Research Article

FeCo Nanoparticle-Loaded Nutshell-Derived Porous Carbon as Sustainable Catalyst in Al-Air Batteries

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Developing a high-performance ORR (oxygen reduction reaction) catalyst at low cost has been a challenge for the commercialization of high-energy density and low production cost aluminium-air batteries. Herein, we report a catalyst, prepared by pyrolyzing the shell waste of peanut or pistachio, followed by concurrent nitrogen-doping and FeCo alloy nanoparticle loading. Large surface area ($1246.4 \text{ m}^2 \text{ g}^{-1}$) of pistachio shell-derived carbon can be obtained by combining physical and chemical treatments of the biomass. Such a large surface area carbon eases nitrogen doping and provides more nucleation sites for FeCo alloy growth, furnishing the resultant catalyst (FeCo/N-C-Pistachio) with higher content of N, Fe, and Co with a larger electrochemically active surface area as compared to its peanut shell counterpart (FeCo/N-C-Peanut). The FeCo/N-C-Pistachio displays a promising onset potential of 0.93 V vs. RHE and a high saturating current density of 4.49 mA cm^{-2} , suggesting its high ORR activity. An aluminium-air battery, with FeCo/N-C-Pistachio catalyst on the cathode and coupled with a commercial aluminium 1100 anode, delivers a power density of 99.7 mW cm^{-2} and a stable discharge voltage at 1.37 V over 5 h of operation. This high-performance, low-cost, and environmentally sustainable electrocatalyst shows potential for large-scale adoption of aluminium-air batteries.

1. Introduction

Electrochemical energy storage and conversion devices, such as batteries and fuel cells, are of utmost importance to improve the utilization of energy [1]. Ideally, energy shall be storable or interconvertible at low cost to allow for economical use anytime and anywhere. Metal-air batteries and fuel cells have great potential to serve the purpose. However, their commonly used scarce and costly platinum-based catalysts impose a formidable barrier to large-scale adoption [1–4]. The platinum is employed to tackle the sluggish kinetics of the oxygen reduction reaction (ORR) on the cathode of metal-air batteries during the discharge [4, 5], lowering the overpotential to improve the round-trip efficiency. Hence,

great effort has been invested on the development of alternatives for the Pt catalyst, which are inexpensive, sustainable, and efficient towards ORR catalysis.

With earth-abundance and known ORR catalytic activities, nitrogen-doped carbon-based materials come out as a natural choice of alternative. They can be produced with a large surface area and high conductivity, enabling high ORR activity and stable physicochemical property [6, 7]. The N atoms doped into the carbon raise the electronic density of states near the Fermi level which will boost the electron transfer. Loading such nitrogen-doped carbon with transition metals optimizes the O_2 reduction pathway, facilitating the bond breaking of O_2 to furnish high catalytic stability and overall ORR activity [2, 3, 8–10]. Interestingly,

the presence of Fe on carbons was found to promote N-doping into carbon, giving an ORR catalyst with a four-electron pathway that promotes high ORR activity [2, 11, 12]. The catalytic activity can be further improved by incorporating Co into Fe/N-doped carbons, which not only activates the Fe sites but also improves the conductivity of the catalyst [10–12]. Hence, both Fe and Co on the N-doped commercial activated carbon (FeCo/N-C) have shown a much-improved ORR performance as compared to the single element Fe or Co on the same type of carbon catalyst (i.e., Fe/N-C and Co/N-C) [13]. In addition to the transition metal alloy, the Fe/Co double hydroxide has recently shown a promising bifunctional catalytic activity due to its improved electrical contact and adhesion to the carbon support [14].

Leguminous plants, such as those of peanuts and pistachio nuts, have a capability of nitrogen fixation in their growth [15], which can be promising to the presence of inherently nitrogen dopant in their carbonized form. With good balance of minerals, vitamins, and calories in their fruits, peanut and pistachio shells as biowaste account for 35–45% of their 47 and 1.1 million tons of annual global production, respectively [16–19]. Furthermore, peanut and pistachio shells have great potential to produce high surface area activated carbon as they contain a large amount of fixed carbon and volatile content as well as a small portion of ash which are beneficial to obtain highly porous carbon [20–22]. This opens an avenue to produce low-cost and environmentally benign carbons as ORR electrocatalysts for fuel cells and metal-air batteries. With aluminium-air battery (Al-air battery) possessing high-energy density (8076 Wh kg^{-1} , i.e., higher than most types of metal-air batteries), good safety, and low aluminium production and recycling costs [8, 23–25], such biomass-derived ORR electrocatalyst is likely a key to economic use of the batteries with good environmental sustainability.

This work reports an improved synthesis method of large surface area carbon-based catalysts prepared from peanut and pistachio shells. A combination of physical and chemical treatments followed by a one-step calcination to introduce FeCo nanoparticles and N dopant successfully yielded a carbon-based catalyst with desirable properties, leading to an improved ORR catalytic activity and enhanced performance of Al-air batteries, subsequently. It is found that the morphology of carbons has an impact on the content of Fe, Co, and N in the resultant catalyst, changing their electrochemical active surface area and thus ORR activity. Onset potential as low as 0.93 V vs. RHE can be achieved by FeCo alloy nanoparticle-loaded N-doped pistachio nut shell-derived carbons which are comparable to the more expensive and less sustainable source of carbon-based ORR catalysts that have been modified with the same elements in the literature [26–29]. An Al-air battery with such a catalyst is able to exhibit a promising power density and stable discharge voltage over 5 h of discharge time.

2. Materials and Methods

2.1. Synthesis of FeCo Alloy Nanoparticle-Loaded N-Doped Peanut/Pistachio-Derived Carbons. The fine powders of dried

pistachio and peanut shells (2 g each) were impregnated with 4 M KOH solution (Merck) for 2 days. The brown mixtures were then collected by filtration and dried in an oven at 80°C overnight. The pyrolysis was carried out at 800°C in a tube furnace (Carbolite Gero) with a heating rate of 7°C min^{-1} for 1 h under N_2 flow to obtain pistachio and peanut shell-derived carbon (C-pistachio and C-peanut, respectively). The obtained biomass-derived carbons were washed with 2 M HCl (Honeywell) and distilled water repeatedly and finally dried in an oven at 80°C for 12 h. 1.0 g of the C-pistachio and C-peanut samples was mixed thoroughly with 2.0 g of urea (EMSURE), 0.85 mmol of iron(III) acetylacetonate (Sigma-Aldrich), and 0.85 mmol of cobalt(III) acetylacetonate (Sigma-Aldrich) in an agate mortar. Aliquots of ethanol (Merck) were added to facilitate the grinding and left to dry naturally. The samples were then sent for heat treatment at 800°C with a heating rate of 7°C min^{-1} for 1 h under nitrogen flow to obtain FeCo alloy nanoparticle-loaded N-doped pistachio shell-derived carbon (FeCo/N-C-Pistachio) and FeCo alloy nanoparticle-loaded N-doped peanut shell carbon (FeCo/N-C-Peanut).

2.2. Material Characterizations. X-ray diffraction (XRD) analysis was performed on a Bruker D8 Advance diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54060 \text{ \AA}$). The morphologies were studied on a scanning electron microscope (SEM, HITACHI SU3500) and TEM (HT7700 and H9500 Hitachi). XPS data was collected on a Thermo Scientific VG ESCALAB 200i-XL spectrometer with monochromatized Al $\text{K}\alpha$ ($h\nu = 1484.6 \text{ eV}$). BET surface area (N_2 adsorption) of the powders was measured using a Nova Touch LX4 and processed using Quantachrome TouchWin v1.2 software. Samples were degassed for 3 h at 300°C under flowing N_2 .

2.3. Electrochemical Measurements. The catalytic activity of the samples during ORR were assessed with a three-electrode setup comprising a glassy carbon rotating disk electrode (diameter: 5 mm, Metrohm), platinum counter electrode, and Ag/AgCl (3 M KCl) reference electrode. The three electrodes were connected to a potentiostat (Metrohm Autolab PGSTAT302N). The catalyst ink was made by dispersing the powder of catalyst (9 mg) and Vulcan XC-72 carbon black (2.25 mg) into H_2O :IPA:Nafion (ratio: 2.5:1.0:0.094) solution. The ink was dropcasted onto the RDE to obtain the mass loading of 0.2 mg cm^{-2} . The same procedure was used to prepare commercial 20 wt% Pt/C (Alfa Aesar) as the benchmark catalyst. The electrodes were immersed into a 0.1 M KOH solution under a constant flow of oxygen gas. Linear scan voltammetry (LSV) was conducted with the sweeping rate of 5 mV s^{-1} at room temperature at various rotating speeds.

Al-air battery was assembled by using a homemade Al-air cell. A polished commercial Al plate (1100) was used as the anode. For each catalyst, the ink was made by mixing 4 mg of the catalyst with $26 \mu\text{L}$ of Nafion solution (5 wt %, Aldrich) in 1.8 mL of ethanol (Merck) followed by 1 h of sonication. The catalyst ink was then dropcast onto $2 \times 2 \text{ cm}^2$ Teflon-coated carbon paper, with a mass loading of about $\sim 1 \text{ mg cm}^{-2}$. Titanium mesh was employed as the current

collector at the cathode. The 20 mL of electrolyte which consisted of 6 M KOH, 0.0075 mol of ZnO, and 0.01 mol of Na_2SnO_3 was injected into the cell after assembly. The effective area of the air cathode was approximately about 0.79 cm^2 . The performance of Al-air batteries was assessed by using a potentiostat galvanostat machine (VersaSTAT 3). The discharge polarization curves were obtained from the galvanodynamic measurements. EIS measurements were performed at a constant voltage of 1.0 V, with frequency ranging from 20 kHz to 0.2 Hz and an amplitude of 20 mV. The discharge test was carried out at a constant discharge current of 10 mA cm^{-2} for 5 h.

3. Results and Discussion

The synthesis of FeCo alloy nanoparticle-loaded biomass-derived carbons is illustrated in Figure 1. The shells of pistachio nut and peanut are first ground into fine powders and immersed in a concentrated KOH solution. The brown mixtures are then filtrated, dried, and pyrolyzed in N_2 environment. The obtained carbons are labelled as C-pistachio and C-peanut. These samples are then mixed with urea, iron, and cobalt salts in a mortar which serve as the source of N, Fe, and Co, respectively. The iron and cobalt acetylacetonate are chosen as the salts due to their easy decomposition to yield the desirable metal compound without other impurities, [13, 30] while urea is preferred as the nitrogen source because of its rich nitrogen source and easy processing [31, 32]. Low amount and same ratio of the transition metal precursors are chosen to prevent the agglomeration and to obtain a relatively small size of the resultant FeCo nanoparticles on the carbon substrate [29, 33–35]. The mixtures were then ground thoroughly before their calcination in N_2 environment. The obtained samples are labelled as FeCo/N-C-Pistachio and FeCo/N-C-Peanut, respectively.

Scanning electron microscope (SEM) images of the four types of carbon-based samples are given in Figure 2. Both carbons derived from biomasses show an integrated hierarchical 3D porous structure with a smooth surface (Figures 2(a) and 2(b)). However, in comparison to the carbon obtained from the pyrolysis of peanut shell, the one from pistachio nut shells has more pores with irregular structures (Figure 2(a)). The finer structure of C-pistachio is desirable in electrocatalyst application where the large surface area will multiply the reaction sites for oxygen reduction reaction which is required during the discharge of Al-air batteries.

The BET measurements show a surface area of 1173.11 and $1246.4\text{ m}^2\text{ g}^{-1}$ for C-peanut and C-pistachio, respectively. The values are higher than those reported previously (about $800\text{ m}^2\text{ g}^{-1}$), benefitting from fine grinding of biomass and KOH treatment prior to the pyrolysis as an innovative attempt in this work [5, 7, 9, 21, 36, 37]. The surface area, especially for peanut shell-derived carbon, can be further improved by optimizing the physical grinding and the activation process (e.g., by using a larger concentration of KOH and higher ratio of KOH:biomass). After calcination with N, Fe, and Co precursors, both carbons retained their original morphology, except that the FeCo alloy nanoparticle-

loaded carbons show rougher surfaces as compared to the pristine carbons.

Transmission electron microscope (TEM) imaging is further performed to explore the morphology of the obtained samples. Clear and smooth layers of pistachio and peanut shell-derived carbons are shown in Figures 3(a) and 3(d), respectively, with their thin-sheet nature suggested by the nearly transparent feature. After calcination, some spherical nanoparticles are placed on the top of a thin carbon layer (Figures 3(b) and 3(e)), which are essentially the FeCo alloy nanoparticles. No free particles were found off the peanut/pistachio shell-derived carbon sheets, suggesting a good adhesion of FeCo alloy nanoparticles onto the carbon support. This firm attachment favors better charge transfer to enhance the catalytic activity [29, 38]. High-resolution TEM images (Figures 3(c) and 3(f)) further reveal the existence of spherical FeCo alloy nanoparticles ($<20\text{ nm}$ in diameter) on the carbon support.

The presence of FeCo alloy in the samples was further confirmed by the phase characterization using X-ray diffraction (Figure 4(a)). Similar XRD patterns are seen for the pistachio and peanut shell-derived carbons. The broad peaks around 2θ of 25° and 44° correspond to the (002) and (100) graphitic planes, respectively [39, 40]. After calcination with N, Fe, and Co precursors, more dominant peaks arise at 2θ of 44° due to the presence of (110) facets from FeCo alloy (JCPDS No. 65-6829) [41]. Additional peaks also appear at 65° and 82° which can be assigned to the (200) and (211) planes of the FeCo alloy, respectively [41, 42]. The XRD peaks reported in this work are similar to our previous work on FeCo alloy/activated carbon [13] and other FeCo alloy/carbon composites in the literature [27, 41].

Chemical composition of the samples is investigated with X-ray photoelectron spectroscopy (XPS), with FeCo/N-C-Pistachio and FeCo/N-C-peanut exhibiting the similar spectra (Supporting Information Figure S1). The C 1s, Fe 2p, Co 2p, and N 1s signals of the FeCo/N-C-Pistachio sample are given in Figures 4(b)–4(e). The C 1s spectra in Figure 4(b) can be deconvoluted into four peaks located at 284.97, 285.17, 286.1, and 288.79 eV, corresponding to C=C/C-C, C-N, C-O, and C=O bonding, respectively [1, 43]. The C-N bond spectra confirm nitrogen doping into peanut/pistachio shell-derived carbons. The core level XPS spectra of Co 2p and Fe 2p regions are consistent with the previous reports on FeCo alloy/carbon composite [44]. Spectrum of Fe 2p (Figure 4(c)) shows a pair of peaks that represent Fe $2p_{1/2}$ and Fe $2p_{3/2}$ doublets [45]. Those peaks can be deconvoluted into several peaks located at 708.43 and 719.33 eV that correspond to Fe^0 originated from FeCo alloy, followed by 715.24 eV and 724.30 eV that are deemed as the iron oxide or Fe-N species [27, 41]. Similarly, the Co 2p spectrum (Figure 4(d)) which confirms the presence of the Co element shows a pair of peaks that represent Co $2p_{1/2}$ and Co $2p_{3/2}$ doublets [46]. The deconvoluted peaks at 779.17 and 794.66 eV confirm the presence of the Co^0 component originated from the FeCo alloy, while the peaks at 780.71 and 797.47 eV are ascribed to the ionic states of cobalt derived from Co-N species [26, 41]. Other peaks can be attributed to the presence of shake-up satellites [41]. The

FIGURE 1: Schematic illustration on the synthesis of transition metal alloy nanoparticle-loaded N-doped nutshell-derived carbons.

FIGURE 2: SEM images of (a) C-Pistachio, (b) C-Peanut, (c) FeCo/N-C-Pistachio, and (d) FeCo/N-C-Peanut.

existence of FeCo alloy in the N-doped carbon matrix ensures the fast electron transport, while the oxidation state of metal active sites (e.g. Fe^0 and Co^0) contributes to the ORR activity significantly [26, 47]. The N 1s spectra in Figure 4(e) that is obtained due to the usage of urea in the experiment can be deconvoluted into three peaks at 398.78, 399.78, and 401.12 eV. Those peaks can be assigned to pyridinic/N-Co, pyrrolic, and graphitic N species, respectively [46, 48]. Despite the nitrogen-fixing property of the leguminous plants, the trace of nitrogen is not detected in C-peanut as well as C-pistachio (Supporting Information Figure S2 and S3) which is probably due to the harsh KOH treatment

prior the pyrolysis and the cooked nutshells that were used in this study [5]. Generally, nitrogen configuration significantly affects the structure and the activity of the doped carbon [49, 50]. Graphitic N and pyridinic N are beneficial to enhance the ORR activity by providing additional active sites for O_2 adsorption and helping to weaken the O-O bond [46, 51]. In addition, pyridinic bonds are known to be advantageous in reducing the energy barrier as well as facilitating the electron transfer during the ORR process [52].

Quantitative XPS analysis further provides atomic composition for the elements that are present in FeCo/N-C

FIGURE 3: TEM images of (a) C-Pistachio, (b) FeCo/N-C-Pistachio, (d) C-Peanut, and (e) FeCo/N-C-Peanut. HRTEM images of (c) FeCo/N-C-Pistachio and (f) FeCo/N-C-Peanut.

Pistachio and FeCo/N-C Peanut (Table 1). Similar at% of Fe and Co has been reported in the FeCo alloy/carbon composite in the literature [41]. The FeCo/N-C-Pistachio contains higher atomic percentage of Fe, Co, and N as compared to the FeCo/N-C-Peanut. The amount of N dopant in the FeCo/N-C-Pistachio is about 1.5 times that of the FeCo/N-C-Peanut, while the composition of Fe and Co in the FeCo/N-C-Pistachio is at least two times that of their respective composition in the FeCo/N-C-Peanut. The higher content of N, Fe, and Co in FeCo/N-C-Pistachio can be associated with the finer structure and large surface area of C-pistachio that helps the incorporation of N as well as enhances nucleation sites of FeCo alloy during the calcination process. The higher amount of FeCo alloy and N dopant on the FeCo/N-C-Pistachio is beneficial to provide abundant defect sites in the carbon matrix, serving as active sites to promote and accelerate the electrochemical reactions [28, 53, 54].

All the catalyst samples are then assessed with respect to their catalytic activity toward oxygen reduction reaction (ORR) in alkaline medium using the rotating disc electrode (RDE) in three-electrode configuration. The linear scan voltammetries (LSV) were conducted to quantify the catalytic activity of the catalysts by measuring their onset potential (E_{onset}), half-wave potential ($E_{\text{half-wave}}$), saturating current density (j_{sat}), and electron transfer number (n) (Table 2). Figure 5(a) shows linear scan voltammetry (LSV) curves of the samples at rotation speed of 1600 rpm in 0.1 M KOH electrolyte. The LSV scans were also performed on the commercial Pt/C and Vulcan XC-72 carbon black as the benchmark catalysts. The onset potential of the catalysts is determined as the potential at the current density of -0.1 mA cm^{-2} [55]. The onset potential and saturating current density of our Pt/C benchmark is consistent with the data reported in the literature [39, 56]. As can be seen in

FIGURE 4: (a) XRD patterns of C-Pistachio, C-Peanut, FeCo/N-C-Pistachio, and FeCo/N-C-Peanut. XPS spectra of (b) C 1s, (c) Fe 2p, (d) Co 2p, and (e) N 1s of FeCo/N-C-Pistachio.

TABLE 1: Element atomic percentage of FeCo/N-C-Pistachio and FeCo/N-C-Peanut measured by XPS spectra.

Sample	Atomic %				
	C 1s	N 1s	O 1s	Fe 2p	Co 2p
FeCo/N-C-Pistachio	90.99	2	4.79	1.11	1.11
FeCo/N-C-Peanut	95.23	1.21	2.98	0.4	0.18

Figure 5(a) and Table 2, all the as-synthesized catalysts show an enhanced catalytic activity as compared to the commercial carbon black.

In general, the pistachio shell-derived carbons show an enhanced catalytic activity as compared to the catalysts which are derived from the peanut shells. Among the pristine biomass-derived carbon catalysts (i.e., C-pistachio and C-peanut), the improved catalytic activity can be related to the large surface area of the material, which leads to a wide electrochemical active surface area of the catalyst. In order to determine the electrochemical active surface area of the catalysts, the electrochemical double-layer capacitance (C_{dl}) is extracted from the cyclic voltammetry (CV) scans of various scan rates at a potential region where no faradaic

TABLE 2: ORR activity of each catalyst as quantified by onset potential, half-wave potential, and saturating current density.

Sample	Onset potential, E_{onset} (V)	Half-wave potential, $E_{\text{half-wave}}$ (V)	Saturating current density, j_{sat} (mA cm ⁻²)	Electron transfer number, n	Electrochemical double-layer capacitance, C_{dl} (mF)	BET surface area, S_{BET} (m ² g ⁻¹)
C-Pistachio	0.89	0.73	3.69	3.3	1.7	1246.4
FeCo/N-C-Pistachio	0.93	0.83	4.49	3.8	0.3	291.6
C-Peanut	0.86	0.69	3.34	3.3	1.6	1173.1
FeCo/N-C-Peanut	0.91	0.79	4.34	3.6	0.1	235.6
Vulcan XC-72 carbon black	0.82	0.68	3.09	2.83	—	—
Pt/C	1.04	0.89	4.40	4	—	—

process is observed (Supporting Information Figure S4) [12]. C_{dl} as high as 1.7 and 1.6 mF can be obtained from C-pistachio and C-peanut, respectively, suggesting the larger electrochemical active surface area of C-pistachio as compared to the C-peanut catalyst.

The FeCo/N-C-Pistachio catalyst shows the most desirable onset potential, half-wave potential, and saturating current density among all the nutshell-derived carbon catalysts. The onset potential of FeCo/N-C-Pistachio catalysts is about 0.93 V, 0.11 V less positive than that of the Pt/C benchmark catalyst, which can be attributed to the low conductivity of the nutshell-derived carbon catalysts. Its promising catalytic activity is further supported by the large saturating current density at about 4.49 mA cm⁻². This high value was attributed by the large surface area and high amount of N, Fe, and Co which enhances mass and charge transfer of the catalysts [57]. By alloying Co and Fe to form the bimetallic FeCo alloy, the d-band center of Fe can be tuned down relative to its Fermi level, enhancing the electrochemical active surface area for better electrocatalytic performance [58, 59]. The enhanced electrochemical active surface area of FeCo/N-C-Pistachio originates from its enlarged area in the cyclic voltammogram as compared to FeCo/N-C-Peanut (Figure 5(f) and Supporting Information Figure S5). Furthermore, despite having a lower C_{dl} (0.3 mF) and surface area (291.6 m² g⁻¹) relative to those of C-pistachio, the onset potential of FeCo/N-C-Pistachio (0.93 V) is more positive as compared to the pristine C-pistachio (0.89 V). This is in agreement with the literature where the large surface area of carbon may not necessarily result in the superior catalytic activity as compared to its counterpart that has been modified with transition metals [60]. Moreover, the low onset potential of FeCo/N-C-Pistachio is comparable to a more expensive and less sustainable source of carbon-based catalysts (e.g., CNT, graphene, and commercial carbon) that have been modified with Fe, Co, and N elements (Supporting Information Table S1) [26–29]. Besides that, the presence of FeCo alloy and N dopant results in the steeper slope and larger saturating current density than that of C-pistachio, suggesting the enhanced reaction kinetics. Similar observation can be seen at FeCo/N-C-Peanut and C-peanut catalysts. These results are aligned with the previous reports where the incorporation of transition metals and N dopant into the carbon-based materials results in the improved ORR catalytic activity. In particular, alloys with two dissimilar transition

metals, such as FeCo, have an intrinsic polarity to allow the exclusive reaction pathways for an efficient ORR process [27].

K-L plots were generated from the LSV polarization curves at various rotation rates to understand the catalytic mechanism of each sample (Figures 5(b)–5(e)). Their average of electron transfer number (n) per oxygen molecule can be extracted from the least-square-fitted slope of the respective K-L plot on the basis of the Koutecky-Levich equation. It is found that FeCo/N-C-Pistachio and FeCo/N-C-Peanut catalysts have electron transfer numbers of 3.8 and 3.6, respectively, indicating a more favored four-electron oxygen reduction pathway in the FeCo/N-C-Pistachio catalyst as compared to the latter. The number is around 3.3 for both C-pistachio and C-peanut catalysts, suggesting the involvement of a two-electron transfer pathway with formation of detrimental peroxide species. The desirable electron transfer number of the FeCo/N-C catalysts is associated with the presence of Fe metal and N dopant (i.e., pyridinic bond) which are known to facilitate the electron transfer during the ORR [2, 11, 12, 52]. In particular, the pyridinic bonds will promote the nearby C atoms as the Lewis basic sites that assist the adsorption of O₂ molecules, hence improving the kinetics of the ORR [61, 62].

The nutshell-derived carbons are used as a catalyst in Al-air batteries to improve the ORR kinetics during the discharge of batteries. The galvanodynamic discharge curves and the corresponding power densities of these batteries are given in Figures 6(a) and 6(b). The good discharge profile and high power density of the Al-air battery with Pt/C catalyst are in agreement with the high ORR activity of Pt/C revealed by the RDE study. Among the batteries with the nutshell-derived carbon-based catalysts, Al-air battery with the FeCo/N-C-Pistachio catalyst shows the smallest overpotential at all current densities, which is agreeable with the trend observed in the RDE study (Table 2). Its power density is up to 99.7 mW cm⁻², higher than that in previous works on Al-air batteries with a reported power density of no greater than 92 mW cm⁻² (Supporting Information, Table S3) [24, 63–65].

The resistance of Al-air batteries was investigated with electrochemical impedance spectroscopy (EIS) measurements (Figure 6(c)). The obtained Nyquist plots of all prepared batteries exhibit a semicircle shape that can be fitted to the equivalent circuit consisting of solution resistance (R_s), solid/electrolyte interface resistance (R_{int}), charge-transfer resistance (R_{ct}), and the constant phase elements (Q_{int} and

FIGURE 5: (a) Oxygen reduction polarization curves of the carbon-based catalysts at rotation speed of 1600 rpm. The performance of the catalysts is compared to Pt/C and Vulcan XC-72 carbon black. Oxygen reduction polarization curves of the carbon-based catalysts in different rotation speeds and their corresponding Koutecky-Levich plots: (b) C-Pistachio, (c) C-Peanut, (d) FeCo/N-C-Pistachio, and (e) FeCo/N-C-Peanut. (f) Cyclic voltammogram of FeCo/N-C-Pistachio and FeCo/N-C-Peanut catalysts at a scan rate of 100 mV s⁻¹.

FIGURE 6: Performance of Al-air batteries with Pt/C and peanut/pistachio shell-derived carbon-based catalysts: (a) galvanodynamic discharge curves, (b) power density plots, (c) Nyquist plots from the electrochemical impedance spectroscopy (EIS) measurements, and (d) full discharge curves at discharge current density of 10 mA cm^{-2} .

Q_{dl}) [63]. A comparable solution resistance (R_s) of battery with FeCo/N-C-Pistachio and FeCo/N-C-Peanut catalysts to the battery with Pt/C catalysts can be associated with the improved intrinsic conductivity of carbon upon the introduction of FeCo alloy and N dopant (Supporting Information, Table S2). The incorporated FeCo alloy and N dopant are also beneficial to provide a facile electron pathway, leading to a lower charge transfer resistance (R_{ct}) of the battery with FeCo/N-C-Pistachio and FeCo/N-C-Peanut catalysts as compared to those with the pristine carbon catalysts. Discharge curves of all batteries are given in Figure 6(d). Al-air batteries with FeCo/N-C-Pistachio and FeCo/N-C-Peanut catalysts are able to provide a stable and high discharge

voltage of 1.37 V (about 0.05 V lower than that of battery with Pt/C catalyst) for 5 h of discharge time at a current density of 10 mA cm^{-2} . These results can be used as further evidence of the promising application of FeCo alloy-decorated N-doped pistachio/peanut shell-derived carbon as a sustainable and efficient ORR catalyst for Al-air batteries.

4. Conclusions

We report a general approach for the synthesis of transition metal alloy nanoparticle-loaded N-doped nutshell-derived carbon for the application of sustainable oxygen electrocatalyst in Al-air batteries. Large surface area of peanut and

pistachio shell-derived carbons (1173.11 and 1246.4 m² g⁻¹, respectively) can be obtained. These results are attributed to the fine grinding followed by immersion of biomass in concentrated KOH, resulting in the improved surface area of nutshell-derived carbon as compared to the previous works. Such a large surface area carbon allows more nitrogen doping and enhances nucleation sites for FeCo alloy nanoparticles in FeCo/N-C-Pistachio which leads to an enhanced electrochemically active surface area of FeCo/N-C-Pistachio as compared to that of FeCo/N-C-Peanut. Among all the synthesized samples, the FeCo/N-C-Pistachio catalyst displays the most promising onset potential and saturating current density which is comparable to the more expensive and less sustainable source of FeCo/carbon-based ORR catalysts in the literature. In addition, its application as an ORR catalyst in Al-air batteries has been demonstrated, achieving a power density of up to 99.7 mW cm⁻². The low-cost, sustainable, and efficient ORR catalyst from the abundant biomass waste reported in this study is paving the path for commercialization of high-performance Al-air batteries.

Conflicts of 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.

Authors' Contributions

A. S. was responsible for the conceptualization, methodology, validation, formal analysis, resources, data curation, writing (specifically the original draft and the review and editing), supervision, project administration, and funding acquisition. B. P. was responsible for the formal analysis, investigation, data curation, writing (specifically the original draft and the review and editing), visualization, and funding acquisition. Y. M. was responsible for the methodology, formal analysis, investigation, data curation, and writing (specifically the review and editing). F. R. I. was responsible for the methodology, formal analysis, investigation, data curation, writing (specifically the original draft), and visualization. J. J. H. was responsible for the formal analysis, investigation, data curation, and writing (specifically the original draft and the review and editing). A. M. was responsible for the investigation, data curation, writing (specifically the original draft and the review and editing), and visualization. M. A. A. M. was responsible for the investigation, data curation, writing (specifically the original draft and the review and editing), and visualization. Y. Z. was responsible for the conceptualization, validation, formal analysis, resources, and writing (specifically the review and editing). Z. L. was responsible for the conceptualization, validation, formal analysis, resources, writing (specifically the review and editing), and supervision.

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Supplementary Materials

S1: calculation of electron transfer number. S2: XPS spectra of FeCo/N-C-Peanut, C-peanut, and C-pistachio. S3: cyclic voltammogram and the corresponding double-layer capacitance of the nutshell-derived carbon-based catalyst. S4: ORR activity of the benchmark catalysts. S5: digital image of aluminium-air battery. S6: performance of FeCo/N-doped carbon as ORR catalyst in the literature. S7: performance of the aluminium-air batteries with various catalysts. S8: performance of aluminium-air batteries in the literature. (*Supplementary Materials*)

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