

Innovative and Economically Beneficial Use of Corn and Corn Products in Electrochemical Energy Storage Applications

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Abstract: The United States is by far the largest corn producer worldwide with corn yields being steadily increasing for the past decades. In many Midwest states such as Iowa, Illinois, and Nebraska, corn farmers currently grow more corn than consumers can utilize as human food or animal feed. To sustain the economic viability of corn farmers, it is critical that new uses and markets for corn, corn by-products from harvesting, corn industrial products, and corn by-products from industrial processing should be discovered, giving the highest return to corn producers. With the increasing popularity of electric vehicles and grid-level energy storage systems for renewable energy, there has been an ever-growing interest in improving existing energy storage technologies as well as developing new ones. During this development, a great amount of effort has been focusing on exploiting cost-effective solutions utilizing sustainable materials derived from renewable biomass. In this article, innovative and economically beneficial uses of corn and corn products in various energy storage applications, such as lithium-ion batteries, solid-state batteries, and redox flow batteries, are comprehensively reviewed, which may shed light on how to establish an innovative and economically beneficial solution to support corn industry.

Introduction

Corn is currently the most produced crop species worldwide. The United States is by far the largest corn producer with corn yields being steadily increasing for the past decades. In many Midwest states such as Iowa, Illinois, and Nebraska, corn farmers currently grow more corn than consumers can utilize as human food or animal feed. To sustain the economic viability of corn farmers, it is critical that new uses and markets for corn, corn by-products from harvesting such as corn stover and corn cob, corn industrial products such as corn oil and corn starch, and corn by-products from industrial processing such as corn gluten feed and corn steep liquor be discovered, giving the highest return to corn producers. As portable electronic devices and electric vehicles are becoming more and more popular, there has been an ever-growing demand of improving existing energy storage technologies as well as developing new ones. In addition, as the issues associated with increased costs of fuels, pollution, and global warming are becoming more and more serious due to our dependence on fossil fuels, developing grid-level energy storage systems to tackle the sporadic property of renewable energy is an increasingly important goal. During this development, a great amount of effort has been focusing on exploiting cost-effective solutions utilizing sustainable materials derived from renewable biomass. In this article, innovative and economically beneficial uses of corn, corn by-products, and corn industrial products in various energy storage applications, such as lithium-ion batteries, solid-state batteries,

and redox flow batteries, are comprehensively reviewed, which may shed light on how to establish an environmentally sustainable, technically feasible, and economically beneficial solution to support corn industry.

Corn and Corn By-Products from Harvesting As the largest botanical riddle worldwide, corn currently has a global annual production of approximately 1.09 billion metric tons [1]. The United States currently produce over 345 million metric tons ever year, corresponding to 30% of the global production [1]. The leading states are Iowa, Illinois, and Nebraska [1]. The second largest corn-producing country is China, which generates 21% of the global corn production, followed by 8% from Brazil, 6% from the European Union, 4% from Argentina, 3% from Ukraine, 2% from India, 2% from and Mexico [2]. Owing to its high yield, dent corn, also known as field corn, is the prevailing variety of corn grown across the globe. A grain of dent corn consists of about 74% starch, 9% protein, 7% fiber, 5% oil, and 10% water [2]. In the United States, approximately 50% of the produced corn is used as livestock feed, 40% is used for either human food or industrial products, and 10% is exported [2].

As shown in Figure 1, the corn kernel consists of three main parts, i.e., pericarp, endosperm, and germ. The endosperm consists of starch for energy storage and protein for germination. The pericarp is the outer covering, protecting the kernel against insects and microorganisms as well as preserving the nutrients inside. Germ is the living organism in the kernel, where genetic information, enzymes, vitamins, and minerals are kept. The kernel is attached to the cob via the tip cap, where water and nutrients flow through. The tip cap is not covered by the pericarp.

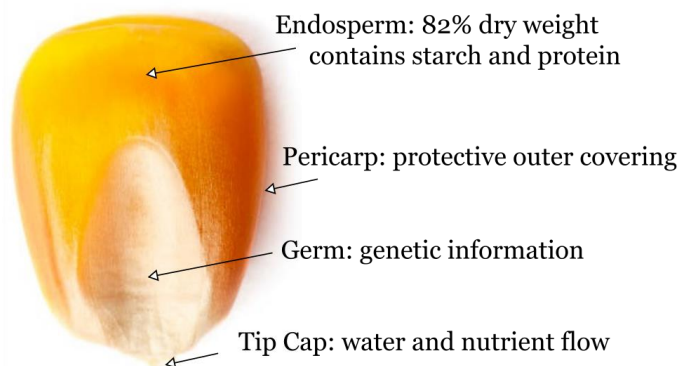


Figure 1. The corn kernel consists of three main parts, i.e., pericarp, endosperm, and germ.

During corn harvesting, significant amounts of by-products are generated, including corn stover and corn cob. Corn stover, also called corn straw, refers to the aboveground plant materials left in the fields after grain harvesting. It includes multiple components, such as stalk, leaves, sheaths, husks, shanks, tassels, lower ears, and silks [3]. Corn stover yields can be estimated based on corn grain yields and the stover mass to grain mass ratio. Since the dry weight harvest index of corn is typically close to one half, the ratio of corn grain to corn stover is approximately one, indicating that every year approximately one billion metric tons corn stover is produced globally [4]. Corn stover has been identified as the most abundant and renewable biomass resource in the United States due to several reasons: the quantity of feedstock is large, the feedstock is fairly uniform, and large quantities are focused on certain regions [5]. As a lignocellulosic biomass, it contains approximately 35% cellulose, 20% hemicellulose, and 12% lignin [2]. In the United States, the majority is harvested and used as animal feed, with a small segment left in the fields to improve soil properties [6]. In China, the current handling approaches involve burning corn stover or disposing of them in landfills [7]. These practices do not make efficient use of this

valuable biomass resource. Even worse, they bring about many environmental issues such as severe air pollution and release of carbon dioxide.

Corn cob refers to the stiff cylindrical core that bears the kernel, constituting one-fifth of the total corn residues [6]. Corn cob contains approximately 70% cellulose, 22% hemicellulose, and 8% lignin [8]. Compared with corn stover, corn cob contains much more cellulose content but much less lignin content. Similar to corn stover, corn cob has been mainly used as animal feed.

It can be concluded that corn and corn by-products from harvesting, such as corn stover and corn cob, are mostly used as human food and animal feed. Value-added applications without pollution or carbon dioxide emission are urgently needed to sustain the corn industry, benefit the rural communities, and preserve the environment.

Corn Industrial Products and Corn By-Products from Industrial Processing The major corn industrial products include corn starch, corn oil, and corn ethanol. As illustrated in Figure 2, there are two different processes for corn processing, i.e., wet milling and dry milling. The details of the two processes are provided by Zhang et al. [2] and Rausch and Belyea [9]. The wet milling process produces corn starch and corn oil, whereas corn ethanol is the primary product of the dry milling process. Each process also generates multiple by-products.

Corn starch predominantly contains two main polysaccharides, i.e., amylopectin with a highly branched, open structure and a very small amount of amylose with an essentially linear, coiled structure [10, 11, 12]. Besides corn starch, the wet milling process generates multiple by-products [13]. Corn steep liquor is known officially as condensed fermented corn extractives. It is a viscous concentrate of corn solubles obtained from the steeping process. Its protein content is 25% on a 50% solids basis [14]. Corn germ meal is ground corn germ, from which most of the solubles have been removed by steeping and most of the oil has been extracted. It contains about 20% to 23% protein and is mainly used as animal feed [15]. Corn gluten feed usually has a dry matter of 88%, which consists of 21% protein, 2% oil, and 10% fiber, minerals, and amino acids [16]. Corn gluten meal contains about 65% protein, and thus it is used for animal feed and zein production [17].

More than one-third of the total annual corn production is used for ethanol production in the United States [2], approximately 90% of which is dry milled. Similar to wet milling, dry milling is also a multistep process, but dry milling is simpler and produces fewer by-products. Condensed distillers solubles, also known in the industry as corn syrup, contains approximately 30% dry matter and is mainly used as animal feed. It can also be combined with the residual solids and dried to become corn distillers dried grains with solubles, which contains remarkable amounts of protein, lipid, and fiber. It is also an important source of minerals, vitamins, and amino acids.

As corn grains usually contain 7% to 11% protein, zein, a commercially available corn protein extracted from distillers dried grains with solubles, has a protein content of at least 90% [18]. Zein is the alcohol-soluble protein of corn and is classified as a prolamin. The zein protein can be categorized as 50% hydrophobic amino acids, supplying nitrogen for the growth of the kernels. Zein consists of a high α -helix content with β -sheet fractions [19]. Its unique molecular structure with amphiphilic characteristics and its self-assembly into two-dimensional periodic patterns can explain zein's ability to form ordered film structures by itself [20].

During the past decade, in our attempts to develop high-performance and cost-effective energy storage technologies, extensive investigation has been conducted focusing on how to utilize sustainable materials derived from renewable biomass. It has been found that corn, corn by-products from harvesting such as corn stover and corn cob, corn industrial products such as corn oil and corn starch, and corn by-products from industrial processing such as corn gluten feed and corn steep liquor exhibit fascinating applications in various energy storage technologies. In this article, 15 representative cases are reviewed in great details, as listed in Table 1.

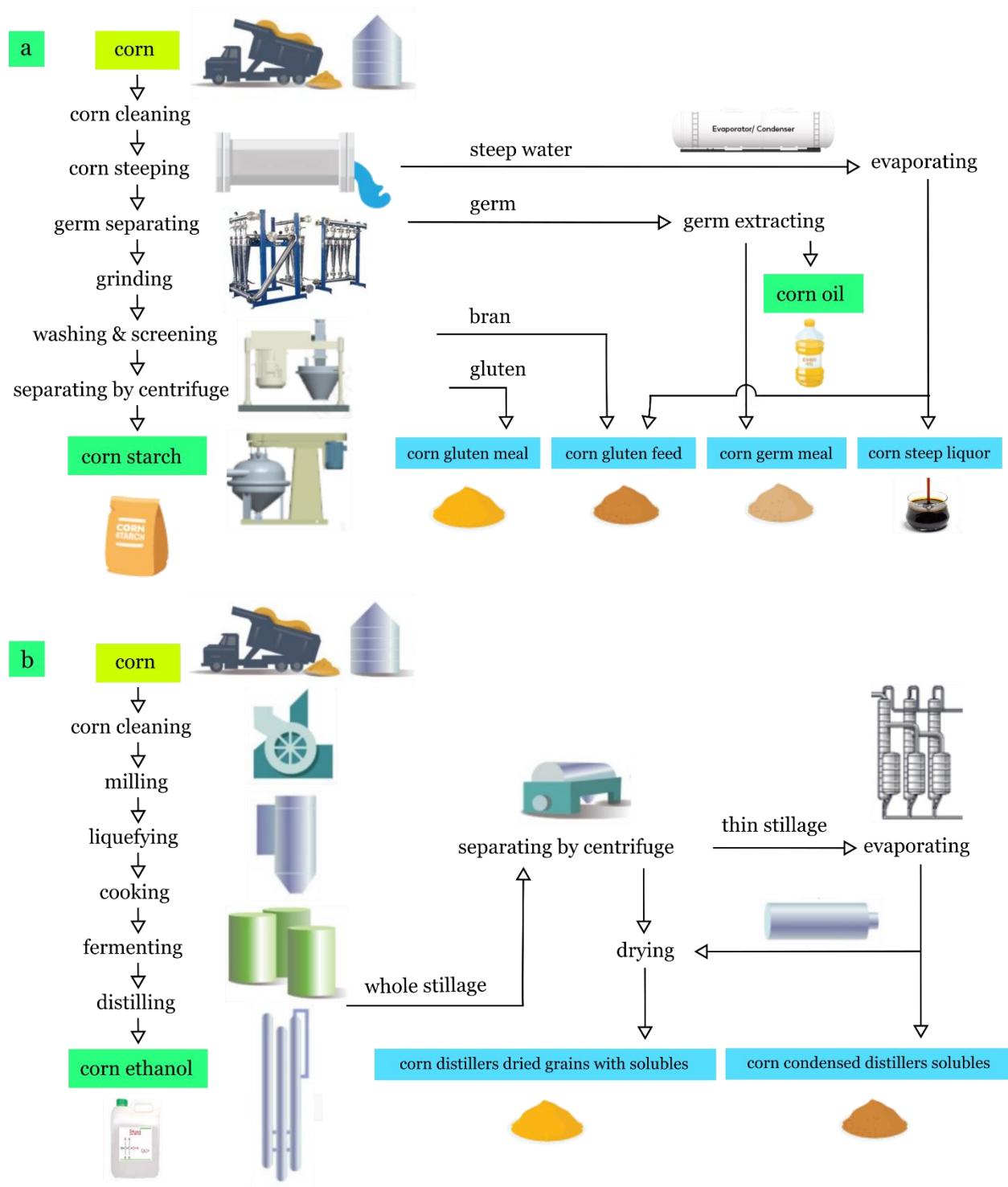


Figure 2. Corn milling processes include (a) the wet milling process and (b) the dry milling process.

Table 1. In this article, 15 representative cases of economically beneficial uses of corn and corn products in energy storage applications are reviewed in detail.

Biomass	Application	References	Year
Corn Stalk	Anode in Lithium-Ion Batteries	[7]	2015

Corn Starch	Anode in Lithium-Ion Batteries	[21]	2015
Corn Stover	Porous Electrode in Supercapacitors	[22]	2020
Corn Gluten Meal	Porous Electrode in Supercapacitors	[23]	2017
Corn Husks	Porous Electrode in Supercapacitors	[24]	2020
Corn Starch	Host Matrix for High-Capacity Electrodes in Lithium-Ion Batteries	[25]	2019
Corn Starch	Host Matrix for High-Capacity Electrodes in Lithium-Ion Batteries	[26]	2020
Corn Stover	Host Matrix for High-Capacity Electrodes in Lithium-Ion Batteries	[27]	2020
Corn Cob	Binder in Lithium-Ion Batteries	[28]	2019
Corn Starch	Binder in Lithium-Ion Batteries	[29]	2018
Corn Starch	Binder in Lithium-Ion Batteries	[30]	2016
Corn Starch	Solid Polymer Electrolyte in Solid-State Batteries	[31]	2016
Corn Steep Liquor	Cathode in Sodium-Ion Batteries	[32]	2017
Corn Starch	Anode in Zinc Batteries	[33]	2020
Corn Protein Zein	Electrocatalyst in Redox Flow Batteries	[34]	2014

Corn-Mediated Carbonaceous Materials as Anodes in Lithium-Ion Batteries

Graphite is the anode material used in most commercialized lithium-ion batteries, but graphite mining in the United States has long stagnated, i.e., it has not been mined since 1990, when the operation was suspended in Montana [35]. China is currently the top producer of graphite. From 2015 to 2016, the total global graphite production was about 2.5 million tons, and 66% was from China, 14% from India, 7% from Brazil, 3% from Turkey, and 3% from Canada [36]. Moreover, with increasing demand for lithium-ion batteries, graphite will soon encounter depletion of resources. Consequently, the price of raw materials for producing graphitic anodes such as petroleum coke, needle coke, and coal tar pitch has increased sharply [37]. Most importantly, graphite delivers an inferior theoretical capacity of 372 mAh/g, critically limiting the energy density of lithium-ion batteries [38]. To address this issue, many newly developed nano-structured materials, such as carbon nanofibers, carbon nanowires, and graphene, etc., have been studied as anode materials [39]. The use of nano-structured materials renders higher capacity and rate performance, but the high costs of the carbon precursors as well as the complex manufacturing processes limit their massive production.

Therefore, carbonaceous materials derived from naturally abundant renewable biomass that can still display a sufficient electrochemical performance have attracted a significant amount of attention in the past few years [40]. For example, Jiang et al. converted bamboo chopsticks waste into carbon nanofibers, which demonstrated a comparable performance to commercially available graphite electrodes [37]. Zhou et al. synthesized carbon nanosheets utilizing wheat stalk as the precursor, and the carbon nanosheets showed excellent rate capability as anode material [38]. Ru et al. found that porous carbon prepared from microalgae demonstrated excellent electrochemical performance as anode material, mainly due to its hierarchical porosity and microcrystalline graphitic carbon domains [41]. Nano-structured carbonaceous materials derived from coconut oil [42], spongy pomelo peels [43], duckweed [44], waste avocado seeds [45], cherry stones [46], apple biowaste [47], mushrooms [48], tea leaves [49], pinecone hull [50], and cotton wool [51] have also been used as anode materials and demonstrated superior electrochemical performance. Some representative cases are summarized in Table 2. Utilizing corn, corn by-products, and corn industrial products to produce nano-structured carbonaceous materials as anodes have been proposed as well [7, 21, 52, 53, 54, 55]. Some representative cases are summarized in Table 3. In this section, two representative cases are reviewed in detail.

Table 2. Recent studies on using low-cost biomass as anode material of lithium-ion batteries.

Biomass	Synthesis	Electrode Parameters	Battery Performance	Reference
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Cattle bone	Pyrolysis at 600°C to 1200°C for 2 h	Mass ratio of active material, polyvinylidene difluoride, and acetylene black: 75:15:15 Mass loading of the active material: 0.8 to 1.0 mg/cm ²	Rate capacity: 1230, 951, 682, 491, 343, and 281 mAh/g at 1, 2, 5, 10, 20, and 30 A/g Cyclability: 1488 mAh/g after 250 cycles at 1 A/g, and 661 mAh/g after 1500 cycles at 10 A/g Initial Coulombic efficiency: 79%	[56] Nano Energy, 2017, 36, 322.
Wheat straw	HCl pretreatment before KOH activation, then pyrolysis at 700°C for 1 h	Mass ratio of active material, polyvinylidene difluoride, and acetylene black: 80:10:10 Mass loading of the active material: 0.64 mg/cm ²	Rate capacity: 1470 mAh/g at 37 mA/g and 344 mAh/g at 18.5 A/g Cyclability: 976 mAh/g at 0.37 A/g and 659 mAh/g at 3.7 A/g, respectively, after 300 cycles Initial Coulombic efficiency: 64%	[57] J. Mater. Chem. A, 2014, 2, 9684.
Rice husks	Formic acid pretreatment, pyrolysis at 900°C for 4 h, and then using NH ₄ HF ₂ for SiO ₂ removal	Mass ratio of active material, polyvinylidene difluoride, and acetylene black: 80:10:10 Mass loading of the active material: no information	Rate capacity: 218, 199, 164, and 137 mAh/g at 0.375, 0.75, 1.875, and 3.75 A/g Cyclability: 403 mAh/g after 100 cycles Initial Coulombic efficiency: 50%	[58] J. Mater. Chem. A, 2013, 1 5269-5273.
Apple and celery	Pyrolysis at 500°C for 3 h	Mass ratio of active material, polyvinylidene difluoride, and acetylene black: 80:10:10 Mass loading of the active material: 0.64 to 0.8 mg/cm ²	Rate capacity: 1600, 1470, 1260, 1070 and 1000 mAh/g at 0.074, 0.185, 0.37, 0.74 and 1.11 A/g Cyclability: 1050 mAh/g at 0.1 A/g after 200 cycles Initial Coulombic efficiency: 73%	[59] Sustainable Energy Fuels, 2018, 2, 2358.
Medium-density fiberboard	Impregnation with FeCl ₃ , then pyrolysis at 500°C for 30 min, and then at 800°C to 2000°C for 30 min	Mass ratio of active material, sodium carboxymethyl cellulose, and acetylene black: 90:5:5 Mass loading of the active material: 2.0 to 2.5 mg/cm ²	Rate capacity: 307 mAh/g at 0.1C Cyclability: capacity retention higher than 90% after 200 cycles Initial Coulombic efficiency: 64%	[60] ChemSusChem, 2018, 11, 2776.
Egg white	Dissolved in (NH ₄) ₂ SO ₄ , pyrolysis at 650°C to 850°C for 2 h, and then using HF for SiO ₂ removal	Mass ratio of active material, polyvinylidene difluoride, and acetylene black: 80:10:10 Mass loading of the active material: 0.8 mg/cm ²	Rate capacity: 205 mAh/g at 4 A/g Cyclability: capacity retention higher than 70% after 100 cycles Initial Coulombic efficiency: 65%	[61] Energy Environ. Sci., 2013, 6, 871-878.

Table 3. Recent studies on using corn products to produce anodes of lithium-ion batteries.

Biomass	Synthesis	Electrode Parameters	Battery Performance	References
Corn stalk	Hydrolyzed under the condition of sulfuric acid, boiled with NaOH, and then carbonized at 600°C under argon atmosphere	Mass ratio of active material, polyvinylidene difluoride, and acetylene black: 80:10:10	Rate capacity: 590, 420, 390, 300, and 240 mAh/g at 0.2C, 0.5C, 1C, 2C, and 5C Cyclability: 577 mAh/g at 0.2C after 100 cycles Initial Coulombic efficiency: 53%	[52] Nanomaterials, 2019, 9, 93. [53] Materials Chemistry and Physics, 2020, 243, 122644.

		Mass loading of the active material: 0.1 mg/cm ²		
Corn stalk	Hydrothermal treatment in KOH and then chemically activated with KOH at 800°C under nitrogen atmosphere	Mass ratio of active material and polyvinylidene difluoride: 90:10 Mass loading of the active material: 3.0 mg/cm ²	Rate capacity: 578, 553, 527, 508, 474, and 454 mAh/g at 0.1, 0.3, 0.6, 1, 2, and 3 A/g Cyclability: 481 mAh/g at 2 A/g after 400 cycles Initial Coulombic efficiency: 76%	[7] Journal of Materials Chemistry A, 2015, 3, 6742-6746.
Corn starch	Enzymolysis, pre-oxidation, and then carbonization at 300°C under nitrogen atmosphere	Mass ratio of active material, polyvinylidene difluoride, and acetylene black: 80:10:10 Mass loading of the active material: no information	Rate capacity: 400, 340, 305, 280, 245, and 150 mAh/g at 0.2, 0.5, 1, 2, 5, and 20 A/g Cyclability: 507 mAh/g at 0.1 A/g after 100 cycles Initial Coulombic efficiency: 66%	[21] Nanoscale, 2015, 7, 1791-1795.
Corn stalk	Pyrolysis with CaCl ₂ at 300°C for 3 h, and then activated by further heating at 600°C for 1 h	Mass ratio of active material, polyvinylidene difluoride, and acetylene black: 80:10:10 Mass loading of the active material: 0.7 mg/cm ²	Rate capacity: 1862.1 mAh/g at 0.2C of discharge Cyclability: 783.8 mAh/g at 0.2C after 100 cycles Initial Coulombic efficiency: 60%	[62] RSC Adv., 2018, 8, 12666.

Wang et al. proposed a simple method to convert corn stalk into a porous carbon hybrid of nanofibers and nanosheets to be used as anodes [7]. As shown in Figure 3(a), hydrothermal treatment is performed for recycled corn stalk in potassium hydroxide solution to remove lignin. The remaining cellulose is then activated by residual potassium hydroxide at 800°C, producing a mixture of nanofibers and nanosheets. As shown in Figure 3(b) to Figure 3(e), the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) observation confirms that the mixture consists of both nanofibers and nanosheets. The result presented in Figure 3(f) and Figure 3(g) shows that the carbon matrix is a mixture of amorphous and polycrystalline carbon. As shown in Figure 3(h), this hybrid material shows an excellent rate capability. As schematically illustrated in Figure 3(i), the hierarchical porosity produces a large electrode/electrolyte interface and smooth diffusion pathways for fast transport of lithium ions. It also contains many defects, facilitating the storage of lithium ions.

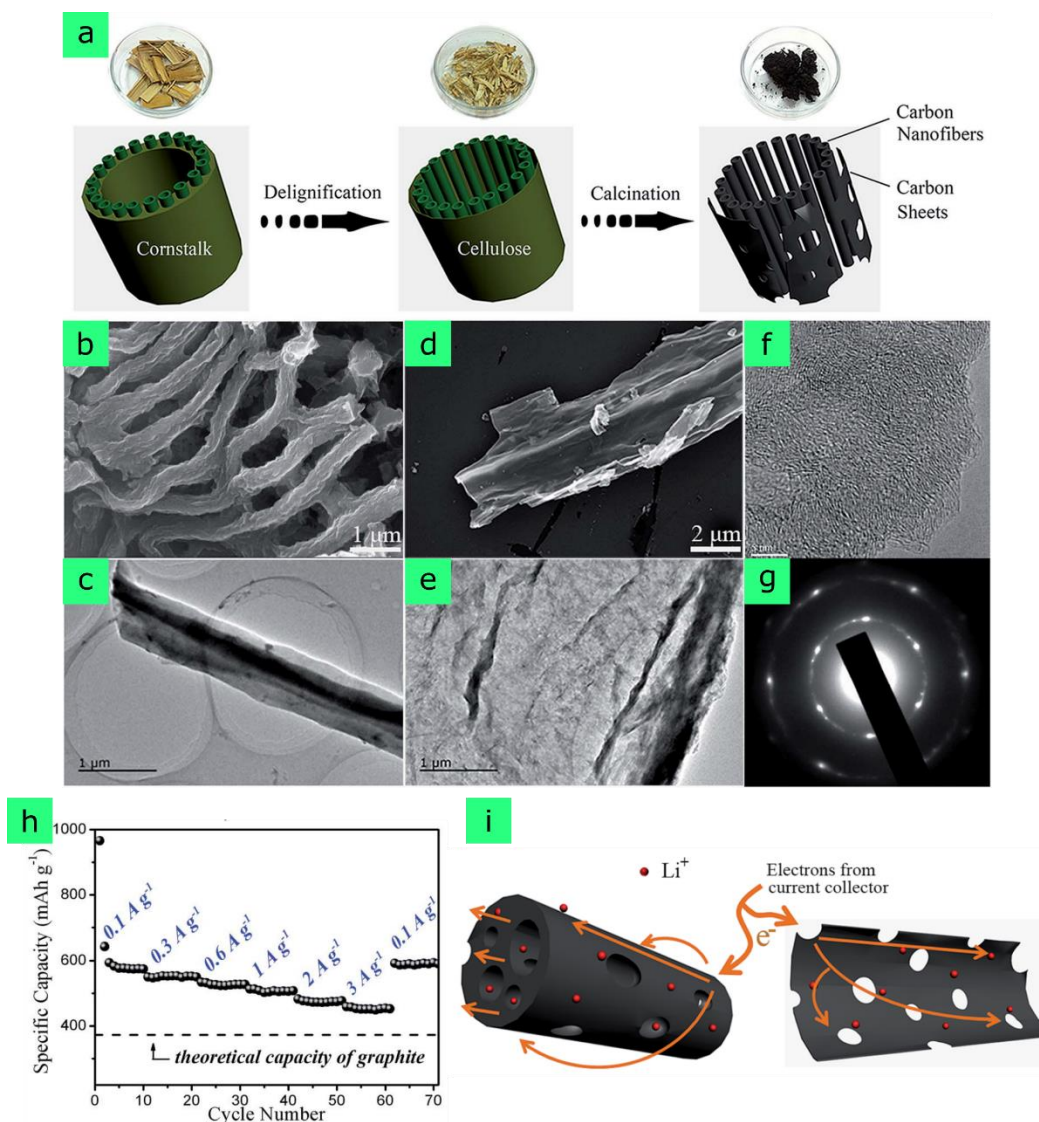


Figure 3. (a) The evolution from corn stalk to carbon nanofibers/nanosheets. (b) and (c) SEM and TEM images of the carbon nanofibers. (d) and (e) SEM and TEM images of the carbon nanosheets. (f) and (g) TEM results of the carbon hybrid of nanofibers and nanosheets. (h) Rate performance of the nanofibers/nanosheets hybrid samples. (i) Schematic illustration of the hierarchical porosity, electronic conducting phase, and lithium ion storage in the nanofibers/nanosheets hybrid samples. Adapted with permission from [7]. Copyright 2015, the Royal Society of Chemistry.

Chen et al. synthesized porous carbon microspheres with rich porosity using corn starch by a multistep process [21]. Corn starch, as shown in Figure 4(a) and Figure 4(b), is dissolved in sodium hydrogen phosphate and citric acid buffer solution to make the first solution, and α -amylase is dissolved in the same buffer solution to make the second solution. The two solutions are then mixed, filtered, separated, and dried at 50°C to make porous starch, as shown in Figure 4(c) and Figure 4(d). The porous starch is pre-oxidized at 180°C in oven, heated to 300°C under a nitrogen flow, kept at 300°C for one hour, heated from 300°C to various temperatures at 5°C/min, and kept at the final temperature for three hours, producing porous carbon microspheres, as shown in Figure 4(e) and Figure 4(f). This fabrication process can be easily scaled up. As shown in Figure 4(g) to Figure 4(i), the microsphere anodes exhibit a high reversible

capacity and excellent cyclability. The rich porosity allows for both ultrafast diffusion of electrolyte and smooth transport of lithium ions.

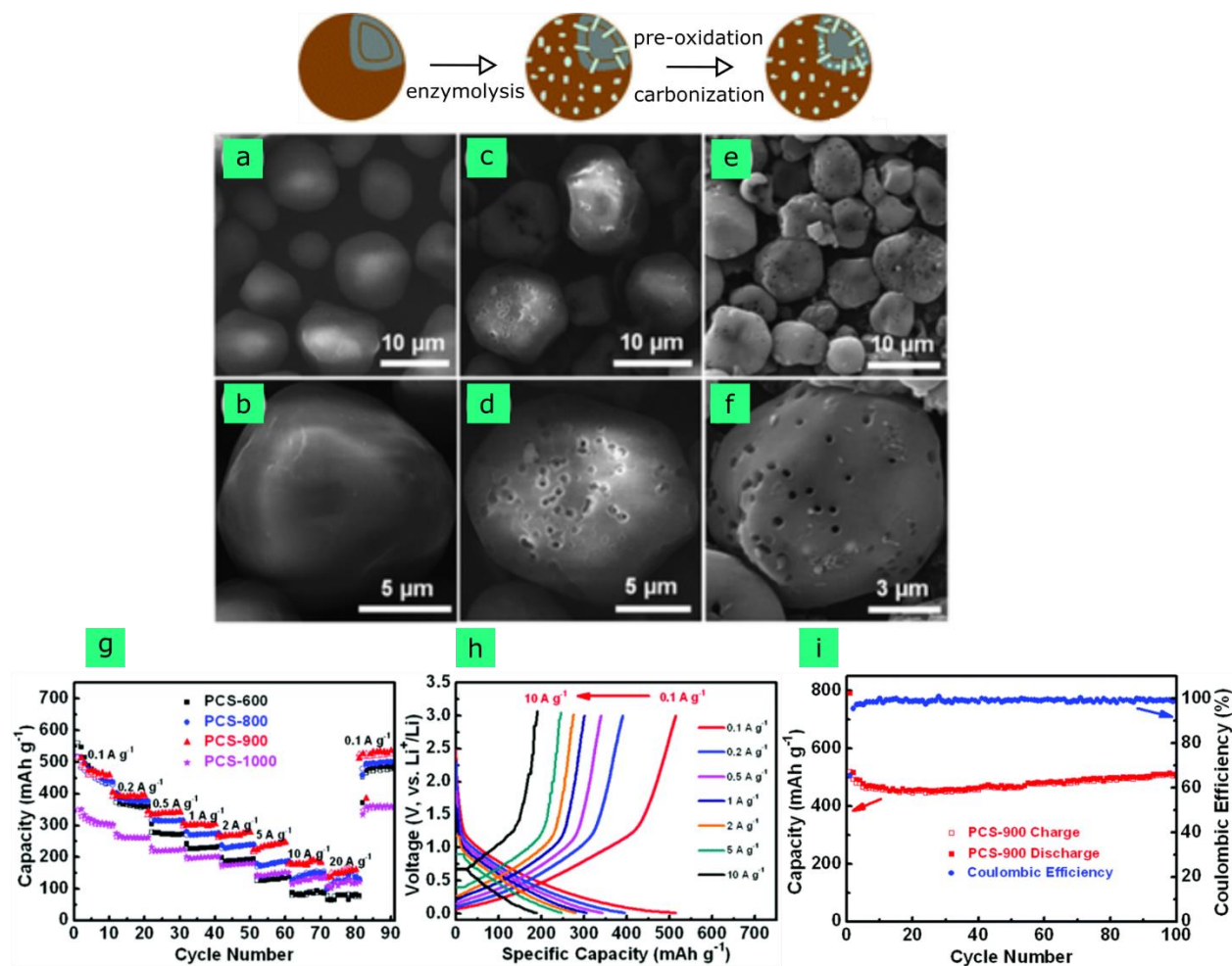


Figure 4. (a) and (b) SEM images of the corn starch. (c) and (d) SEM images of the porous starch. (e) and (f) SEM images of the porous carbon spheres. (g) Rate capabilities of the porous carbon spheres. (h) Charge/discharge curves of the sample fabricated at the carbonization temperature of 900°C. (i) Cycling performance of the sample fabricated at the carbonization temperature of 900°C at 0.1 A/g between 0.01 V and 3.0 V. Adapted with permission from [21]. Copyright 2015, the Royal Society of Chemistry.

In summary, the corn wastes and products can be carbonized to synthesize anodes for lithium-ion batteries. The biochar typically needs chemical modification, such as activated by potassium hydroxide, to increase surface area and enhance electrochemical properties. It is worthy to note that these biomass-derived nano-structured anodes have a slightly higher lithiation and delithiation electrochemical potential than graphite anodes. While it is beneficial to alleviate lithium plating to some extent, it will slightly reduce the operating voltage of full cells. Thus, the capacity needs to be higher to offset their higher electrochemical potential and maintain same energy density as graphite anodes. In addition, when using biomass-derived nano-structured anodes, the initial irreversible capacity loss also rises because of their higher surface area, originating from the decomposition of the electrolyte to produce both a solid electrolyte interphase (SEI) layer and gaseous products on the carbonaceous electrode during the initial charging/discharging processes [63]. Therefore, surface area, morphology, and structure of the

biomass-derived nano-structured anodes need to be optimized to achieve the best performance at high charging/discharging rates, which can be done by adjusting the carbonization process, such as temperature and atmosphere. Adjusting the process parameters leads to different properties of the resulting material, catering to various specific battery requirements.

Corn-Mediated Carbonaceous Materials as Porous Electrodes in Supercapacitors

Supercapacitor is a unique ultra-high capacitance device that is governed by the same working principle as conventional capacitors but utilizes electrodes with larger surface area and thinner dielectrics. There are three types of supercapacitors, i.e., electrochemical double-layer capacitors, pseudocapacitors, and hybrid capacitors [64]. Electrochemical double-layer capacitors store charges electrostatically, as there is no actual charge transfer between electrolyte and electrode. Electrodes of pseudocapacitors are normally based on functionalized porous carbons, conducting polymers, and metal oxides, which possess much higher specific capacitance than electrochemical double-layer capacitors, with the charge storage mechanism utilizing fast redox reactions taking place on the electrode surface, not in the bulk as in the case of batteries [65]. Relying on both faradaic and non-faradaic processes to store charges, hybrid capacitors have demonstrated energy and power densities greater than electrochemical double-layer capacitors without compromising cycling stability and affordability that have hampered the development of pseudocapacitors.

While a wide range of materials can be utilized as supercapacitor electrodes, porous carbon materials enjoy a place of pride mainly due to higher surface area, lower cost, higher chemical stability, and better electronic conductivity than other materials such as conducting polymers and metal oxides [66, 67, 68]. In the past few years, porous carbon materials derived from low-cost renewable biomass, such as seaweed [69], banana stems [70], sugar cane bagasse [71], bamboo stems [72], coffee beans [73], pistachio shells [74], silk cocoons [75], and human hair [76], have been shown to be excellent candidates as supercapacitor electrodes. Some representative cases are summarized in Table 4. Many innovative uses of corn and corn products to produce porous carbon materials as electrodes in the three types of supercapacitors have been proposed as well [77, 78, 79, 80, 24, 23, 81, 82, 83, 84]. Some representative cases are summarized in Table 5. In this section, three representative cases are reviewed in detail.

Table 4. Recent studies on using low-cost biomass as porous electrodes of supercapacitors.

Biomass	Synthesis	Surface Area	Electrolyte	Performance	References
Bamboo stems	Hydrothermal treatment at 200°C for 12 h and then activated with KOH at 800°C for 1 h	1472 m ² /g	KOH (6 M)	Specific capacitance: 301 F/g and 193 F/g at 0.1 A/g and 100 A/g, respectively	[85] J. Mater. Chem. A, 2015, 3, 5656–5664.
Hemp stems	Pyrolysis at 600°C for 2 h, activated at 800°C with steam for 2 h, and then loading with MnO ₂	438 m ² /g	Na ₂ SO ₄ (1 M)	Specific capacitance: 340 F/g at 1.0 A/g	[86] Langmuir, 2017, 33, 5140–5147.
Watermelon	Hydrothermal treatment at 180°C for 12 h, then activated with FeCl ₃ and FeSO ₄ at 550°C for 4 h	No information	KOH (6 M)	Specific capacitance: 358 F/g at 0.5 A/g	[87] ACS Nano, 2013, 7, 3589–3597.
Soybean roots	Pyrolysis at 500°C for 2 h and then activated with KOH at 800°C for 2 h	2143 m ² /g	KOH (6 M)	Specific capacitance: 276 F/g at 0.5 A/g	[88] ACS Appl. Mater. Interfaces, 2016, 8, 33626–33634.
Almond shells	Pyrolysis at 700°C to 900°C for 4 h and then	1363 m ² /g	KOH (6 M)	Specific capacitance: 286 F/g at 1.0 A/g	[89] ACS

	activated with KOH at 800°C for 2 h				Appl. Mater. Interfaces, 2016, 8, 15288-15296.
Sawdust	Pyrolysis with FeCl ₃ at 800°C for 1 h	421 m ² /g	K ₂ SO ₄ (0.5 M)	Specific capacitance: 128 F/g at 0.5 A/g	[90] Environ. Sci. Technol., 2014, 48, 13951-13959.

Table 5. Recent studies on using corn products to produce porous electrodes of supercapacitors.

Biomass	Synthesis	Surface Area	Electrolyte	Performance	References
Corn cob	Hydrothermal treatment at 180°C for 16 h and secondary low-temperature heat treatment from 100°C to 300°C for 5 h under air conditions	1024.8 m ² /g	H ₂ SO ₄ (1 M)	Specific capacitance: 289 F/g at 0.09 A/g	[81] J. Wood Chem. Tech., 2019, 39, 343-359.
Corn stover	Hydrothermal treatment with KOH and then put into a microwave reactor heated at 1000 W and 2450 MHz for 40 to 100 min	1781 m ² /g	TEABF ₄ /PC (1 M)	Specific capacitance: 98 F/g at 1.0 A/g	[22] ACS Omega, 2020, 5, 26084-26093.
Corn gluten meal	Fast pyrolysis at 300°C to 500°C and then activated with KOH at 600°C to 900°C for 1 h	3353 m ² /g	KOH (6 M)	Specific capacitance: 488 F/g at 0.5 A/g	[23] Sustainable Energy Fuels, 2017, 1, 891-898.
Corn husks	Carbonized at 1000°C under argon atmosphere for 1 h and then activated with KOH at 600°C to 800°C for 2 h	1378 m ² /g	KOH (6 M) and TEABF ₄ /AN (1 M)	Specific capacitance: 127 F/g at 1.0 A/g in organic electrolyte and 80 F/g at 1.0 A/g in KOH electrolyte	[24] J. Power Sources, 2020, 471, 228387.
Corn silks	Refluxing with KOH at 80°C for 4 h and pyrolysis at 900°C for 1 h	2285 m ² /g	TEABF ₄ /PC (1 M)	Specific capacitance: 160 F/g at 1.0 A/g	[91] J. Electrochem. Soc., 2018, 165, A3369

Liu et al. proposed a microwave-aided hydrothermal activation method to fabricate supercapacitor electrode materials using corn stover with the presence of potassium-based catalyst [22]. Dried corn stover and potassium hydroxide powders in a weight ratio of 2:1 are put in a hydrothermal tank and mixed with deionized water, as shown in Figure 5(a). The reaction tank is put into a microwave reactor, heated at 1000 W and 2450 MHz, and held for 40 min, 70 min, and 100 min, respectively. With the radiation time increasing from 40 min to 100 min, the hydrochar becomes more porous with the pores swelling from micropores to hierarchical pores, as shown in Figure 5(b) to Figure 5(d), and the microstructure changes from amorphous to graphene-like, as shown in Figure 5(e) to Figure 5(g). Microwave irradiation not only accelerates the hydrolysis, facilitating strong depolymerization and reorganization of the carbon framework, but also promotes the movement of the potassium catalyst between the carbon layers to display a graphitization effect. The sample made with the longest radiation time of 100 min has very large surface area and highly ordered microstructure, demonstrating the best electrochemical performance. The rich porosity and the high graphitization extent are extremely helpful for the transmission of ions and electrons in the electrolyte.

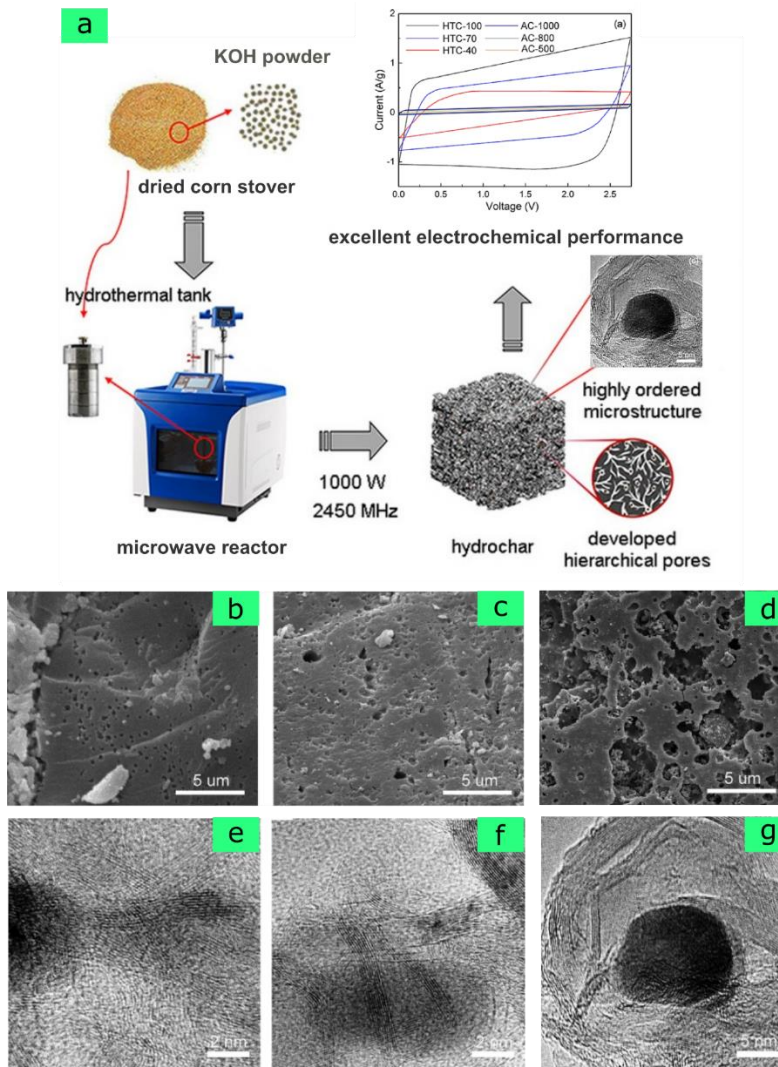


Figure 5. (a) The evolution of corn stover into hydrochar samples. (b) to (d) SEM image of the hydrochar sample made with a radiation time of 40 min, 70min, and 100 min, respectively. (e) to (g) TEM image of the hydrochar sample made with radiation time of 40 min, 70min, and 100 min, respectively. Adapted with permission from [22]. Copyright 2020, American Chemical Society.

Cheng et al. prepared porous carbonaceous materials using corn gluten meal. The resulting porous carbonaceous materials demonstrated excellent capacitance performance [23], showing that fast pyrolysis combined with chemical activation by potassium hydroxide could be a very promising technique for industrial production of supercapacitor electrodes from renewable biomass. As introduced in the first section, corn gluten meal, one of the by-products from the wet milling process, contains about 65% protein and has historically been used as livestock feed. As shown in Figure 6(a), after fast pyrolysis, 60% to 75% of the feedstock is converted into pyrolysis oil. The obtained biochar has plenty of oxygenated functional groups and thus can be used as raw materials to make supercapacitors electrodes with the functionalities acting to significantly improve the pseudocapacitance performance. Compared with the hydrothermal carbonization method, fast pyrolysis can be completed within a very short amount of time. As shown in Figure 6(b), the specific capacitance of the porous carbonaceous materials obtained at fast pyrolysis temperature of 500°C is the best. This excellent performance mainly results from the large surface area and rich porosity, as shown in Figure 6(c) to Figure 6(g). As shown in Figure 6(h), the TEM

result reveals a highly disordered porous carbon structure without graphite ribbons or crystalline impurities.

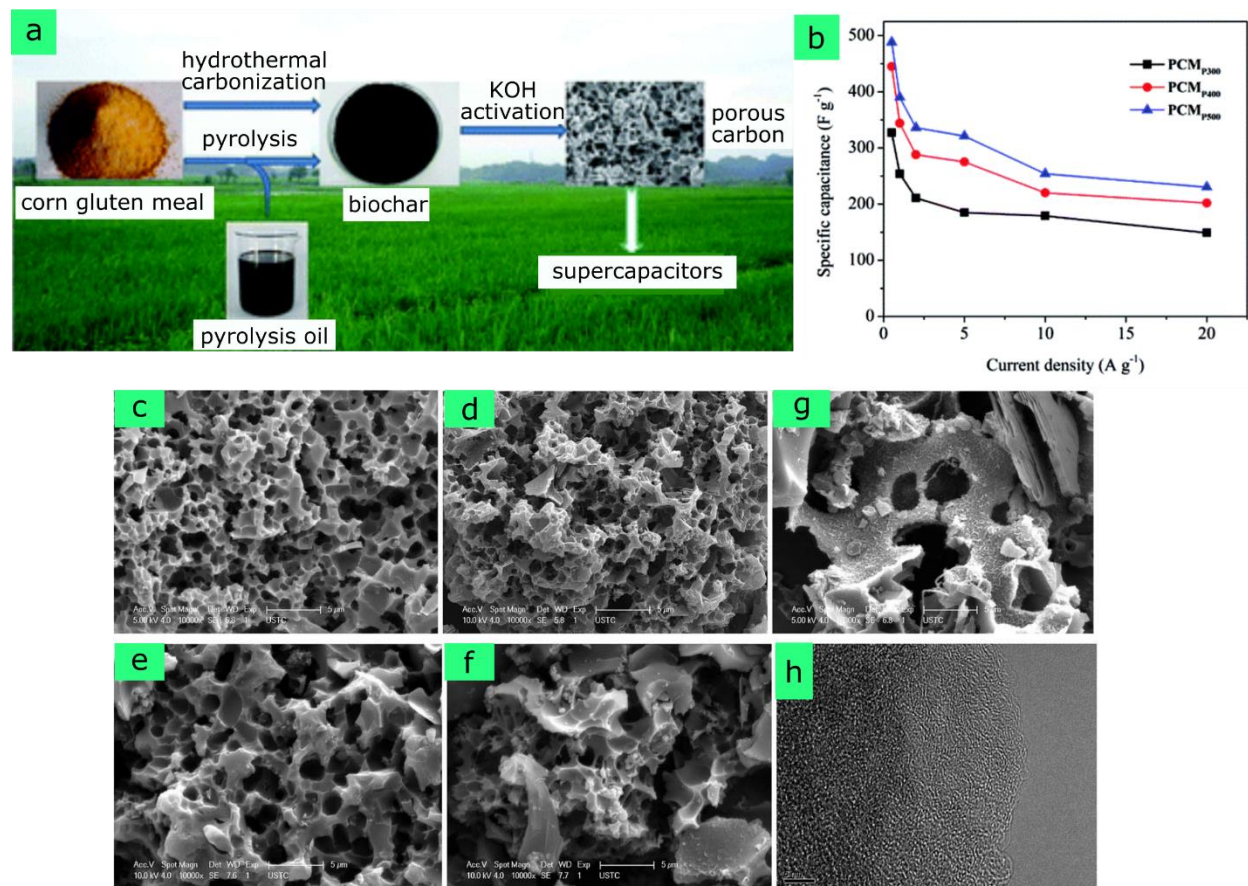


Figure 6. (a) The evolution of corn gluten meal into porous carbonaceous materials. (b) Specific capacitance of the samples. (c) to (g) SEM images of the porous carbonaceous materials. (h) TEM image of the porous carbonaceous materials. Adapted with permission from [23]. Copyright 2017, the Royal Society of Chemistry.

Rani et al. used corn husks to synthesize porous carbonaceous materials, which demonstrated great potential as electrodes for high operating voltage supercapacitors [24]. As shown in Figure 7(a), dried corn husks are first carbonized under an argon atmosphere at 1000°C for one hour, and the resultant carbon is then activated using potassium hydroxide. The morphology of dried corn husks, which possess lamellar structure as shown in Figure 7(b) and Figure 7(c), separates into layers after activation because of the exfoliating function of potassium hydroxide in addition to generating the porous network. The morphology of corn husks after carbonization, as shown in Figure 7(d) to Figure 7(f), resembles that of dried corn husks with white silica particles on its surface. These particles are detached during the activation process, which creates extra porosity. The porous structure is shown in Figure 7(g) to Figure 7(i). Figure 7(j) and Figure 7(k) show the TEM results of the morphology of non-activated carbon. The black particulates shown in Figure 7(j) correspond to the silica particles. As shown in the TEM images of activated carbon presented in Figure 7(l) and Figure 7(m), potassium hydroxide penetrates the layered structure during the activation process and separates it into layers as well as creates porosity. The electron mobility increases in the layers, helping improve its electrochemical performance. As shown in Figure 7(n) to Figure 7(s), when used as supercapacitor electrode, it shows excellent performance in both

potassium hydroxide electrolyte and organic electrolyte. It also demonstrates very good cyclic stability.

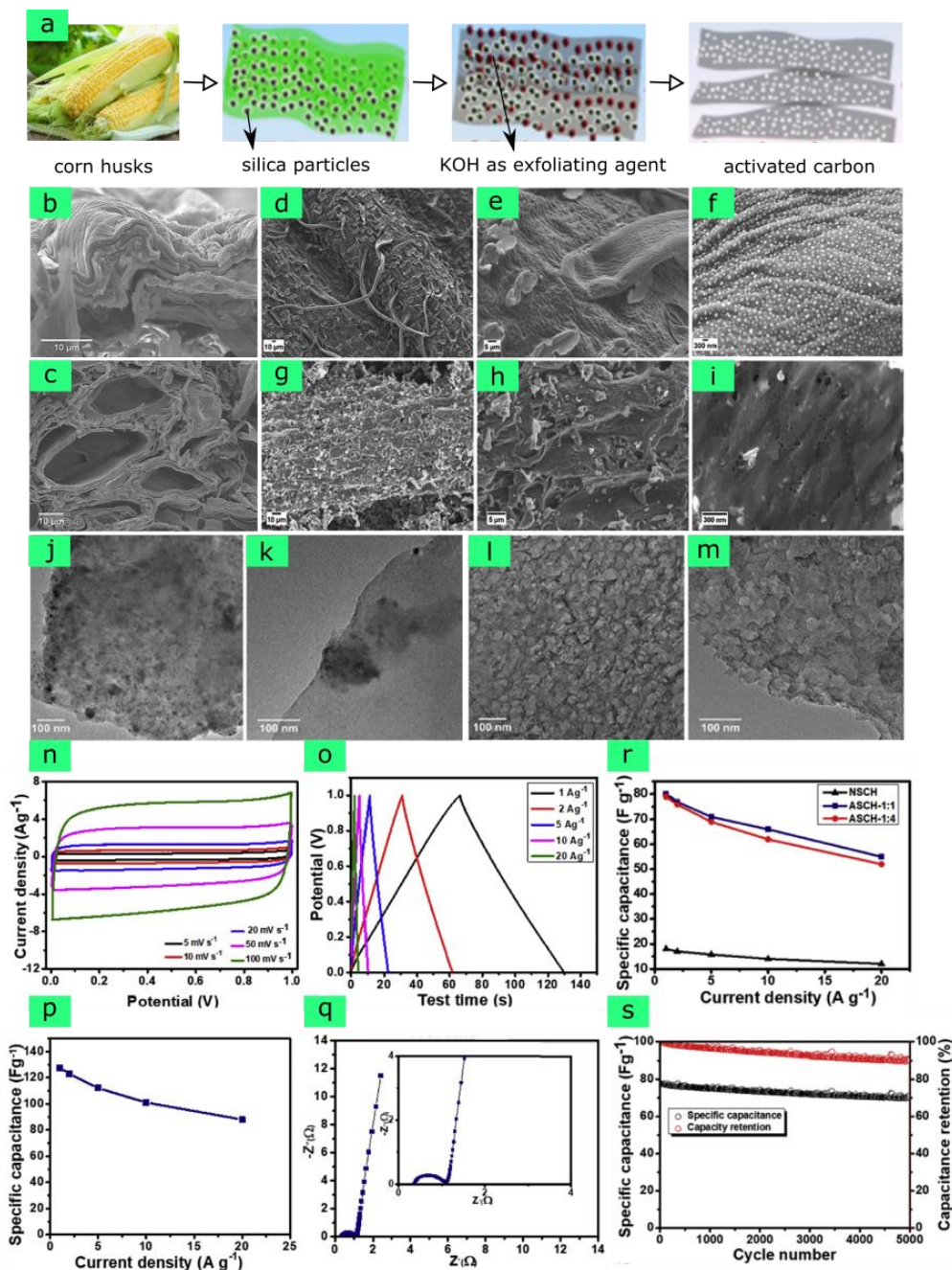


Figure 7. (a) The evolution of corn husks into activated carbon. (b) and (c) SEM images of the dried corn husks. (d), (e) and (f) SEM images of the non-activated carbon. (g), (h) and (i) SEM images of the activated carbon. (j) and (k) TEM images of the non-activated carbon. (l) and (m) TEM images of the activated carbon. (n) Cyclic voltammety curves at different scan rates when using potassium hydroxide electrolyte. (o) Charge/discharge curves at various current densities when using potassium hydroxide electrolyte. (p) Specific capacitance when using potassium hydroxide electrolyte. (q) Electrochemical Impedance Spectroscopy (EIS) spectrum when using potassium hydroxide electrolyte. (r) Rate capability of the samples when using organic electrolyte.

(s) Cyclic stability of the sample over 5000 cycles at 2 A/g when using organic electrolyte. Adapted with permission from [24]. Copyright 2020, Elsevier B.V.

It can be concluded that the electrode, as an essential component of a supercapacitor, can be successfully synthesized based on corn biochar. According to the existing literature, most of the corn-based electrodes are used in electrochemical double-layer capacitors and pseudocapacitors, and only a few are used in hybrid capacitors [92, 93, 94]. In both cases, the modified corn biochar derived from various parts of the corn has demonstrated satisfactory energy and power densities. Since hybrid capacitors incorporate the advantages and alleviate the disadvantages of the two systems, it is believed that future investigation will be focusing on the application of corn biochar in hybrid capacitors.

Corn-Mediated Carbonaceous Host Matrixes for High-Capacity Electrodes in Lithium-Ion Batteries

Graphite only possesses a theoretical capacity of 372 mAh/g, and most of the commonly used performing cathodes are only 150 mAh/g to 250 mAh/g, severely limiting the energy density of energy storage systems [95]. Thus, high-capacity electrode materials have attracted a great amount of attention, but the mechanical degradation due to their dramatic volume change during lithiation and delithiation has been recognized as a bottleneck issue. For example, anode materials based on silicon, germanium, and tin possess a high theoretical capacity of 4200 mAh/g, 1625 mAh/g, and 994 mAh/g, respectively [96]. However, their volume change caused by lithiation and delithiation can be as high as 420%, 370%, and 260%, respectively, often leading to high stresses and particle pulverization [97]. Moreover, the significant morphology variation can either delaminate a portion of the electrode or even detach the entire electrode from the current collector. Furthermore, the volume variation and cracking of high-capacity electrode can break down the SEI layer deposited on the electrode surface.

Therefore, tremendous effort has been made to explore the fundamental basics of high-capacity and high-energy electrode materials and many strategies have been proposed to conquer the obstacles of boosting energy density of the batteries [98, 99, 100, 101]. One strategy is to reduce particle size to nanoscale to alleviate mechanical strain. For example, Liu et al. found that, during the first lithiation process, the nanoparticles with diameters less than 150 nm undergo volume expansion without fracturing or cracking, suggesting that nanoparticles can tolerate huge volume change [102]. Another innovative strategy is to utilize hierarchical porous structure to accommodate volume change. For example, Li et al. demonstrated that silicon sponge with hierarchical porous structure can restrain the particle volume increase at full lithiation to 30%, preventing particle pulverization [103]. Another smart design is to wrap high-capacity electrode particles using self-healing polymers. For example, Wang et al. showed that self-healing polymers can be self-repaired by the randomly branched hydrogen bonds in itself [104]. It was observed that silicon particle of several micrometer demonstrated amazingly long cycle life owing to the containing effect of the self-healing polymer. The focus of this section, though, is the remarkable idea of dispersing high-capacity electrode particles in a carbonaceous host matrix to accommodate volume change and simultaneously improve conductivity [25, 26, 27, 105, 106, 107, 108]. Three representative cases of using corn, corn by-products, and corn industrial products to produce the carbonaceous host matrixes are reviewed in detail.

Kwon et al. proposed an innovative method of using corn starch as a precursor to produce silicon/carbon hybrid composite anodes [25]. As shown in Figure 8(a), silicon nanoparticles are dispersed in oil to form the first solution, whereas corn starch and cetrimonium bromide are dissolved in water to form the second solution. Cetrimonium bromide works as a surfactant. Then the two immiscible solutions are homogenized to form an emulsion. During homogenization, the oil droplets are coated by a thin layer called micelle, comprising surfactants. The mixture is then

heated to 320°C and stirred vigorously for one day. Via the collision reaction, silicon nanoparticles nucleate inside the oil droplets. The obtained powders are preheated to 230°C in a vacuum oven and then carbonized under propene gas at 800 °C to produce the silicon/carbon hybrid composite. The SEM image and the particle size distribution of the hybrid composite are shown in Figure 8(b) and Figure 8(c), respectively. As shown in the scanning TEM (STEM) image in Figure 8(d), silicon nanoparticles are well immersed in the carbon matrix, which is further verified by energy dispersive X-ray spectroscopy (EDX) as presented in Figure 8(e) to Figure 8(g). As shown in the HRTEM image in Figure 8(h), the hybrid composite is composed of silicon nanoparticles placed in micron-sized amorphous carbon balls, and each ball is covered by a thin graphitic carbon layer. As shown in Figure 8(i), the hybrid composite anode shows a high capacity and an outstanding cyclability.

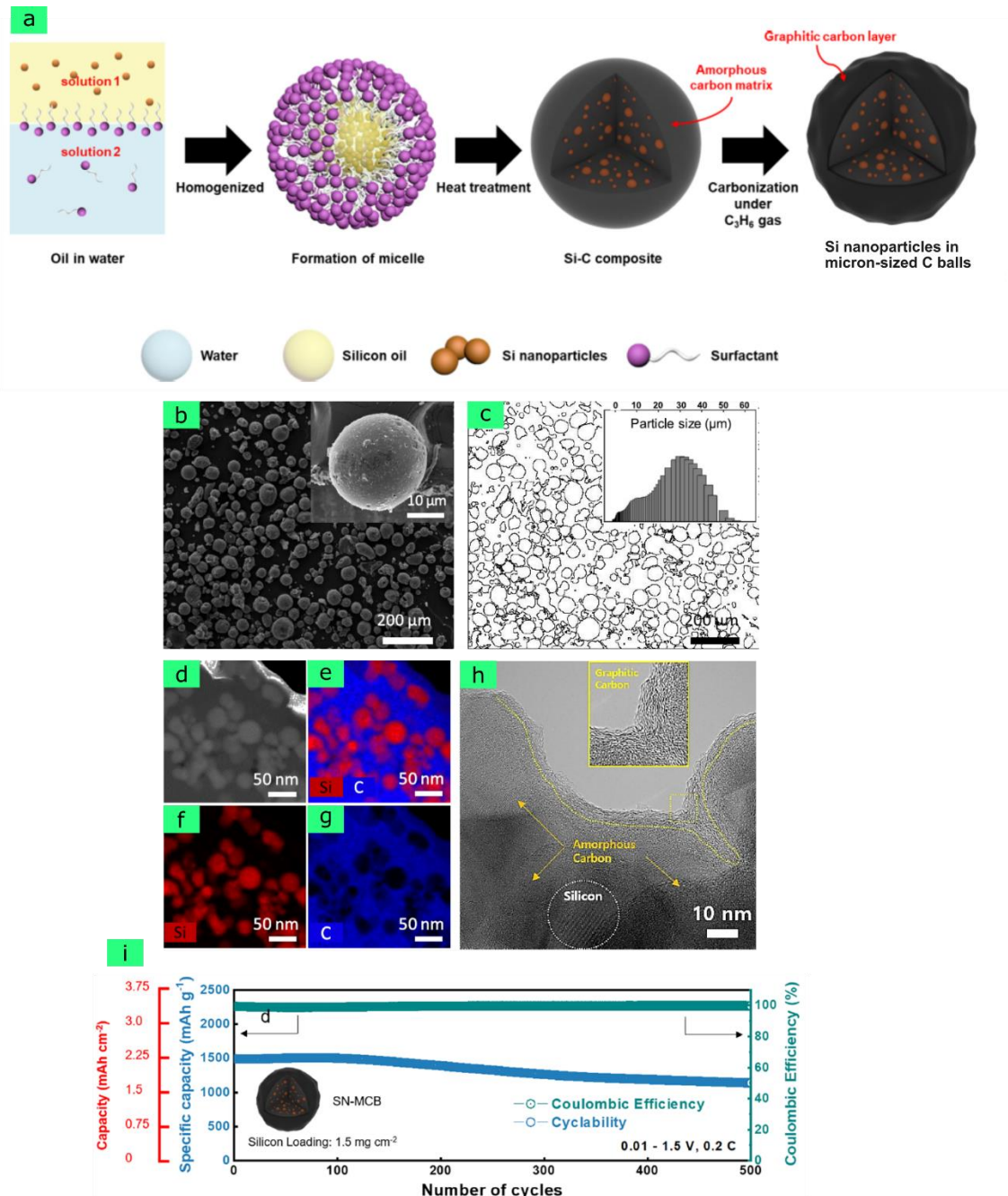


Figure 8. (a) The synthesis process of the silicon/carbon hybrid composite. (b) SEM image of the hybrid composite. (c) Particle outline diagram and particle size distribution of the hybrid composite. (d) STEM image of the hybrid composite. (e) to (g) The EDX mapping of the hybrid composite. (h) HRTEM image of the interface with yellow lines indicating the boundary between graphitic and amorphous carbon. (i) Cycling stability at 0.2 C. Adapted with permission from [25]. Copyright 2019, American Chemical Society.

Wei et al. also fabricated silicon/carbon hybrid composite anodes based on low-cost corn starch but using a different approach [26]. The synthesis process is shown in Figure 9(a). In this study, corn starch, mainly comprising spherical particles, as shown in Figure 9(b), is first hydrolyzed by amylase. The corn starch emulsion is then filtered and separated into porous starch and starch slurry. The porous starch particles remain spherical but possess rich porosity, as shown in Figure 9(c). Most pores have a radius of approximately 100 nm, not only facilitating embedment of silicon nanoparticles but also promoting the electrolyte diffusion and ion transfer after carbonization. The silicon nanoparticles are then dispersed by ultrasonication in the porous starch. As shown in Figure 9(d) and Figure 9(e), many clusters of silicon nanoparticles are observed on the carbon framework. These silicon nanoparticles are then coated with starch slurry. Finally, the porous starch/silicon/starch slurry precursor is placed in an inert atmosphere and carbonized at 650°C to obtain the hybrid composite. As shown in Figure 9(f) and Figure 9(g), the silicon nanoparticles are uniformly distributed over the carbon, mainly due to the successful deposition of the carbon layer. As shown in Figure 9(h) to Figure 9(j), the presence of the carbon layer, which is 50 nm to 500 nm thick, guarantees a secure bonding between the silicon nanoparticles and the carbon framework. As shown in Figure 9(k) and Figure 9(l), outstanding electrochemical performance is obtained, largely due to the rich porosity of the starch derived carbon, which enhances the structural stability and electrochemical kinetics.

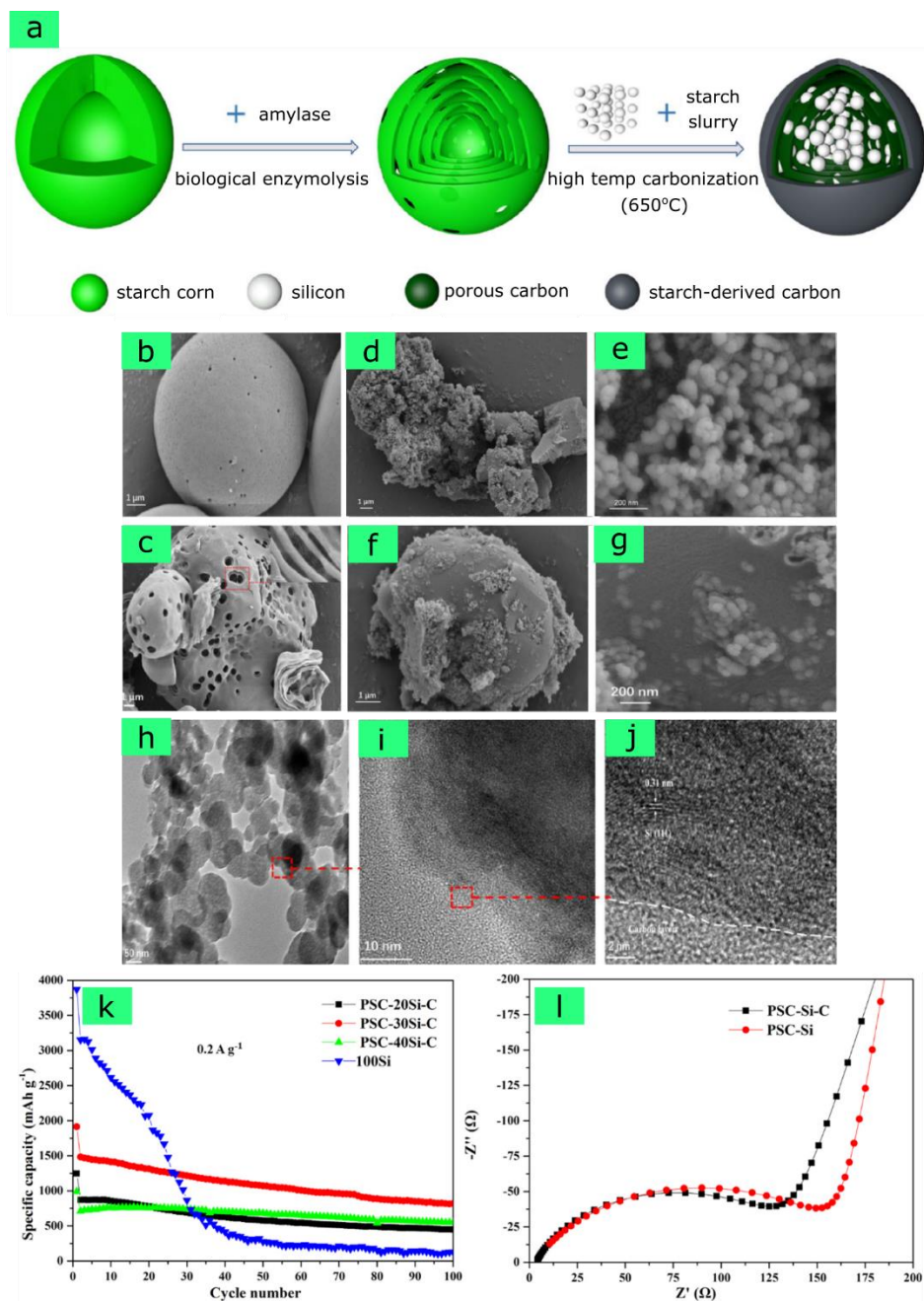


Figure 9. (a) The synthesis process of the silicon/carbon hybrid composite. (b) SEM image of the corn starch. (c) SEM image of the porous starch. (d) and (e) SEM images of the silicon nanoparticles introduced into the porous starch. (f) and (g) SEM images of the obtained hybrid composite. (h) and (i) TEM images of the hybrid composite. (j) HRTEM image of the hybrid composite. (k) Cycling performance of the samples. (l) EIS curves before electrochemical cycle. Adapted with permission from [26]. Copyright 2020, IOP Publishing.

Hu et al. synthesized a composite anode using tin dioxide nanoparticles anchored in a porous carbon framework derived from corn stover via a facile hydrothermal method [27]. As shown in Figure 10(a), the crushed corn stover powders are impregnated in calcium chloride solution for 48 hours and dried at 90°C. The powders are then pre-carbonized at 300°C for three hours in a muffle oven and then heated to 600°C for one hour. Figure 10(b) presents the SEM image of the

obtained porous carbon, which shows an irregular, amorphous block structure with rough surfaces. The pretreated porous carbon and tin dioxide nanoparticles are then dispersed in deionized water, vigorously stirred, placed in an autoclave, and heated to 200°C. The black precipitates are collected by centrifugation, washed, and dried at 90°C for three days. The sample is then annealed at 500°C for three hours under an argon atmosphere. The SEM images presented in Figure 10(c) and Figure 10(d) show that the tin dioxide nanoparticles are filled in the porous carbon matrix. Figure 10(e) to Figure 10(g) show the EDX element mappings of the composite with carbon, oxygen, and tin denoted by red, blue, and green, respectively. Carbon, oxygen, and tin are uniformly distributed throughout the composite. The porous carbon matrix provides plenty of accommodation sites and firmly anchors the tin dioxide nanoparticles. The TEM images presented in Figure 10(h) and Figure 10(i) show that the carbon matrix possesses a translucent amorphous structure with rich porosity clearly observed. The TEM image presented in Figure 10(j) reveals that the tin dioxide nanoparticles denoted by yellow circles are evenly distributed in the amorphous carbon framework. As shown in Figure 10(k) and Figure 10(l), the composite anode demonstrates excellent electrochemical performance. The pores and inner channels in the porous carbon matrix not only mitigates the significant volume change of tin dioxide during cycling but also increases the conductivity of the tin dioxide electrode.

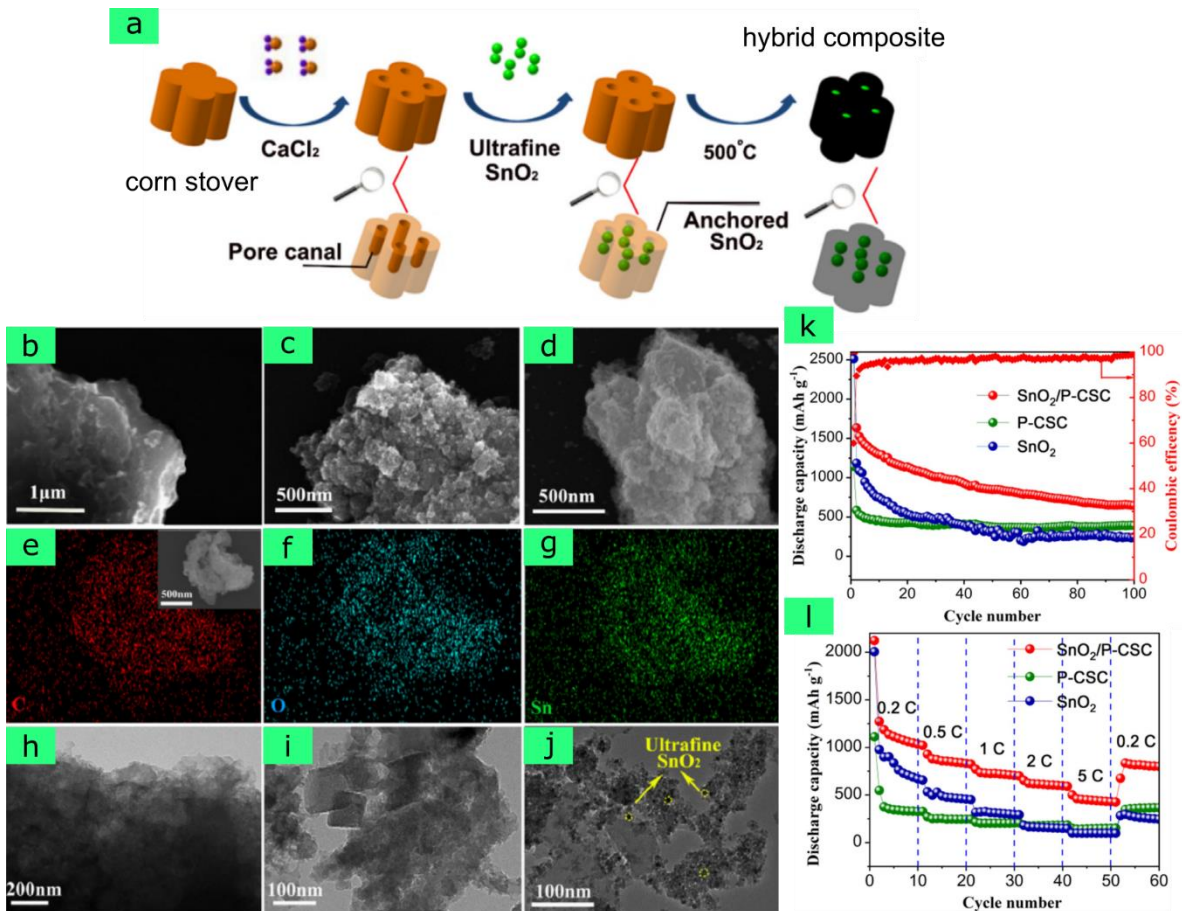


Figure 10. (a) The synthesis process of the tin dioxide/carbon hybrid composite. (b) SEM image of the porous carbon. (c) and (d) SEM images of the hybrid composite. (e), (f) and (g) EDX element mappings of the composite with carbon, oxygen, and tin denoted by red, blue, and green, respectively. (h) and (i) TEM images of the porous carbon. (j) TEM image of the hybrid composite. (k) Cycling performance of the samples. (l) Rate capability of the samples. Adapted with permission from [27]. Copyright 2020, Elsevier B.V.

Corn-Mediated Binders for Lithium-Ion Batteries

To conquer the obstacles of using high-capacity electrode materials, most research has been focusing on innovative electrode structural design, but recent studies have shown that the role of the binder, the electrically inactive component of the electrode, is pivotal to keep the electrode intact as well as exhibit a satisfactory cycling performance [109]. Particles of high-capacity electrode materials that possess huge volume changes pose a significant challenge to binder characteristics to ensure electrode integrity during repeated cycles of lithium insertion and extraction. Polyvinylidene fluoride (PVDF), the most commonly used binder, is attached to electrode material particles and metallic current collector via weak van der Waals forces and incapable of accommodating significant changes in particle spacing. As a result, it is unable to hold the particles together or maintain electrical conductivity within the anode. In addition, extensive usage of PVDF causes environmental issues as its handling typically necessitates toxic organic solvents.

Owing to these limitations of PVDF, in the past decades, more efficient and more eco-friendly binders have been proposed to stabilize high-capacity electrodes [109, 110, 111, 112, 113, 114, 115, 116, 117, 118]. For example, recent research has shown that biomass-derived polysaccharides and synthetic polymers, such as carboxymethyl cellulose (CMC) [110, 113, 114, 117, 119], polyacrylic acid (PAA) [112, 120], and sodium alginate (SA) [111], can function as binders for silicon-based anodes by utilizing their abundant carboxyl and hydroxyl functional groups that facilitate a series of ester-like covalent bonds or hydrogen bridge bonds with the hydroxyl groups on the silicon surface. The enhanced adhesion due to the chemical bonds between the binder and the silicon nanoparticles demonstrates a self-healing effect when locally broken [110]. Many innovative uses of corn, corn by-products, and corn industrial products have been proposed as well [121, 30, 29, 28, 122]. In this section, several representative cases are reviewed.

CMC has been considered as the precedent that opened the avenue for the investigation of water-soluble binders for high-capacity electrode materials. Chen et al. used a mixture of commercial acrylic adhesive and CMC for silicon-based anodes [113]. The addition of CMC favorably affects battery performance. Hochgatterer et al. later confirmed the existence of a chemical bond between the CMC binder and the silicon particles using Fourier-transform infrared spectroscopy [117], which is found to be the main reason for the long-lasting reversible cycling. According to Mazouzi et al. [119], a silicon-based composite electrode prepared using aqueous processing in an acidic medium can accomplish over 700 cycles at the capacity of 960 mAh/g. When a buffer solution with a pH value of 3 is used for the electrode fabrication, a grafting esterification reaction between the hydroxyl groups on the silicon surface and the carboxyl groups of CMC is greatly favored, and as a result, the electrode displays a remarkable cycle life. It has been demonstrated that CMC binder can be fabricated based on corn stover through an eco-friendly and economical approach [28, 122, 123]. For example, Hidayat et al. synthesized CMC binder for lithium-ion batteries using corn cob [28].

Corn starch has been extensively studied as the binder for silicon-based anodes due to its low cost and biodegradability [30, 121]. One example was provided by Rohan et al. [29]. As shown in Figure 11(a) and Figure 11(b), corn starch and maleic anhydride are dissolved in hot water, stirred for one hour at room temperature, and then heated at 120°C for 12 hours for cross-linking. As shown in Figure 11(c), the peeling force of the starch binder is significantly increased by cross-linking. As shown in Figure 11(d), the silicon-based composite anode with the cross-linked corn starch binder demonstrates a high specific capacity with enhanced cycling stability.

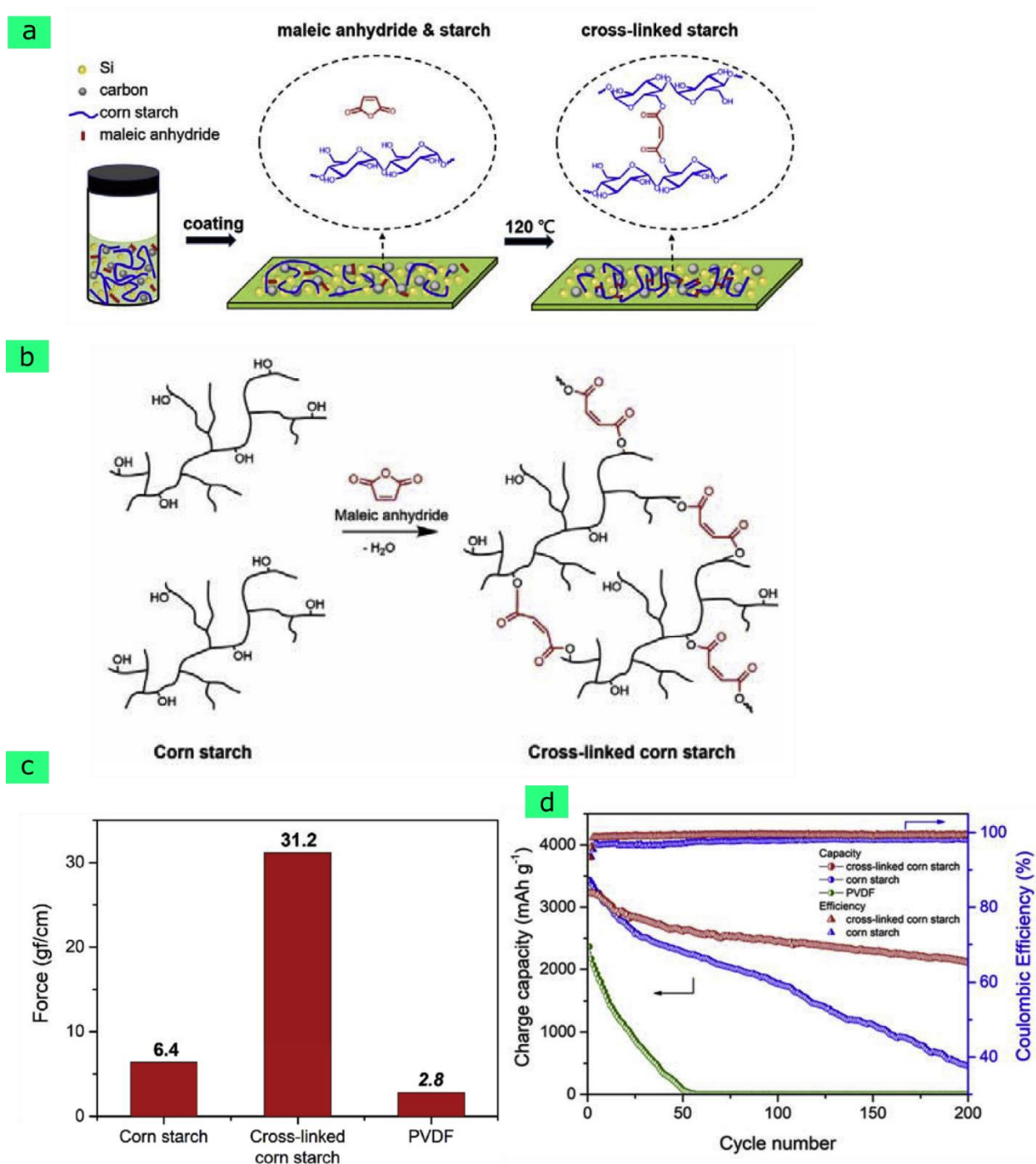


Figure 11. (a) Synthesis process of silicon-based composite electrode with cross-linked corn starch binder. (b) Corn starch cross-linked by maleic anhydride. (c) Results of 180° peel tests. (d). Charge capacity and coulombic efficiency at 0.5 C. Adapted with permission from [29]. Copyright 2018, Elsevier B.V.

Besides the adhesion strength of the binder with the silicon particles and the copper current collector, the mechanical properties of the binders are also crucial, i.e., too stiff binders are incapable of accommodating the stress and strain caused by the huge volume change of silicon particles, resulting in macroscopic cracking of the electrode. For polysaccharides characterized by

glycosidic linkages, it is generally believed that β -glycosidic linkages lead to stiffer mechanical properties than α -glycosidic linkages. For example, pectin that is based on α -glycosidic linkages has been confirmed to perform better for silicon anodes than CMC that is based on β -glycosidic linkages [118]. Based on this finding, Bie et al. proposed to use oxidized corn starch featuring oxidized amylose and oxidized amylopectin as the binder for silicon anodes [30]. The molecular structures of CMC, SA, and oxidized corn starch, respectively, are shown in Figure 12(a). Since β -glycosidic linkages result in stiffer mechanical properties than α -glycosidic linkages, both CMC and SA are less elastically deformable than oxidized corn starch. Oxidized amylopectin, the major component of oxidized corn starch, is multi-branched, which is beneficial for holding silicon particles together. In addition, the plentiful polar groups in oxidized corn starch facilitate a robust interaction between oxidized corn starch and silicon particles. As shown in Figure 12(b), the silicon anode can cycle for 120 times with a capacity retention of 74%. As shown in Figure 12(c), in the cases of CMC and SA binders, distinct cracks appear after battery cycles, indicating that such stiff binders are incapable of handling repeated particle expansion and extraction. On the other hand, oxidized corn starch only shows minor crevices. This work demonstrates that the excellent binding capability, ultralow cost, and nontoxicity make oxidized corn starch an outstanding candidate to be a binder for silicon anodes.

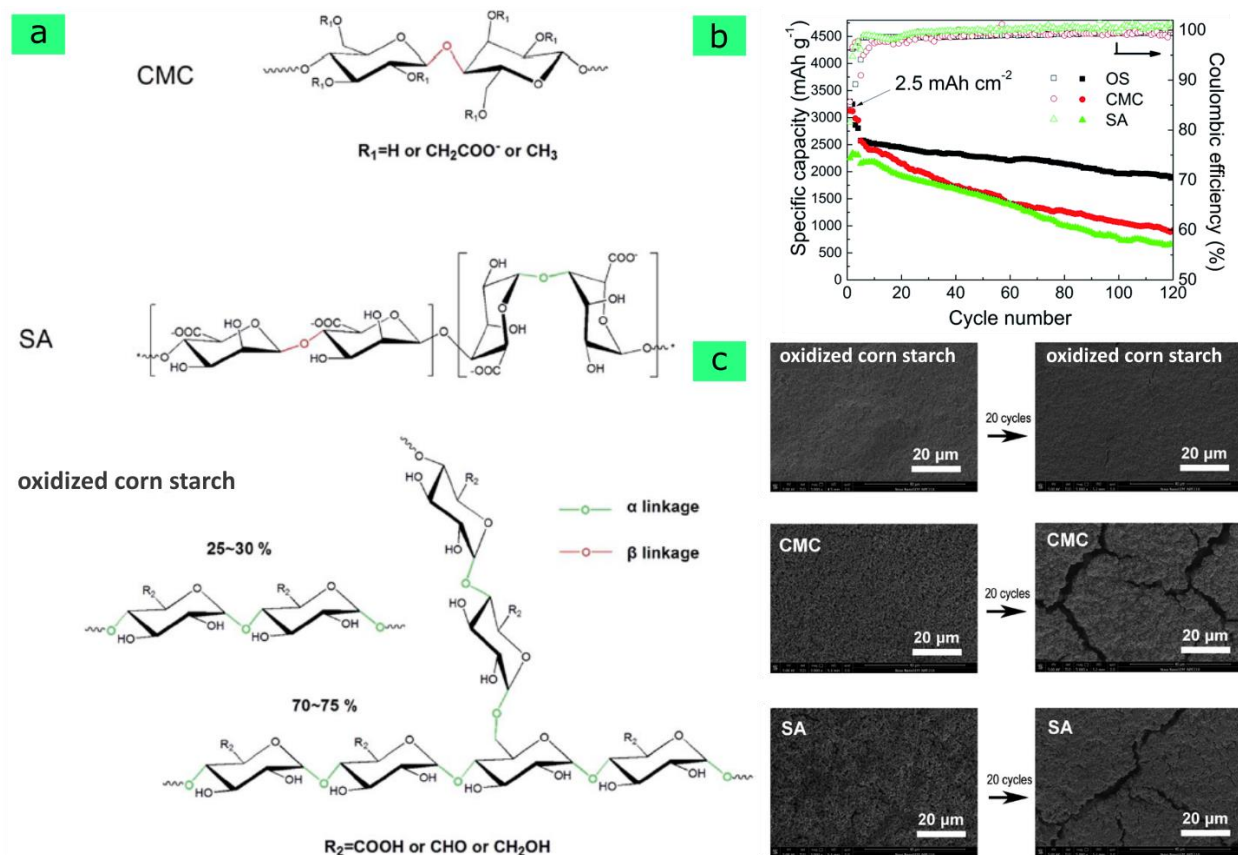


Figure 12. (a) Molecular structures of CMC, SA, and oxidized corn starch, respectively. (b) Cycle performance and coulombic efficiencies of the samples. (c) SEM images of the silicon anode with oxidized corn starch, CMC, and SA, as the binder, respectively, before and after battery cycles. Adapted with permission from [30]. Copyright 2016, the Royal Society of Chemistry.

It can be concluded that binders for lithium-ion batteries can be successfully fabricated based on corn and corn products. These binders show a very promising future since they are compatible with the current manufacturing of silicon/graphite composite anodes [124]. In addition, they are

water-soluble binders and enable the recovery of chemical compounds from spent electrodes using water [125]. Recent research demonstrated that the recovered cathode compounds can be regenerated to display comparable performance to the original one [125]. However, there exists very little literature about corn-based binders, indicating that this issue can be more thoroughly investigated as future endeavors.

Corn-Mediated Solid Polymer Electrolyte for Solid-State Batteries

A solid-state battery uses a solid-state electrolyte [126]. Compared with liquid electrolyte, solid-state electrolyte has better safety and thermal stability. Out of the various solid-state electrolytes, solid polymer electrolyte has the highest possibilities to be used in next-generation batteries, mainly due to its excellent electrochemical performance, great safety, and mechanical robustness [127]. In the beginning stage, synthetic polymers, such as polyethylene oxide [128], polyacrylic acid [129], and polyvinyl alcohol [130], were tested, but this practice causes environmental concerns associated with their toxicity and slow degradability. Biopolymers were then regarded as a promising alternative since they do not cause safety or environmental issues. Chitosan [131], cellulose [132], xanthan gum [133], and gelatin [134] have thus been explored as solid polymer electrolyte. Corn starch consists of repeating glucose monomers joined by glycosidic linkages shaping a stable helix structure, beneficial for the reversible transportation of ions. Therefore, solid polymer electrolyte based on corn starch has been investigated [135, 136, 137, 138, 31].

Lin et al. fabricated a novel solid polymer electrolyte film using corn starch [31]. Figure 13(a) shows the fabrication process. The corn starch is first dissolved into dimethyl sulfoxide (DMSO), and a certain amount of silane coupling agent KH-560 is then added to the solution so that the corn starch is crosslinked with KH-560 to enhance stretchability of the electrolyte film. The reaction at 90°C produces a yellowish viscous solution. The solution is then dried at 60°C to generate the starch host. The molecular weight distribution and molecular structure of the obtained starch host are examined by gel permeation chromatography, as shown in Figure 13(b), and nuclear magnetic resonance spectroscopy, as shown in Figure 13(c), respectively. According to the results, a suggested structure of the host is shown in Figure 13(d). As shown in Figure 13(e), to fabricate the electrolyte film, the starch host solution is blended with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and dried at 60°C. This electrolyte demonstrates an outstanding ionic conductivity of 0.339 mS/cm and ion transference number of 0.80 at 25°C. Using this electrolyte, the lithium sulfur batteries demonstrate excellent electrochemical performance.

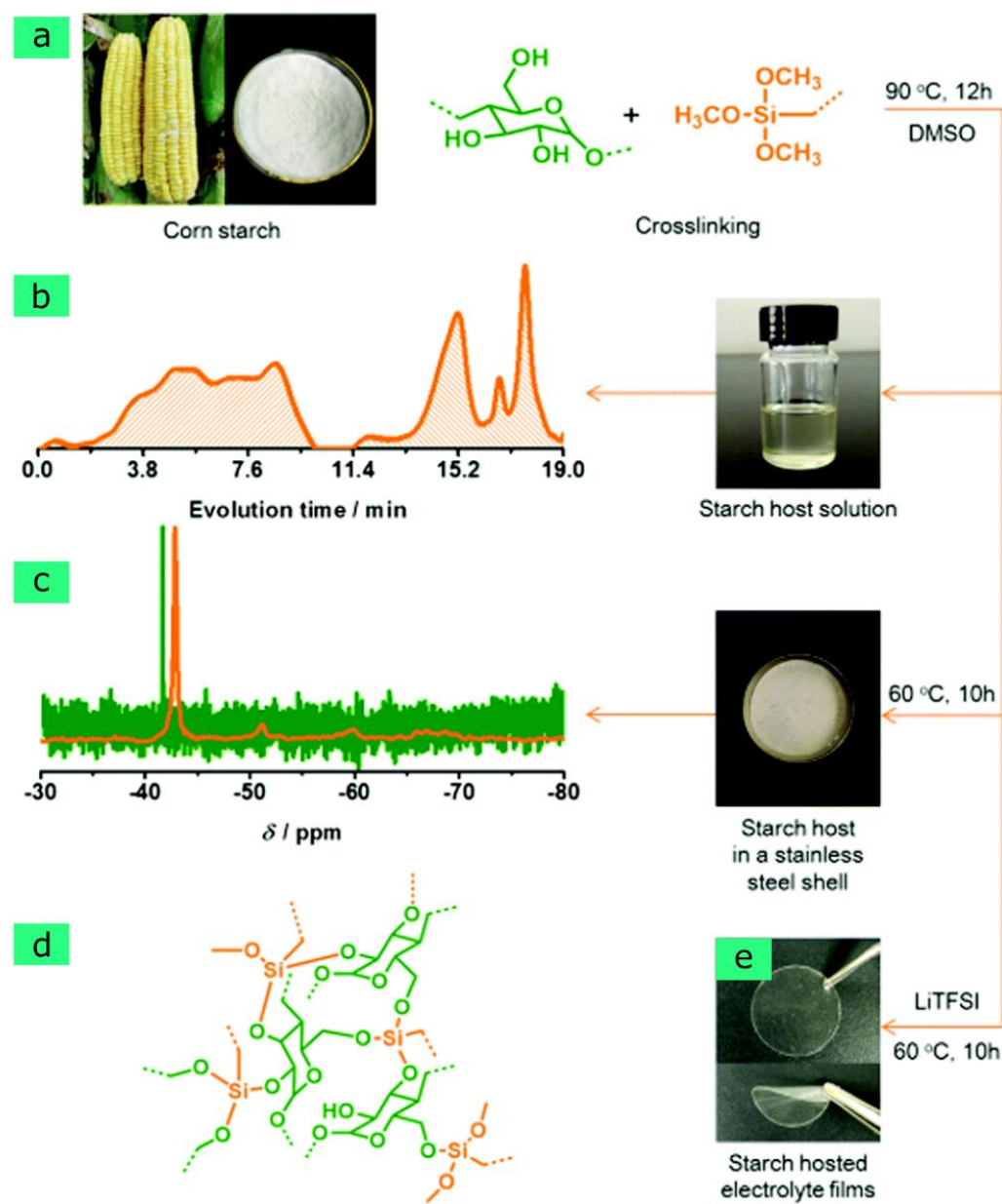


Figure 13. (a) The process of the starch host synthesis. (b) and (c) Results from gel permeation chromatography and nuclear magnetic resonance spectroscopy, respectively. (d) Suggested structure of the starch host. (e) Images of the obtained electrolyte film. Adapted with permission from [31]. Copyright 2016, the Royal Society of Chemistry.

Corn-Mediated Materials for Beyond-Lithium-Ion Technologies for Grid-Level Energy Storage

Numerous approaches have been explored for grid-level energy storage [139, 140], and among them, battery technologies possess many advantages thanks to their effortless modularization, rapid response, and adaptable installation. Lithium-ion battery is among the most developed battery technologies [141], but the use of lithium-ion battery in grid-level energy storage is too expensive, since most of the components are not based on earth-abundant elements. The current production rate could rapidly deplete known reserves of cobalt and nickel, making the batteries even more costly in the near future [142]. Although lithium makes up only a tiny segment of the

total cost, there will still be a severe pressure on lithium suppliers to cater to demand [143]. Even worse, current battery recycling technology is still in its infancy, i.e., it does not make any economic sense to recycle lithium-ion batteries [144, 145]. Thus, various other battery technologies are explored to meet the increasing demand for grid-level energy storage.

Sodium-ion batteries are promising candidates for grid-level storage of intermittent renewable energies, where specific volumetric and gravimetric energy density requirements are not as strict as in electric vehicles [146, 147], due to the high natural abundance and broad distribution of sodium resources [148]. Rhodizonate ionic crystals that can be prepared from a natural compound myo-inositol are promising active compounds due to their excellent theoretical energy density [149]. Myo-inositol, also known as inositol or hexahydroxycyclohexane, is a component of cell membranes and is an essential nutrient for human cells for growth and survival in culture. Corn steep liquor is the traditional industrial source of myo-inositol [150]. In this process, phytin is first precipitated as a calcium salt and then hydrolyzed with a strong acid. However, the production of myo-inositol in this fashion was terminated in the United States in 1987, mainly due to the high production cost [150]. Thus, supplies of myo-inositol currently either come from China, where it is extracted from corn steep liquor, or Japan, where it is produced from rice bran. Recently, Lee et al. demonstrated that rhodizonate ionic crystals prepared from corn steep liquor help realize four-sodium storage and high-rate capability of cathodes, opening a cheaper and greener way to establish sodium-based energy storage systems [32].

Zinc batteries also hold particular promise for grid-level energy storage [151], since zinc is the fourth most abundant metal on earth [152]. Historically, zinc batteries showed limited cycle life, but recent technologies have dramatically improved rechargeability [153]. Hopkins et al. proposed a low-cost synthesis of zinc sponge using corn starch [33]. The fabrication process is shown in Figure 14(a) to Figure 14(d). Previously published protocols used expensive polymer resin porogen that constitutes more than 73% of the material cost, i.e., \$9.7/kg. Those resins, typically CMC, which costs \$420/kg, are generally considered as required for the fabrication of zinc sponges. When tested in zinc-air cells, the electrode demonstrates a significant enhancement in rechargeable areal capacity compared with the published results. This study shows that corn starch, which costs only \$0.3/kg, is an exceptional alternative to polymer resin. The corn starch particles are 5 μm in radius, comparable to the thickness of the CMC polymer resin branches, as shown in Figure 14(e) and Figure 14(f), respectively. In addition, as little as 4% of char is left after baking, which is highly desired since the carbon residue blocks the sponge pores. By using corn starch, the cost is lowered by 74% to \$2.5/kg, as shown in Figure 14(g) and Figure 14(h).

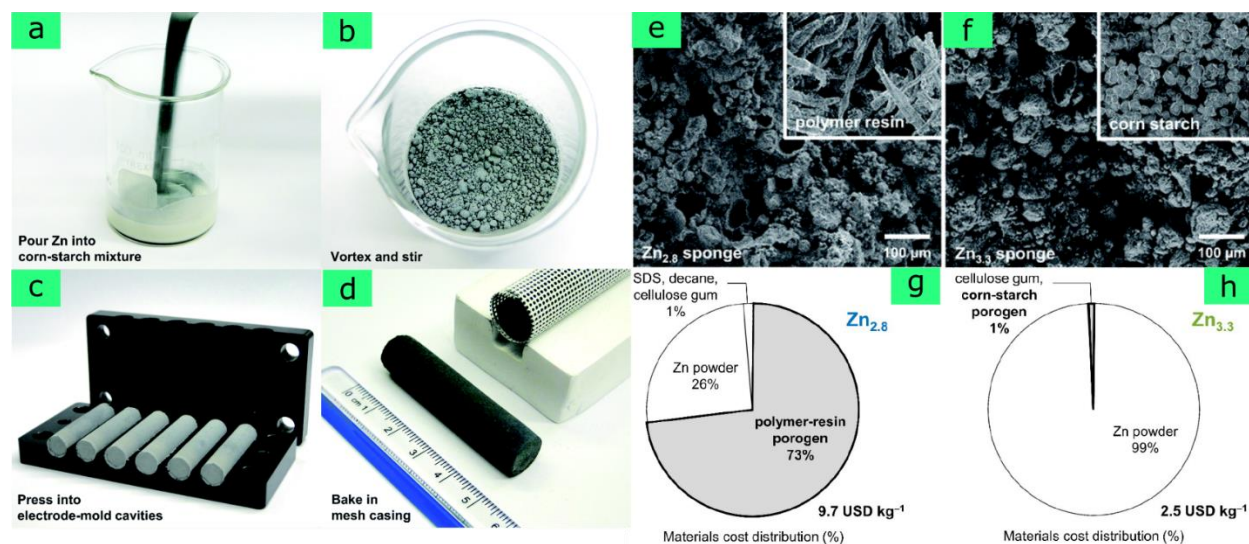


Figure 14. (a) Mix zinc powders into the mixture of water, corn starch, and cellulose gum. (b) Vortex and stir the mixture. (c) Press the paste into electrode-mold cavities. (d) Place dried preforms into a mesh casing for baking: (center) baked zinc sponge; (right) mesh casing filled with zinc sponges. (e) SEM image of a cross-sectioned $Zn_{2.8}$ sponge and CMC polymer resin (top right). (f) SEM image of a cross-sectioned $Zn_{3.3}$ sponge and corn starch (top right). The previously reported sponge synthesized using conventional CMC has a density of $2.83 \pm 0.09 \text{ g/cm}^3$ and thus denoted as $Zn_{2.8}$, whereas the sponge synthesized using the proposed synthesis has a density of $3.26 \pm 0.10 \text{ g/cm}^3$ and thus is denoted as $Zn_{3.3}$. (g) Materials cost distribution of $Zn_{2.8}$. (h) Materials cost distribution of $Zn_{3.3}$. Adapted with permission from [33]. Copyright 2020, the Royal Society of Chemistry.

Redox flow batteries have also been studied for grid-level energy storage applications since the 1970s and show a promising future [154]. Unlike traditional batteries, the electrode is separated from the electrolyte. Among the various redox flow batteries, all-vanadium redox flow batteries have been most extensively studied, mainly due to their superiority of decreased cross-contamination by applying the same element in both electrolytes [154]. Their electrode materials are typically graphite felts, which demonstrate high stability, high conductivity, and high surface area. On the other hand, their inferior kinetic reversibility and electrochemical activity restrain the battery operation to low current densities. Therefore, electrocatalyst is often introduced on the electrode surface to lower the activation barrier for redox conversion [155].

Park et al. developed a carbon-based electrocatalyst for all-vanadium redox flow batteries using a green synthesis method based on corn protein zein [34]. As introduced in the first section, zein is a commercially available corn protein extracted from the by-products of the wet milling process. It has been produced in the United States in large quantities and at an ultralow cost of \$10/kg. As shown in Figure 15(a), zein powders are dissolved in a binary mixture of ethanol and water, and carbon black is then poured into the solution. As the solution evaporates in an oven, zein self-assembled on the carbon black. The dried powders are transformed into the nitrogen-doped carbon black catalyst by a carbonization process at 800°C , and then the catalyst ink is obtained by mixing the catalyst in Nafion suspension in ethanol. To prepare the electrode, the carbon felt is coated with the catalyst using the ink as presented in Figure 15(b). The electrochemical performance of the prepared electrodes is shown in Figure 15(c) and Figure 15(d). This study demonstrates that the rearrangement of zein molecules and the film assembly behavior greatly aid heteroatom doping on the surface of the carbon black particles. In comparison with the carbon black catalyst, the nitrogen-doped carbon black catalyst demonstrates superior catalytic activity towards vanadium redox reactions.

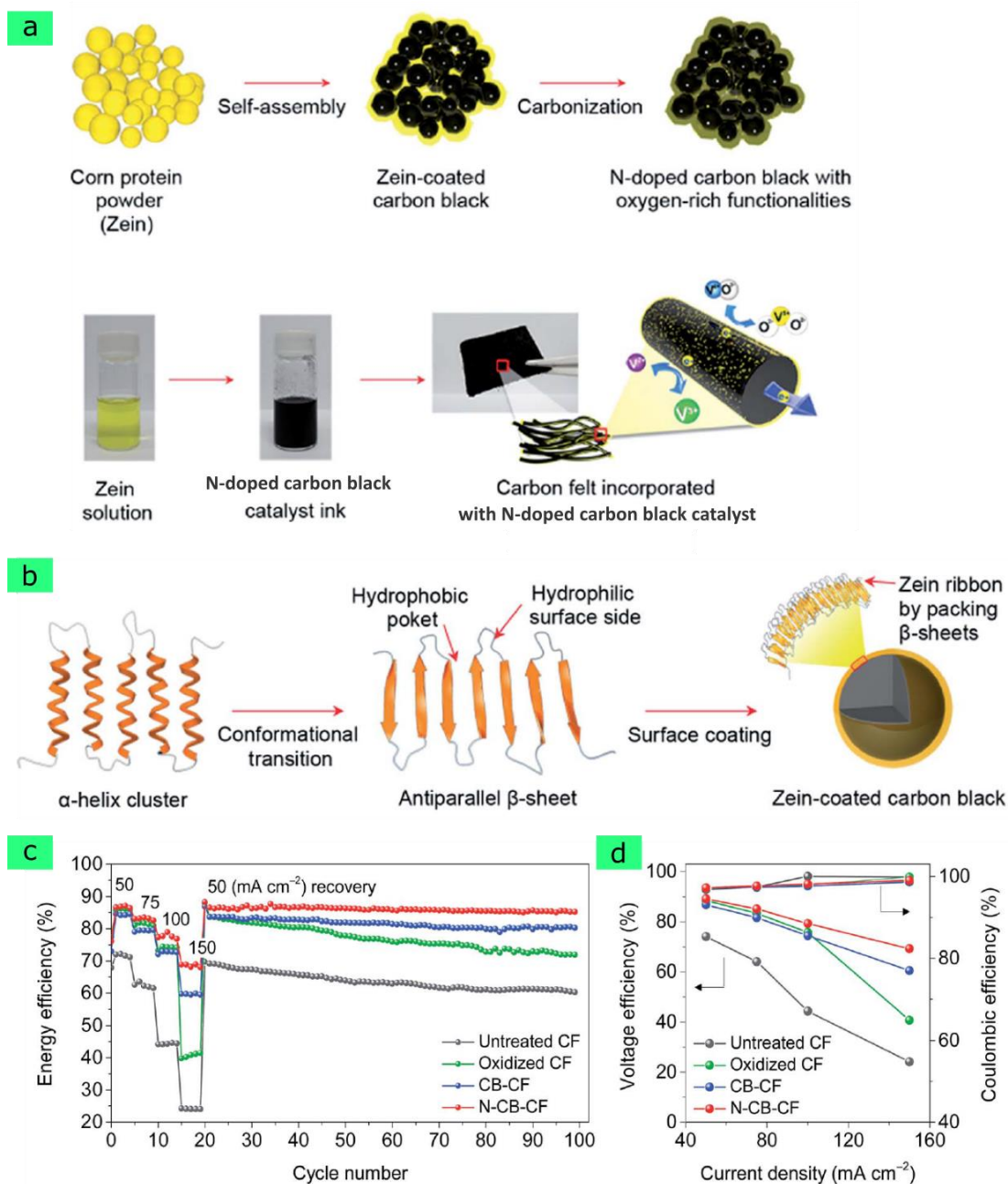


Figure 15. (a) Schematic diagram of the nitrogen-doped carbon black catalyst fabrication process. (b) The mechanism for self-assembly of the zein coated carbon black nanoparticles. (c) Energy efficiency of the samples. (d) Voltage efficiency of the samples. Adapted with permission from [34]. Copyright 2014, the Royal Society of Chemistry.

Concluding Remarks and Future Perspectives

Corn is often called “yellow gold”, because it has been used to manufacture various products and by-products that end up throughout the economy, from food store shelves to industrial chemical plants. This article summarizes their potential application in energy storage devices, which could provide new insights into how to establish an environmentally sustainable, technically feasible, and economically beneficial solution to support corn industry.

Although this review appears quite comprehensive, there are still many innovative applications of corn and corn products in electrochemical energy storage systems that are not included. For example, Zhu et al. coated a porous activated carbon derived from puffed corn on a polypropylene separator to enhance the electrochemical performance of lithium-sulfur batteries [156]. However, this research is the only one that one could find from the existing literature on exploring the possibility of using corn and corn products for the synthesis of membrane separators, which could become one of the focuses of future investigations.

It can be concluded that, according to the existing literature, a broad set of materials synthesized from corn biomass containing inherently favorable properties hold promise for reducing costs while elevating the performance of the energy storage systems. However, the establishment of design principles for corn-derived materials has been complicated by the heterogeneity of viable biomass sources, synthesis routes, and resulting properties. So far, all the proposed technologies reviewed in this article are still at the laboratory-scale stage. Our understanding of the feedstock-processing-property-performance relationship of corn-derived materials used in energy storage systems remains very limited due to a lack of systematic study. Scattered research on different feedstocks is rather unsuitable for comparison due to high variability in the experimental design. Many questions remain unanswered, such as how to adjust the processing conditions to tailor the structure of the obtained carbonaceous material at the atomic scale, microscale, and mesoscale for energy storage applications, how to adjust processing temperature and heating rate to tune the properties of the carbonaceous materials such as the volume fraction of the graphitic domain and the size of the graphitic crystallites, to what extent the impurities on the carbon structure influence its electrochemical performance, and how to properly select the biomass enriched in certain elements to obtain the desired functionalities and heteroatom doping of the resulting carbonaceous material to be used as electrodes. Advancing our understanding of the feedstock-processing-property-performance relationship is urgently needed to optimize the properties of corn-derived materials, paving their way for full-scale industrial production.

Data science is becoming increasingly popular in the field of material science and has, in fact, led to the emergence of the new field of material informatics [157], which applies data science techniques to materials science and engineering to improve our understanding, use, selection, development, and discovery of materials. Currently, the field of material informatics is still pretty much in its nascent stage, similar to bioinformatics twenty years ago. Data science can be utilized to enable timely discovery of highly reliable causal linkages among feedstock selection, processing parameters, material properties, and battery performance, as shown in Figure 16. The results will provide us multiple optimal solutions for any specific type of batteries, so that we can select the production processes and material properties that can be attained in the most cost-effective manner.

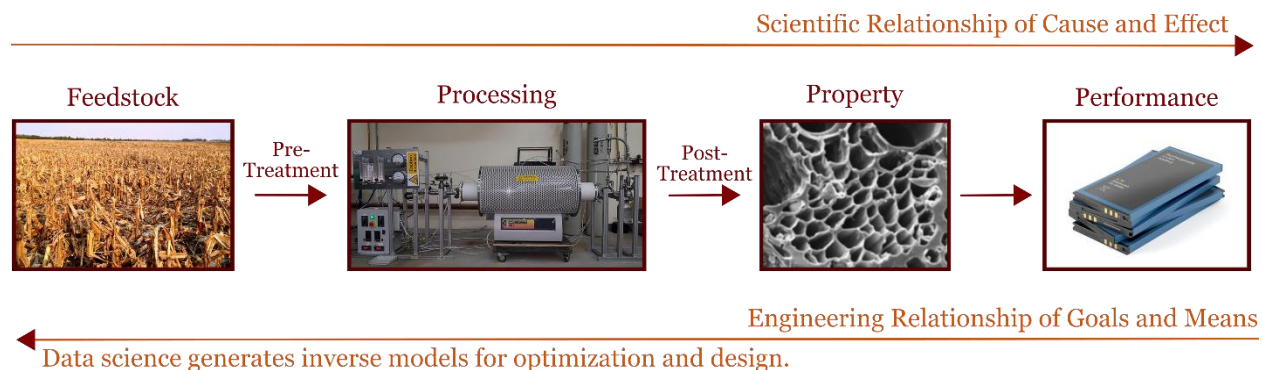


Figure 16. Data science can be used to establish the feedstock-processing-property-performance relationship of corn-derived materials to pave their way for full-scale industrial production.

Future research can also be focusing on conducting life-cycle assessment and life-cycle cost analysis to understand the environmental and economic impacts of corn-derived materials quantitatively. Life-cycle assessment is a technique to estimate the possible environmental impacts and resource consumption throughout a product's life cycle. Life-cycle cost analysis is a technique built upon well-ground principles of economic analysis to determine the most cost-effective option among competing alternatives. In the last decade, many life-cycle assessment and life-cycle cost analysis studies related to corn-derived products have been performed [158, 159]. However, their application in energy storage systems has never been systematically investigated. As future work, the two analyses should be conducted to evaluate how to use corn and corn products to minimize the greenhouse gas emissions and maximize the economic benefits. The recycling potential of some of the corn-derived materials after the final life of the battery needs to be assessed as well.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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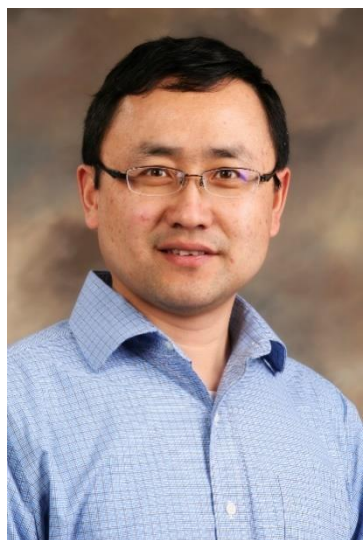
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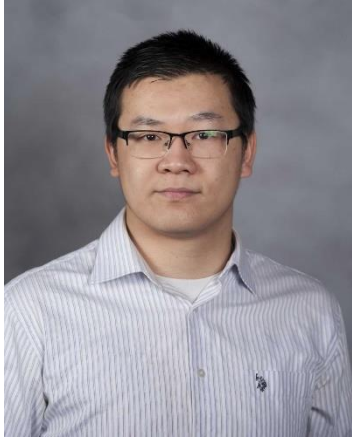
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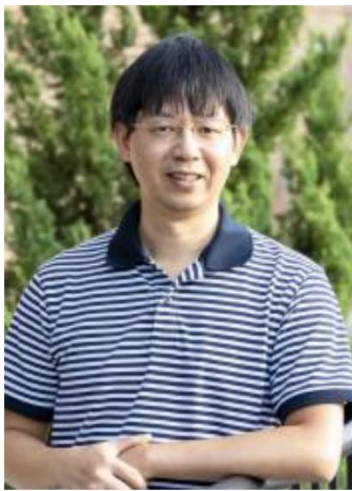
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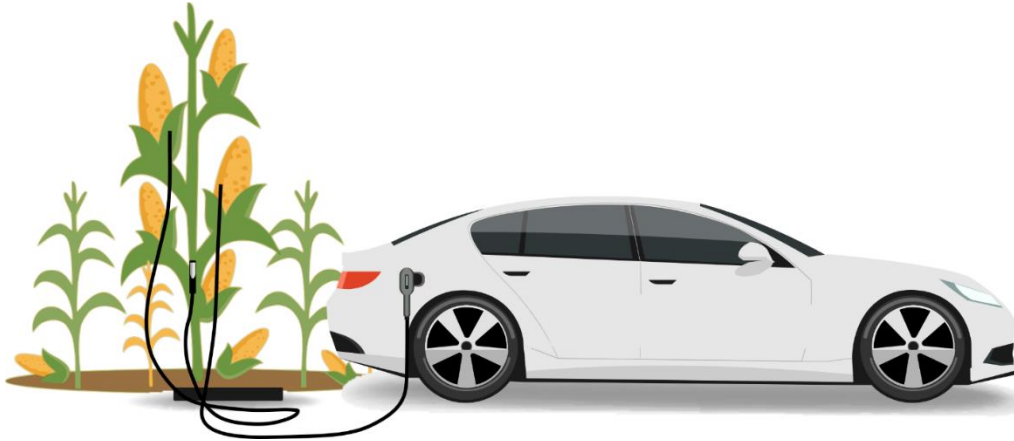


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The United States is by far the largest corn producer worldwide. To sustain the economic viability of corn farmers, it is critical that new uses and markets for corn and corn products should be discovered, giving the highest return to corn producers. In this article, innovative and economically beneficial uses of corn and corn products in various energy storage applications are comprehensively reviewed.