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Lithium storage in structurally tunable carbon anode derived from sustainable source

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ABSTRACT

A meticulous solid state chemistry approach has been developed for the synthesis of carbon anode from a sustainable source. The reaction mechanism of carbon formation during pyrolysis of sustainable feedstock was studied *in situ* by employing Raman microspectroscopy. No Raman spectral changes observed below 160 °C (thermally stable precursor) followed by color change, however above 280 °C characteristic D and G bands of graphitic carbon are recorded. Derived carbon particles exhibited high specific surface area with low structural ordering (active carbons) to low specific surface area with high graphitic ordering as a function of increasing reaction temperature. Carbons synthesized at 600 °C demonstrated enhanced reversible lithiation capacity (390 mAh g^{-1}), high charge-discharge rate capability, and stable cycle life. On the contrary, carbons synthesized at higher temperatures (>1200 °C) produced more graphite-like structure yielding longer specific capacity retention with lower reversible capacity.

1. Introduction

The increased demand for efficient energy storage devices has intensified the development of advanced high-performance rechargeable batteries during the last two decades. Currently considered the state-of-the-art battery technology, lithium ion batteries (LIBs) are the energy storage solution of choice for portable consumer electronics, and are poised to enter new markets such as electric vehicles and grid storage [1,2]. With the rising demand for LIBs, the search for inexpensive, more sustainable high-capacity electrode materials has become ever more imperative. Carbonaceous materials are still the primary anode material, with graphitic carbons accounting for the majority of all anodes utilized in commercial LIBs [3,4].

The specific capacity of a perfectly graphitic structure cannot exceed 372 mAh g^{-1}, thus limiting the energy density of graphite-based anodes. In contrast, owing to a different storage mechanism, a variety of disordered carbons were found to exhibit significantly higher capacities, reaching 1000 mAh g^{-1} or more [5–8]. From a cost and sustainability perspective, disordered carbons derived from biomass are of particular interest.

To date, a wide variety of biomass sources have been investigated (Table 1), including sugar, oak, walnut, almond, lignin [6]; starch [6,9,10], mangrove [11], peanut [12], coffee shells [13], sisal [14], banana fibers [15], rice husk [16,17], straw [18], alginic acid [19], olive [20], and cherry stones [20,21]. More recently, bamboo chopsticks [22], and wheat straw [23] have been used. Unfortunately, many of these precursors have their individual short comings, including the need for acid/base treatments before pyrolysis [12,13,15–18,20–22]; salt baths for impregnation of catalytic metal particles [15,20]; or high temperature treatment (>1000 °C) [11]. In addition, the resulting carbons often exhibit high capacity fade [13,14,18,21] and/or suffer from poor cyclability [17]. The above studies have revealed that among all the biomass-derived carbons, starch offers the highest control over structure and properties of the resulting carbon [9,10,24]. In recent electrochemical studies, spherical porous carbon particles were obtained from potato starch, achieving specific capacities of 475 mAh g^{-1} after 20 cycles at 1C [9] and 513 mAh g^{-1} after 50 cycles (C-rates were not reported) [10].

In spite of the great progress in the morphological control from starch-derived carbons, to the best of our knowledge, wheat flour

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Table 1
Literature survey of the various biomass derived carbons, their synthesis methods and their respective half - cells reversible capacities with respect to lithium at similar C-rates (0.1C), otherwise noted.

Precursor	Synthesis	C_{rev} (mAh g^{-1})
Potato Starch Granules [9]	Baking (200–300 °C) + Pyrolysis (1000 °C)	540
Mangrove charcoal [11]	Pyrolysis (1000 °C)	463
Sisal Fibers [14]	Pyrolysis (900 °C) + Hydrothermal activated (140 °C)	250
Rice Husk [16]	Autoclave (230 °C) + Pyrolysis (900 °C) + SiO_2 etching NH_4HF_2	403 @0.2C
Alginic Acid [19]	HCl bath + Pyrolysis (1500 °C)	255 @0.7C
Cherry stones [20]	H_2SO_4 bath + $ZnCl_2$ impregnation + Pyrolysis (500 °C)	267 @0.2C
Cherry stones [21]	KOH bath + Pyrolysis (500 °C)	348
Bamboo chopsticks [22]	KOH bath + Various heating process and washing process (150 °C + 60 °C) + Pyrolysis (800 °C) + HCl Bath	355 @0.37C
Wheat Straw [23]	HCl Bath + KOH Bath + Pyrolysis at 700 °C	1470

derived from cereal grains of the *Triticum* genus comprising mostly carbohydrates (starch), protein, minerals, and minor vitamins has not been explored as potential carbon precursor for anode materials in lithium ion batteries. This comes as a surprise given the fact that in 2013, the world wheat production was around 713 million tons, which is about 25% of the global cereal grain production, ranking third compared to maize and rice [25]. Moreover, the granule size of wheat starch ranges from 1 to 45 µm, which is smaller and thus more favorable than that of potato starch [26]. At the same time, amylopectin-amylose-ratio, the two main components in starch, for wheat (72:28) is similar to that of potato starch (79:21) [26]. These two main components will be the primary source for the structurally tunable carbon content in the wheat flour, making it a promising candidate as precursor material for lithium-ion battery anode applications. Hence, in this paper, we report on the utilization of a sustainable, inexpensive wheat flour-derived carbons as a promising anode material in lithium ion batteries. Our primary focus is the critical structure-property-relation, with emphasis on the electrochemical performance of the resulting carbons.

2. Experimental

2.1. Material preparation

Raw wheat flour (Aashirvaad, ITC Limited) were used as feedstock precursor for carbon synthesis. Approximately 3 g of wheat flour were inserted into an alumina boat for carbonization in a tube furnace under inert argon atmosphere, with a constant flow rate of ~10 ml min^{-1}. The ramping rate was set at 5 °C min^{-1} and the holding time was 2 h. Carbonization temperatures were set to 300, 400, 500, 600, and 700 °C. For selected samples, a secondary high-temperature treatment (graphitization) was conducted. Two samples, carbonized at 600 °C, were further annealed for 2 h at 1200 and 1600 °C, respectively. The step towards structural ordering of pre-synthesized carbons was conducted in an argon atmosphere (flow rate of 100 ml min^{-1}) using a high temperature alumina tube furnace and a ramping rate of 3 °C min^{-1}.

2.2. Material characterization

Thermogravimetric analysis (TGA) was performed using a TGA Q50 from TA instruments. Carbonization of wheat flour was measured under a constant Ar purge, whereas thermal stability studies of the as-produced carbons were conducted in air (~ 40 ml min^{-1}). All heating and cooling rates were set to 5 °C min^{-1}.

In situ Raman spectroscopy studies were carried out to study the formation mechanism of carbon from the wheat-flour employing a DXR Raman microscope (Thermo Scientific) with an Ar-ion laser (532 nm), and a 50 × microscope objective with a 25-µm slit. All *in situ* experiments were carried out in a programmable temperature stage (Linkam THMS600) under inert Ar atmosphere with O_2 levels <1 ppm, and a constant argon purge of 10 ml min^{-1}. Samples were dispersed on a quartz slide and placed in the temperature stage. Each Raman spectrum was collected for ~45 s using a laser power density of 3.5 mW cm^{-2}. *Ex situ* Raman spectra of the as produced carbon samples were collected as well with the as described parameters.

Particle morphology was characterized using a scanning electron microscope (SEM, FEI XL40 at 5 kV), and transmission electron microscope (TEM, FEI Titan ETEM 80–300 at 300 kV). Surface area and pore size were analyzed using a Micromeritics Tristar 3000, the samples were outgas at 300 °C for 12 h.

Powder X-ray diffraction (XRD) was performed using a Rigaku (Cu source), at an acceleration voltage of 40 kV and a current of 44 mA. Data were collected in the range $2\theta = 10–80°$ using a step size of 5° min^{-1}. The Scherrer Equation (1) was used to determine the dimension of the crystallite thickness (L_c), and L_a the cluster diameter or the in-plane coherent length.

$$L = \frac{\kappa\lambda}{(\beta cos\theta)} \tag{1}$$

where κ is the geometrical factor, λ is the X-ray source wavelength, θ is the scattering angle in radians, and β is the full width at half maximum (FWHM) for the peaks used in radians. The (002) peak center is used to calculate L_c, and κ equals 0.9. For the dimensions of the cluster diameter (L_a), the peak center of (100) data is used and κ equals 1.84 [27]. Transmission electron microscopy (TEM, FEI Titan ETEM 80–300 at 300 kV) is used for the structuring understanding.

2.3. Electrochemical studies

Electrode slurries were prepared by mixing 80 wt.% wheat-derived carbon with 10 wt.% polyvinylidene fluoride (MTI) binder and 10 wt.% of conductive carbon (Timcal SuperP). The powder mixture was then dispersed in *N*-methyl-2-pyrolidone (MTI) and casted on a copper foil using an automated doctor blade applicator. The electrode was subsequently dried in a vacuum oven (80 °C for ~8 h). Coin cells were assembled in half-cell configuration using a lithium metal electrode (MTI) and a standard electrolyte (MTI) containing 1 M $LiPF_6$ in EC: DMC: DEC (1:1:1) with Celgard 2500 separator. Cell assembly was conducted in an Ar-filled glove box (H_2O and O_2 less than 1 ppm). Galvanostatic charge-discharge cycles were conducted on a Maccor 4000 series with the cycling voltage range of 0–3.0 V at various C-rates, C-rates were normalized to the electrode mass, assuming theoretical capacity of graphite, 372 mAh g^{-1}. Electrochemical impedance spectroscopy (EIS) were conducted on cells at a charged state with an oscillation of 5 mV amplitude over the frequency of 100 kHz to 0.01 Hz.