Electronic Supplementary Information (ESI):

Rice Husk-derived Carbon Anodes for Lithium Ion Batteries

Liping Wang,^a Zoe Schnepp^b and Maria Magdalena Titirici^a*

^a Max Planck Institute of Colloids and Interfaces, Am Mühlenberg 1, 14476 Potsdam, Germany, E-mail: Magdalena.Titirici@mpikg.mpg.de

^b School of Chemistry, University of Birmingham, Birmingham, UK

Supplementary method

The rice husk was sourced from a local farmer in ibaraki prefecture, Japan and ground to a maximum size of 0.8 mm for easier processing. Typically, 3.0 g rice husk powders were dissolved in 40 ml formic acid (95 wt %) at 80 °C for 4 h with magnetic stirring. After cooling to room temperature, the mixture was filtered and washed with distilled water to neutral pH. The collected solid product (~ 2.0 g) was placed in a 25 ml Teflon-sealed autoclave and kept at 230 °C for 48 h. After reaction, the autoclave was cooled down in a cold water bath, and the obtained black powder (~1.1 g) was centrifuged and washed several times. After drying at 80 °C overnight, the powder was calcined at 900 °C for 4 h at a heating rate of 10 K minute⁻¹. Finally, the powder was soaked in 4 M NH₄HF₂ for dissolving SiO₂ and consequently washed by water and dried. The carbon derived from rice husk after HTC is denoted as RH-Acid-HTC, after pyrolysis at 900 °C, denoted as RH-Acid-HTC-900, and after removal of SiO₂ as RH-Acid-HTC-900-HF.

Characterization

Thermo-gravimetric analysis (TGA) was carried out using a NETZSCH TG 209 at a heating rate of 10 K min⁻¹ from RT to 1000 °C in air. The size and morphology of samples were visualized using SEM Gemini Leo-1550. Nitrogen adsorption/desorption isotherms were measured at 77 K

using a Quantachrome Adsorption Instrument. XRD patterns were recorded with a Bruker-D8 apparatus with Cu radiation. Each pattern was recorded with a step size of 0.03° . Elemental composition was determined using a Vario E1 elemental analyzer.

Electrochemical test

The electrode was prepared by mixing powder (80 wt %), carbon black (10 wt %), and polyvinylidene fluoride (PVDF, 10 wt %) in N-methylpyrrolidone (NMP) to form a homogenous slurry. The slurry was then spread onto a copper foil and dried at 100 $^{\circ}$ C for overnight in a vacuum oven. Commercial electrolyte LP30 (1 M LiPF₆ in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) (1:1 by volume)) was used as the electrolyte. The assembly of the test cells was carried out in an argon-filled glove box. The batteries were charged and discharged at different rates from 0.2 C to 10 C between 0.0 and 3.0 V on a LAND CT2001A cell test apparatus (1 C corresponding to 372 mA g⁻¹ of current rate).



Figure S1 a) Pictures of original rice husk, b) SEM micrograph of pristine rice husk, c) SEM micrograph of rice husk after formic acid treatment, d) SEM micrograph of rice husk after formic acid treatment combined with HTC (denoted as RH-Acid-HTC), e) SEM micrograph of rice husk after formic acid treatment combined with HTC and pyrolysis (denoted as RH-Acid-HTC-900), f) SEM micrograph of rice husk- formic acid - HTC-900-NH₄HF₂ (denoted as RH-Acid-HTC-900-HF).



FigureS2 XRD profiles for pristine rice husk (RH), RH after formic acid treatment (RH-Acid), hydrothermal carbonization of formic acid treated rice husk (RH-Acid-HTC), and carbon from RH-Acid-HTC- 900-HF.



Figure S3 The morphology of rice husk after HTC treatment without formic acid pretreatment.



Figure S4 SEM images of rice husk after formic acid treatment then directly calcined at 900 $^{\circ}$ C for 4 h in N₂.



Figure S5 Thermogravimetric analysis of original rice husk heated from RT to 1000 $^{\circ}$ C in air with a ramp 10 K min⁻¹. It shows that 29 wt % ashes (mainly SiO₂) takes up the total weight of rice husk.



Figure S6 Rice husk ash obtained by combustion rice husk in air 900 °C for 4 h.



Figure S7 (a) Nitrogen sorption isotherms and (b) Pore size distributions (QSDFT model) obtained for sample RH-HTC-900 before and after silica removal.

Table S1 Calculated parameters from the nitrogen adsorption-desorption analysis at 77 K from Figure 2 for carbon materials derived from rice husk.

Sample	Surface	area [r	$n^2 g^{-1}$]	Pore Volume $[cm^3 g^{-1}]$			
	S _{BET} [a]	S _{total}	S _{micro}	S _{meso}	V _{total} [b]	V _{mic}	V _{meso}
RH-Acid-HTC	52	40	23	17	0.12	0	0.12
RH-Acid-HTC-900	135	155	133	22	0.15	0.05	0.10
RH-Acid-HTC-900-HF	243	219	66	153	0.41	0.09	0.32

[a] S_{BET} surface area is calculated by using BET equation in the relative pressure range of 0.05-0.35, other parameters are obtained by quenched solid density functional theory method (QSDFT).

[b] Total pore volume determined at $P/P_0 = 0.99$.

Sample	Surface area $[m^2 g^{-1}]$				Pore Volume $[cm^3 g^{-1}]$			
	S _{BET} [a]	S _{total}	S _{micro}	\mathbf{S}_{meso}	V _{total} [b]	V_{mic}	V _{meso}	
RH-HTC-900	65	90	77	13	0.08	0.03	0.05	
RH-HTC-900-HF	98	111	62	49	0.26	0.03	0.23	

Table S2 Calculated parameters from the nitrogen adsorption-desorption analysis at 77 K (Figure S7) for sample RH-HTC-900 before and after silica removal.

[a] S_{BET} surface area is calculated by using BET equation in the relative pressure range of 0.05-0.35, other parameters are obtained by quenched solid density functional theory method (QSDFT).

[b] Total pore volume determined at $P/P_0 = 0.99$.