

Communication

Inkjet-printed silicon as high performance anodes for Li-ion batteries

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ABSTRACT

Herein we report the fabrication, optimization, and characterization of inkjet-printed thin film silicon anodes for lithium-ion batteries using commercial silicon nanoparticles. By comparing four different polymer binders, we demonstrate the critical role of binder on achieving good electrochemical performance of inkjet-printed silicon electrodes. Inkjet-printed silicon nanoparticle electrodes with conductive polymer PEDOT:PSS binder exhibit superior performance and durability, with a capacity retention of over 1000 cycles at a depth-of-discharge of 1000 mA h g⁻¹. The working mechanism of the impact of the binders on inkjet-printed silicon electrodes is investigated and explained in detail via various characterization techniques, including scanning electron microscopy, Raman and infrared spectroscopy.

1. Introduction

Portable energy storage has been receiving worldwide interest as the recent demand for mobile power sources has sky-rocketed. With the miniaturization of wireless devices, rechargeable batteries have had to decrease in size without compromising the amount of energy stored. Thin film batteries are poised to meet this challenge, as they exhibit a number of unparalleled features including high energy and power densities [1,2], short ion diffusion lengths [3,4], and intrinsic flexibility [5,6]. The successful development of high capacity thin film batteries will enable advances in the fields of wireless sensors, RFID tags, implantable medical devices, and robotics. Up to now thin film batteries have mostly been fabricated by traditional thin film growth technologies such as physical vapour deposition (PVD) or chemical vapour deposition (CVD). However, these methods generally require expensive equipment and harsh conditions for thin film growth, including high vacuum or high temperatures, which limits the wide adoption of thin film batteries.

Inkjet printing is a promising technique for fabricating thin film electrodes. It can be used to deposit films of precisely controlled thickness, which can be tuned by the number of layers printed on top of one another. It has many advantages over other thin film fabrication techniques, including ease of use, cost-effectiveness, minimal wasted material, scalability, and the ability to deposit patterns easily. It does not require expensive equipment and deposition can be performed at room temperature and ambient conditions. For these reasons, inkjet printing has been successfully developed to fabricate supercapacitors [7–9], transistors [10,11], solar cells [12–14], and battery electrodes

[15–19]. However, current research on inkjet-printed fabrication of thin film electrodes for lithium-ion batteries (LIBs) has mainly focused on the cathode, while few studies have focused on the anode (Table S1). Zhao et al. reported both inkjet-printed SnO₂ and Li₄TiO₁₂ thin films as anodes for LIBs [20,21]. Nonetheless, the discharge capacity of these reported thin film anodes (below 1000 mA h g⁻¹) are still insufficient to meet increasing requirements of energy density for future thin film LIBs.

Silicon has been proposed and widely studied as a candidate anode material for LIBs to at least partially replace the state-of-the-art commercial graphite anodes [22–25], due to its high theoretical gravimetric capacity (4200 mA h g⁻¹, compared to 372 mA h g⁻¹ for graphite), low lithium insertion/extraction potential, and low cost [26,27]. Accordingly, thin film Si electrodes have also attracted wide research interest for thin film LIBs (Table S2). However, one well-known challenge of Si anode material is its 400% volume expansion upon full lithium insertion [28], causing pulverisation of the particles and loss of electrical contact which results in decreased capacity during cycling. Nano-scale Si is more resistant to mechanical fracture than micro-scale Si [29,30], and many studies have focused on developing novel nanostructured Si electrodes, such as nanowires [31], nanotubes [32], hollow nanospheres [33], and core-shell structures [34,35], to overcome the poor cycling stability of Si. However, the synthesis of these nanostructured Si electrodes typically requires large amounts of energy and is not easily translated to commercial mass production. One simpler alternative strategy is to use a polymer binder that can accommodate the volume expansion of Si nanoparticles (SiNPs) and maintain electron conduction across the electrode. Previous reports

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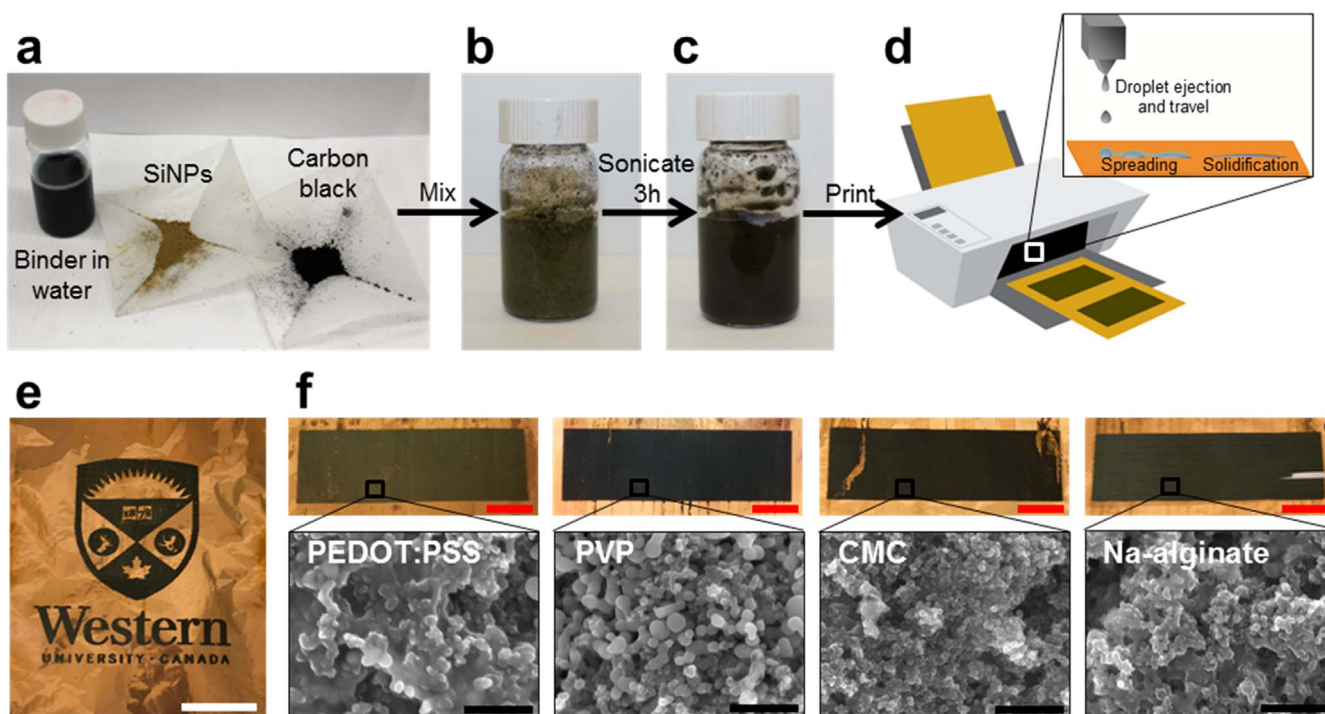


Fig. 1. Procedure used to print SiNP anodes on copper foil. (a, b) First, the ink was prepared by mixing SiNPs, carbon black, and the polymer binder in water. (c) After 3 h of sonication, the solution was well-mixed and (d) injected into an inkjet printer cartridge and printed. (e) Photograph of the Western University logo printed with the SiNP ink. (f) Optical photographs and SEM images of the inkjet-printed SiNP anode films on copper foil. Scale bars red, white, and black represent 3 cm, 5 cm, and 500 nm, respectively.

have shown that the mechanical, chemical, and electronic properties of different binders have a significant effect on the cycling performance of SiNP electrodes [36–41].

Herein we report preparing inkjet-printed SiNP anodes with four commercially available polymer binders, i.e. poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT:PSS), polyvinylpyrrolidone (PVP), carboxymethyl cellulose (CMC), and Na-alginate, and investigated their effects on the electrochemical performance of the electrodes in LIBs. We demonstrate that SiNP anodes printed with PEDOT:PSS binder exhibit the most stable cycling at high discharge capacity, due to its excellent jetting properties [42] and electrical conductivity. Scanning electron microscopy (SEM) shows that PEDOT:PSS conformally coats the SiNPs as a conductive layer, allowing for rapid electron transport while binding the electrode together. In addition to the improved electronic conductivity due to the conductive nature of PEDOT:PSS, which has been previously demonstrated as an effective binder for battery electrodes [43–47], we also noticed the unexpected behaviour of PEDOT:PSS acting as a self-healing polymer. Using various characterization techniques, including SEM, Fourier transform infrared (FTIR) spectroscopy, and Raman spectroscopy, we observed the PEDOT:PSS binder stretching during cell discharge to effectively accommodate the volume expansion of SiNPs and shrinking during charge to preserve the continuous conductive network. Thereby, the optimized inkjet-printed SiNP electrode exhibits high electrochemical performance as an anode for Li-ion batteries.

2. Experimental

2.1. Silicon ink preparation

Inks were prepared by mixing SiNPs (50 nm, Hongwu Nano), carbon black (50 nm, Gunbai), and polymer binder at a ratio of 2:2:1 by weight in an appropriate volume of DI-water to achieve a viscosity of 10 mPa s, as measured with a U-tube viscometer (Cannon Instrument Company). Four polymer binders were used: PEDOT:PSS (Sigma-

Aldrich), PVP (Sigma-Aldrich), CMC (Calbiochem), and sodium alginate (Sigma-Aldrich). Inks were sonicated for at least 3 h to break up large agglomerates and ensure uniform dispersion prior to use.

2.2. Electrode and coin cell preparation

The ink was transferred into a well-cleaned HP 61 ink cartridge and printed using a Hewlett-Packard Deskjet 2540 inkjet printer. Twenty-five layers of each ink were printed on copper foil to ensure sufficient thickness and uniformity. After printing, the films were dried in a vacuum oven at 60 °C overnight. The printed films were then cut and assembled in CR-2032 coin cells with lithium metal foil as the counter electrode in an argon-filled glove box. The mass loading of Si in the inkjet-printed thin film electrodes are around $125 \mu\text{g cm}^{-2}$. The two electrolytes used were composed of 1 M LiPF_6 salt dissolved in different solvent mixtures: (1) 1:1:1 ratio by volume ethylene carbonate, diethyl carbonate, and ethyl methyl carbonate (EC:DEC:EMC) and (2) 1:9 ratio by weight dimethyl carbonate and fluoroethylene carbonate (FEC:DMC). The coin cells were stored overnight at room temperature before testing.

2.3. Characterization

A field emission SEM (Hitachi S-4800) equipped with an energy dispersive X-ray (EDX) spectrometer was used to observe the microstructure and elemental composition of the printed films. Galvanostatic charge-discharge measurements were performed on an Arbin BT-2000 Battery Tester between 0.01 and 1.0 V vs. Li/Li^+ . The charge/discharge rates and capacities were calculated based on the mass of Si in the anode, as determined by thermogravimetric analysis (TGA, TA Instruments SDT Q600) (see Fig. S1). Cyclic voltammetry (CV) (Fig. S2) and EIS were performed on a multichannel potentiostat 3/Z (VMP3). FTIR spectroscopy (Nicolet 6700) and Raman spectroscopy (532.4 nm laser, HORIBA Scientific LabRAM HR) were performed to analyze anodes with PEDOT:PSS binder before cycling, after first cycle lithiation, and after first cycle delithiation.

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