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Research Update: Hard carbon with closed pores from pectin-free apple pomace waste for Na-ion batteries

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Herein, we report a hard carbon derived from industrial bio-waste, i.e., pectin-free apple pomace. The structural, morphological, and electrochemical properties of the hard carbon are reported. The impact of the bio-waste on the closed porosity is discussed, providing valuable insights into the sodium storage mechanism in hard carbons. Most importantly, the hard carbon delivers good electrochemical performance, high specific capacities of 285 mAh g⁻¹, and a very good capacity retention of 96% after 230 cycles at 0.1 C. © 2018 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). <https://doi.org/10.1063/1.5013132>

Sodium ion batteries (SIBs) are considered to be a promising alternative battery technology for stationary energy storage¹⁻³ due to the low cost and high abundance of sodium-based raw materials and the feasible use of aluminum as a current collector for the negative electrode. However, it needs to be considered that these advantages, unfortunately, are not sufficient in order to establish SIBs as a competitive battery technology for cost-effective energy storage.⁴ In fact, SIBs also require high performance active materials that are composed of abundant, cheap, and environmental-friendly elements and that are synthesized from raw materials that fulfill the same criteria. One bottleneck for the commercialization of SIBs is the lack of low-cost anode materials with high electrochemical performance [i.e., close to or exceeding that of graphite in lithium ion batteries (LIBs)]. Graphite only shows a poor electrochemical performance in SIBs,⁵ which is why the development of powerful anode materials is of high interest in the recent years.⁶ In this regard, hard carbons are in the focus since they can be derived from abundant and cheap waste resources while offering promising electrochemical performance. Indeed, industrial bio-waste is an appealing raw material as it is available in very large scale and at very low cost if not for free. This is due to the fact that many wastes have little commercial value and limited usability. For example, crop residues are frequently burned on site, which is leading to the emission of greenhouse gases and other pollutants.

As a consequence, the use of waste as hard carbon precursor is attracting wide attention. Various raw materials were investigated such as pomelo peels,⁷ corn cobs,⁸ and ox horns⁹ for hard carbons. The use of industrial waste such as tires¹⁰ has been reported but is still relatively unexplored although its use is certainly beneficial with respect to cost, availability (e.g., megaton-scale), quality (composition and homogeneity), and logistic efforts (collection, processing, and transport). In our recent study, we showed that the use of waste for the synthesis of hard carbons can decrease the environmental impact associated with their production, which finally results in more environmental-friendly batteries.¹¹ In another work, we showed that waste-apple-derived hard carbon, in fact, can be used as an anode material in SIBs.¹² Furthermore, we recently determined the influence of the biomass waste composition, e.g., the content of pectin, lignin, and hemicellulose, on the electrochemical performance and behavior of the corresponding hard carbons.¹³

Herein, we report the use of an industrial bio-waste, which is pectin-free apple pomace, as a raw material for the synthesis of hard carbon with high electrochemical performance. The resulting hard

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carbon (named AP-HC) is thoroughly characterized, and the results are compared with our previous work on waste-apple-derived hard carbon (A-HC).¹²

The hard carbon was synthesized via a facile synthesis route that is schematically illustrated in Fig. 1(a) and detailed in the [supplementary material](#). Compared to our previous studies on waste apples,^{12,13} no phosphoric acid treatment of the industrial-waste was performed because this step is applied during the pectin extraction process.^{14,15} Further acid treatment of the pectin-free apple pomace, in fact, led to hard carbon yields below 0.1% because of the absence of pectin, which is a stabilizing cross-linking component in the biomass.¹³ Instead, direct carbonization of the pectin-free apple pomace led to a high yield of about 30%, i.e., more than two-fold higher than that obtained for waste-apple derived hard carbon (14%) synthesized via initial phosphoric acid activation and subsequent carbonization under the same conditions.¹²

The morphology of AP-HC is shown in Figs. 1(b) and 1(c). Interestingly, SEM reveals spherical bubble-like structures on the surface of the hard carbon particles. TEM measurement and energy dispersive X-ray (EDX) mapping were used to investigate structure and composition of this unique bubble-like surface morphology [Figs. 1(d) and 1(e)]. TEM reveals that the hard carbon is porous and that the bubbles are indeed hollow, i.e., closed, pores. EDX mapping shows uniform elemental distribution, thus, suggesting homogenous composition for the material surface. So far, the formation of these bubbles has not been observed in other biomass-derived hard carbons, including our previous study on waste-apple-derived hard carbon.⁸ Possibly, the absence of pectin, i.e., the cross-linking component, facilitates the formation of semifluid-components, which trap the gas formed during

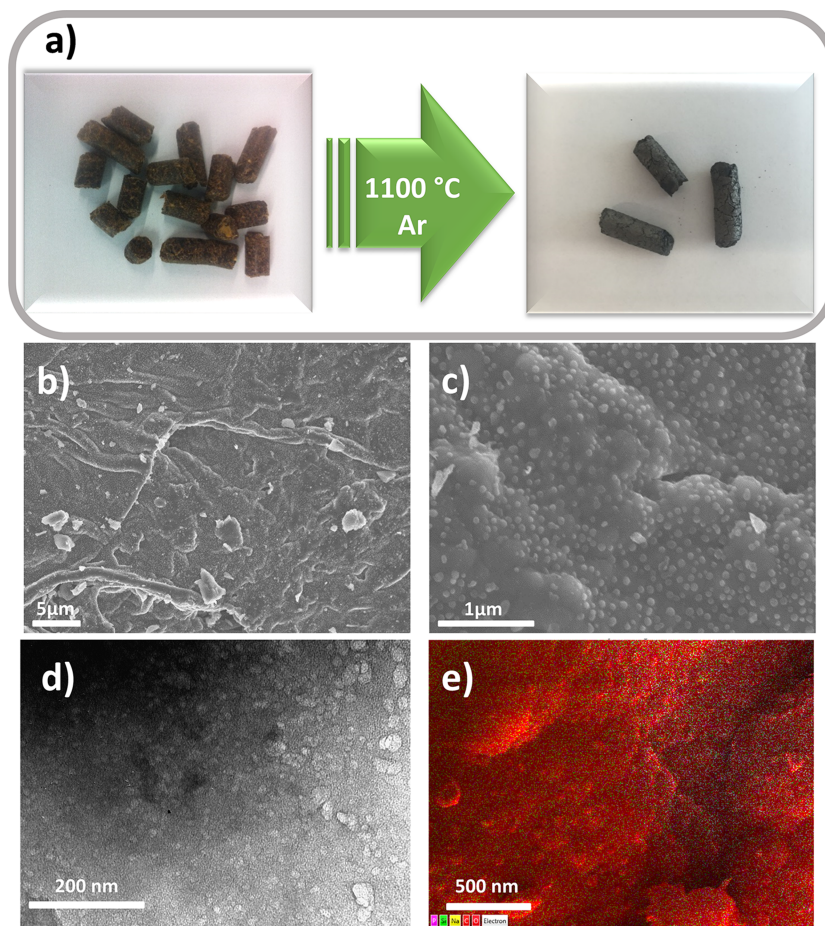


FIG. 1. (a) Schematic synthesis of pectin-free apple pomace-derived hard carbon and images of educt and product. SEM morphology of AP-HC at a magnification of (b) 10k \times and (c) 70k \times . (d) TEM image of AP-HC and (e) EDX mapping of the surface.

carbonization.¹⁶ Besides, as the pectin-free apple pomace (precursor) is extruded into compact pellet [see Fig. 1(a)], large particles are evident in the SEM images.

The structural properties of AP-HC were characterized by Raman spectroscopy, X-ray diffraction (XRD), N₂-adsorption measurements, and X-ray photoelectron spectroscopy (XPS). Results are displayed in Fig. 2 and Table S-I of the [supplementary material](#). Further details on the experimental conditions are given in the [supplementary material](#).

The structural properties of AP-HC are quite different from those of the apple waste-derived hard carbon of our previous work in which the biomass contained pectin (A-HC).¹² This observation is in accordance with the particular particle morphology observed via SEM in Figs. 1(b) and 1(c). The intensity ratio of the D and G bands ($I_D/I_G = 1.08$), calculated average interlayer spacing ($d_{002} = 0.377$ nm), and BET (Brunauer-Emmett-Teller method) surface area (1.54 m² g⁻¹) are decreased compared to the A-HC material with $I_D/I_G = 1.26$, $d_{002} = 0.385$ nm, and a surface area of 187.3 m² g⁻¹.^{12,13} Once more, the different structural properties can be explained with the very low content of pectin inside AP-HC. This facilitates the formation of a semifluid during carbonization which finally yields hard carbons with more graphitic character.¹⁶ The reflections at about 31.4° 2θ and 34.1° 2θ in the XRD diffraction pattern of AP-HC [Fig. 2(b)] are originating from alkali impurities that have not been removed from the biomass.¹⁷ The nitrogen adsorption-desorption isotherm of AP-HC [Fig. 2(c)] can be classified as type III, which is typical of non-porous materials.¹⁸ The pore size distribution (Fig. S-1 of the [supplementary material](#)), indeed, confirms that AP-HC only contains few open pores. The observed low surface area (BET) and large porosity (TEM) suggest that AP-HC contains substantial amount of closed pores. Additional pycnometry measurements and calculations were performed to determine the volume ratio of closed and open pores according to a published patent (detailed calculation in the [supplementary material](#)).¹⁹ The volume of closed and open pores for AP-HC accounts for 22.8% and 0.7% of the total volume, respectively, confirming the majority of the pores to be closed. The X-ray photoelectron (XP) C 1s core level spectra in Fig. 2(d) can be fitted with five peaks at binding energies of 286.6 eV, 285.1 eV, 286.7 eV, 290.5 eV, and 293.5 eV, which are associated to C=C/C-C, C-C/C-H, C-O,

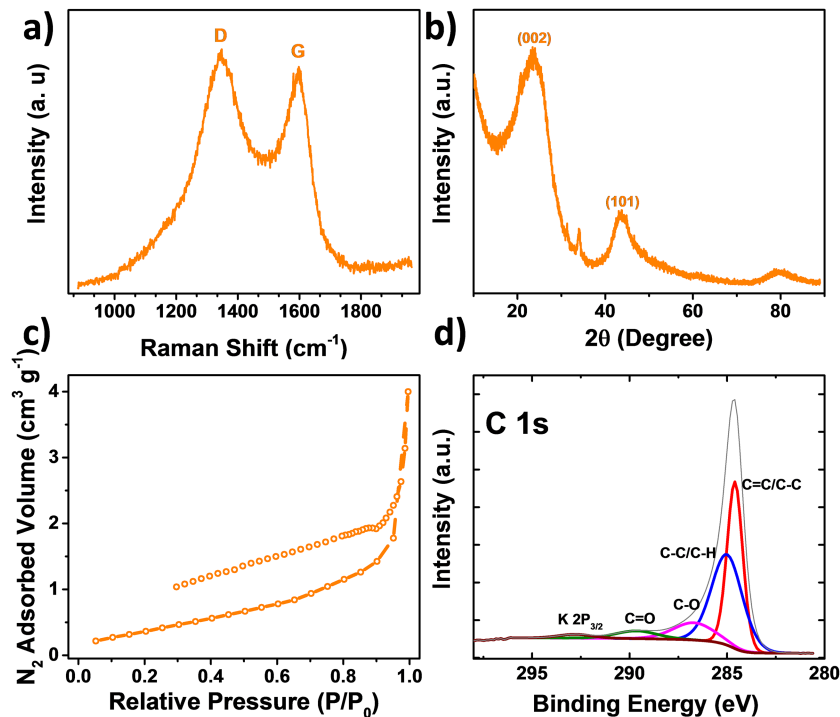


FIG. 2. (a) Raman spectrum; (b) X-ray diffraction pattern; (c) N₂ adsorption-desorption isotherm; and (d) XP C 1s core level spectra of AP-HC.

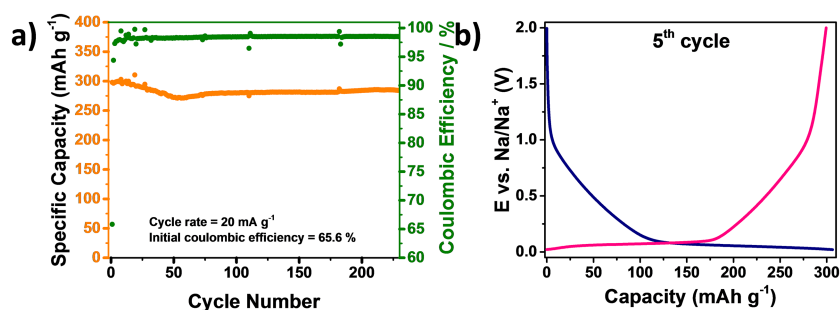


FIG. 3. Electrochemical performance of AP-HC. (a) Long-term cycling performance at 0.1 C and (b) potential profile of the 5th cycle.

C=O, and K 2p_{3/2}, respectively. Compared with A-HC,¹³ AP-HC contains about 8% less C=C/C—C (45.4% *vs.* 53.7%) and 6% more C—C/C—H (38.3% *vs.* 32.0%) on the surface. The I_D/I_G ratio of AP-HC is lower than that of A-HC, which shows that AP-HC contains more sp²-carbon. The presence of the K 2p_{3/2} peak in XPS is in accordance with the additional reflection in XRD and once more suggests the presence of alkali impurities.

The electrochemical performance of AP-HC is shown in Fig. 3. The cycling performance at 1 C is shown in Fig. S-2 of the [supplementary material](#).

Figure 3(a) shows that AP-HC delivers a good overall performance during the galvanostatic long-term cycling at 0.1 C. In detail, AP-HC still delivers a specific capacity of 285 mAh g⁻¹ after 230 cycles, which corresponds to a capacity retention of 96% (*vs.* 2nd cycle). Interestingly, the capacity is also about 50 mAh g⁻¹ higher than that delivered by A-HC.^{12,13}

AP-HC also shows a bit higher initial Coulombic efficiency (65.6%) than A-HC (61.2%). However, the irreversible capacity is still too high considering the rather low BET surface area and open porosity. This may indicate that the irreversible capacity is mostly related to processes occurring in the bulk of the material rather than at the surface, indicating that closed pores and impurities have a strong impact.

The AP-HC potential profile upon sodiation [Fig. 3(b)] is the one typical for hard carbons, exhibiting a slope between 2.00 V and 0.12 V (110 mAh g⁻¹) and a plateau between 0.12 V and 0.02 V (175 mAh g⁻¹). Interestingly, AP-HC delivers very similar capacities within the slope-like region [see Fig. 3(b)], suggesting that the surface area does not have any impact on the Na-storage capacity. However, it shows a much larger capacity within the plateau as compared to A-HC (108 mAh g⁻¹).¹³ Such a different electrochemical behavior at low potentials provides some insights into the sodium storage mechanism of hard carbons, which is still controversially discussed.^{20–23} In fact, the sodium storage along the plateau is commonly explained with charge accumulation in the hard carbon's porosity. AP-HC interestingly delivers much more capacity along the plateau than A-HC although it contains very little open porosity that is measurable by N₂ adsorption measurements. This indicates that close porosity plays a major role for the sodium storage in this region. The amount of closed pores and their characteristics (inner surface, shape, and size) as well as impact on the Na-storage mechanism deserves to be investigated in greater detail in future work.

Summarizing, we have synthesized a hard carbon from industrial bio-waste, *i.e.*, pectin-free apple pomace, via a very facile carbonization method. The hard carbon delivers excellent electrochemical performance with respect to the state-of-the-art despite being synthesized from very cheap and abundant waste.²⁴ Most importantly, the hard carbon exhibits a unique morphology and very interesting structural properties, resulting in high sodium storage capacity and good retention upon cycling. Finally, the investigations enlightened the role of closed porosity on the sodium storage mechanism.

See [supplementary material](#) for a detailed description of the experimental section.

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