



## Fabrication and performance of electrochemically grafted thiophene silicon nanoparticle anodes for Li-ion batteries



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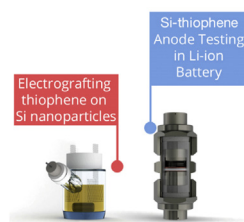
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### HIGHLIGHTS

- Thiophene is grafted to silicon to allow for intimate contact.
- Modification with the thiophene layer acts as a pre-existing SEI layer.
- The thiophene layer results in improved cycle life.
- Further improvements will be possible by forming conducting polymer composites.

### GRAPHICAL ABSTRACT



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In this work, we developed thiophene-grafted Si nanoparticle anodes for Li-ion batteries. The surface of Si nanoparticles was chemically modified with thiophene molecules via an electrochemical grafting process. This study is an overture for future

endeavours where the thiophene layer on the modified Si-nanoparticles will function as an anchor point when co-polymerised with conducting polymers to produce a chemically bonded Si/conducting polymer anode composite. This in principle should mitigate the loss of electrical connection with Si due to any structural breakdown that may occur during cell cycling. Furthermore, the effect of the thiophene layer on the capacity and the cyclability of the Si electrode was apparent where the new material retained ~39% of the starting capacity after 60 cycles, compared to the unmodified Si electrodes, that merely lasted for 10 cycles with only 4% capacity retention. This is due to the thiophene layers which create an artificial solid electrolyte interphase around the Si nanoparticles protecting them from degradation. Additionally, the viability of using conducting polymers as anode composites under charging/discharging conditions was investigated via electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) to conclude whether or not n-doping of the conducting polymer is required in such applications.

### 1. Introduction

In a modern age characterised by the inevitable transformation from using fossil fuels to greener renewable energy sources, new cutting-edge materials for energy storage are being pursued by

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scientists to keep up with the surging demand for clean energy. Such materials should be able to store or generate high amounts of energy in devices that ultimately should be cheap, lightweight, environmentally friendly and easily produced to maximise cost efficiency. Traditionally, energy storage devices such as Li-ion batteries utilise graphite based materials as anodes, but a significant drawback is that graphite exhibits low capacity that can't match the full energy capacity of lithium [1–3]. In order to overcome this problem, other materials, such as silicon, are being utilised as anode materials instead of graphite. This is due to silicon's extraordinarily high gravimetric capacity (3572 mAh g<sup>-1</sup> vs. 372 mAh g<sup>-1</sup> for graphite) as well as high volumetric capacity (8322 mAh L<sup>-1</sup> vs. 818 mAh L<sup>-1</sup> for graphite) [4,5]. However, silicon-based anodes have their own disadvantages due to their massive volume expansion that can reach up to ~400% during the lithiation process [6]. This massive volume expansion results in a structural fracture and hence, loss of electrical contact with the collector electrode [7,8] as well as breaking and reformation of an unstable solid electrolyte interphase (SEI) layer in the subsequent cycles which consumes the electrolyte [9–11]. All of this results in a large fade in capacity [4]. Additionally, the conductive mixture, which is required for the anode to work properly, adds extra weight to the battery without contributing to its capacity which is detrimental to its applicability in applications such as electric vehicles.

Many strategies have been attempted to tackle these problems [1,12]. Nano-sized silicon particles were utilised to better accommodate the colossal strain which mitigated the cracking issue [6,13–17]. Furthermore, Si nanoparticles were mixed with various polymeric binders, such as polyacrylic acid (PAA), polyvinylidene difluoride (PVdF), and carboxyl-methyl cellulose (CMC), to provide strong bonding between the Si nanoparticles and the conductive carbon material in order to improve the cycle life [18–20]. The cycle life of Si/PAA and Si/CMC composites anodes were improved due to the binding between the functional groups on the polymers and the oxide layer on the silicon particles [1]. Recently, various types of conducting polymers (CPs) were utilised with Si electrodes. An exotic variant of CPs was tested by Liu et al. where the polyfluorene-type polymers served as a conductive binder to overcome the volume expansion problem [20]. Furthermore, Cui et al. achieved a high-performance Li-ion battery by developing a silicon/polyaniline (PANI) hydrogel composite anode [2]. They encapsulated the Si nanoparticles within the PANI 3D porous network via *in situ* polymerisation. In both cases, the CPs served as conductive networks for fast electron and ion transport as well as providing the proper support for the Si to accommodate any volume expansion. However, for Li-ion batteries, the charging/discharging process on the anode takes place at a very negative potential (vs. Li/Li<sup>+</sup>) [3] in a region where the CPs are n-doped, as in PEDOT and polypyrrole, or undoped, as in the case of polyaniline. Due to this phenomenon, the use of CPs as battery electrode materials receives some criticism. That is because at this very negative potential range the conductivity of the CPs is thought to be at its lowest where the polymer structure lacks counter ions, as in polyaniline, or contains a very low concentration of counter ions, as in n-doped PEDOT. Furthermore, the n-doping process of PEDOT has been found to diminish and disappear in the presence of Li<sup>+</sup> ions in the solution [21].

The aforementioned work on developing Si/CPs composite anodes relied on the physical incorporation of Si nanoparticles within the CPs. These methods do not provide strong chemical bonding between the CPs and the Si nanoparticles whether the composites were prepared via physical mixing of CPs and Si, or via *in situ* polymerisation of CPs with the nanoparticles. In the presented work, a new approach is taken, whereby the surface of Si nanoparticles was chemically modified with thiophene molecules via an electrochemical grafting process. In future studies, this thiophene

layer is proposed to serve as anchoring points for poly(3,4-ethylenedioxythiophene) (PEDOT) to attach to during polymerisation in order to yield a chemically bonded Si/CPs composite anode. The relatively strong Si–C covalent bond [22] formed between the Si surface and the C atom from thiophene should ensure the lasting connection between the Si nanoparticles and the CP matrix and hence mitigate the effects of volume expansion exhibited by the Si electrodes. This study serves as a preface for these future studies and focuses on the electrochemical grafting process of thiophene onto silicon and what effect the thiophene layer, alone, has on the behaviour and performance of the modified Si electrodes and if it offers a viable route to protecting the Si nanoparticles against degradation during lithiation and de-lithiation processes. Additionally, the study investigates the viability of using conducting polymers such as PEDOT as anode composites in Li-ion batteries via electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) to determine whether or not n-doping of the conducting polymer is required for such applications.

## 2. Experimental Section

### 2.1. Materials

3,4-ethylenedioxythiophene (97%, EDOT), bromo-thiophene, acetonitrile (≥99.0%), *N*-methyl-2-pyrrolidone (99%, NMP), Tetra-butylammonium hexafluorophosphate (NBu<sub>4</sub>PF<sub>6</sub>), hydrofluoric acid (HF), and carboxymethyl cellulose (CMC, Mw = 90000) were purchased from *Sigma-Aldrich* and 1 M Lithium hexafluorophosphate in ethylene carbonate and dimethyl carbonate (LP30 battery standard electrolyte, LiPF<sub>6</sub> EC/DMC) was purchased from *Solvionic*. Tetraethylammonium tetrafluoroborate (NEt<sub>4</sub>BF<sub>4</sub>) was purchased from *Novolyte*. Lithium foil for electrode construction was purchased from *Targray*. The Si nanoparticles (~150 nm in diameter) were synthesised by CEA-LITEN (Grenoble, France). For the characterisation studies, a *Kratos Nova* XPS instrument, *Bio-Logic* battery testing unit, *FEI Nova* SEM, and *Hitachi HF-2000 Field Emission Gun (FEG)* TEM were used.

### 2.2. HF treatment of Si nanoparticles

The Si nanoparticles (150 nm diameter) were treated with HF to etch away the oxide layer from the Si surface to generate an H-terminated surface. The H–Si bond is crucial for the grafting of the thiophene layer onto the Si nanoparticles. First, 0.5 g (±0.05) of Si nanoparticles were loaded into two centrifuge tubes and then 30 mL of 2% HF solution (in NMP) was added to each tube. Both tubes were then ultrasonicated for 30 min in order to suspend the nanoparticles in the HF solution and expose more surface area to the etching reaction. After the ultrasonication for 30 min, the nanoparticles suspension was vacuum filtered through a Teflon filter membrane and then washed with NMP for 5 times and an excessive amount of absolute ethanol until the pH of the filtrate was ~7.

### 2.3. Thiophene grafting

The electrochemical grafting was achieved via a modified version of the Gurtner et al. method [23]. Following the etching, the Si nanoparticles were resuspended into 25 mL of 50 mM bromothiophene in acetonitrile and 100 mM NEt<sub>4</sub>BF<sub>4</sub> as supporting electrolyte. The new suspension was placed in an electrochemical cell and purged with argon for 30 min. The working and counter electrodes were a 2 cm<sup>2</sup> stainless steel mesh and Ag/AgNO<sub>3</sub> (10 mM AgNO<sub>3</sub> + 100 mM NBu<sub>4</sub>PF<sub>6</sub> in acetonitrile) was used as a reference electrode (Fig. 1a).

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