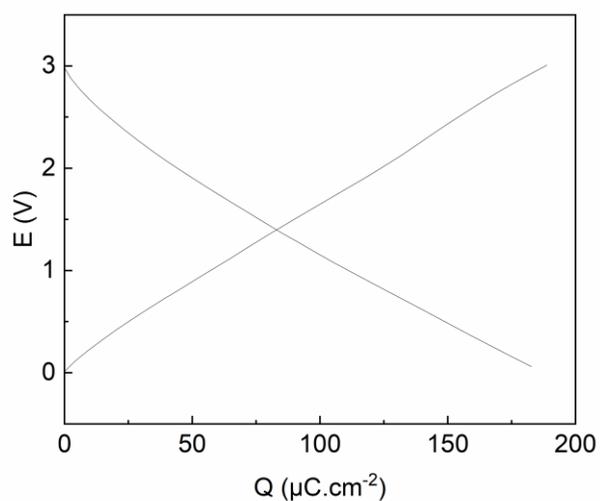
**Figure S5:** First discharge followed by first charge (1<sup>st</sup> and 2<sup>nd</sup> cycle) of thin TiO<sub>2</sub> cycled in liquid cell within [0.5 – 3V] potential range vs Li<sup>+</sup>/Li at 1  $\mu\text{A}\cdot\text{cm}^{-2}$ .



**Figure S6.** (a, b, c) CV plotted for scan rates between 10 and 100  $\text{mV}\cdot\text{s}^{-1}$  for 6nm, 11 and 21nm films respectively in liquid half-cell configuration. (d, e, f) Peaks potential shift as function of the scan rate for 6nm, 11 and 21nm films respectively.



**Figure S7.** CV profiles of 6nm, 11nm and 21nm TiO<sub>2</sub> films at a scan rate of 1 mV.s<sup>-1</sup>. (Inset:  $I_{\text{peak}}$  vs TiO<sub>2</sub> thickness).



**Figure S8:** 10,000<sup>th</sup> charge and discharge profile with constant current of 10  $\mu\text{A}\cdot\text{cm}^{-2}$ .