ABSTRACT: Carbon black nanospheres were turned to hollow carbon nanospheres (HCNs) and were used as the conductive additive in the cathodes of Li-ion batteries (LIBs). The results show that 10 wt % HCN added to the LIB cathodes, such as LiMn$_2$O$_4$, LiCoO$_2$, LiNiMnCoO$_2$, and LiFePO$_4$, can provide significantly higher specific capacity than those using spherical carbon black. For example, a specific capacity of the LiMn$_2$O$_4$/HCN/PVDF cathode at 80:10:10 wt % with a bulk electrical conductivity of 1.07 $\Omega$ cm$^{-1}$ is 125 mA h g$^{-1}$ at 0.1 C from 3.0 to 4.3 V versus Li$^+/\text{Li}$, which is 3.85-fold higher than that using Super P. The stability tested at 1 C remains over 95% after 800 charge/discharge cycles with 100% Coulombic efficiency. Replacing the present carbon black conductive additive with HCN in this work may be one of the best choices to increase the charge storage performance of LIBs rather than only focusing on the development of active cathode materials.

INTRODUCTION

Li-ion batteries (LIBs) have been widely used in many applications, for example, mobile phones, laptops, electric vehicles, and hybrid electric vehicles because of their high energy densities ($\sim$100–170 Wh kg$^{-1}$) and long cycle life. The present materials used in the cathode of LIBs consist of three main components: (i) ca. 80 wt % of active materials such as LiCoO$_2$ (LCO), LiMn$_2$O$_4$ (LMO), LiNi$_x$Co$_{1-x}$Al$_{1/3}$O$_2$ (NCA), LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ (NMC), and LiFePO$_4$ (LFP) and composite materials, (ii) ca. 10 wt % conductive additives (i.e., spherical carbon black, Super P), and (iii) ca. 10 wt % polymer binders [i.e., polyvinylidene fluoride (PVDF) and poly(tetrafluoroethylene) (PTFE)].

For example, LiMn$_2$O$_4$ having a spinel structure (space group Fd$\beta$m) with a poor electrical conductivity ($\sim$10$^{-6}$ S cm$^{-1}$) mixed with carbon black (e.g., Super P) and PVDF at a weight ratio of 8:1:1 can provide a discharge specific capacity of 82.6 mA h g$^{-1}$ at 0.05 A g$^{-1}$. The LiMn$_2$O$_4$ rods were mixed with carbon black and PTFE (8:1:1 by weight), providing 96.8 mA h g$^{-1}$ at 0.5 C. The LiMn$_2$O$_4$ nanowires (NWs) mixed with acetylene black and PVDF at a weight ratio of 8:1:1 exhibit 94.7 mA h g$^{-1}$ at 1 C. Up to now, about 10–20 wt % spherical carbon black (Super P) is routinely used in the fabrication process of the LIB cathodes. However, those specific capacities are still far lower than a theoretical value of LiMn$_2$O$_4$. Besides, a simple question is why spherical carbon is extensively used as a conductive additive in LIBs.

In this work, spherical carbon black nanoparticles (CNs) were turned to oxidized CNs (OCNs) and hollow carbon nanospheres (HCNs). They were then used as the conductive additive in fabricating the cathodes of LIBs. For comparison, four grades of the CN widely used, namely, EC300J (CN-1), Super P (CN-2), Denka (CN-3), and ENSACO (CN-4), were also employed as the conductive additives. The LIB cathodes include LiMn$_2$O$_4$, LiCoO$_2$, LiNiMnCoO$_2$, and LiFePO$_4$ which are currently used in the commercial LIBs. Interestingly, we have found in this work that among carbon conductive additives, HCN can provide rather high specific capacities for all LIB cathodes because of its outstanding physicochemical property. The as-fabricated coin cell LiMn$_2$O$_4$ battery with a CR-2025 size using 10 wt % HCN as a conductive additive in the cathode exhibits 125 mA h g$^{-1}$ at 0.1 C, which is 3.85-fold higher than that using the conventional conductive additive, CN (Super P), and higher than that in other previous reports.

RESULTS AND DISCUSSION

Morphological and Structural Characterizations. Transmission electron microscopy (TEM) images in Figure 1a–d show the spherical shapes of EC300J (namely, CN-1), Super P (CN-2), Denka (CN-3), and ENSACO (CN-4), with a diameter of around 30–50 nm in the primary spherical particles. All of them are stable in an aggregated structure, forming a so-called high structure, leading to high electrical conductivity. Especially, CN-1 particles aggregated have a void fraction in their particles. Obviously, the spherical shape of the primary particles is not geometrically ideal for entirely coating...
The microscale particles such as LiMn$_2$O$_4$, LiCoO$_2$, LiNiMnCoO$_2$, and LiFePO$_4$, which are used as the active materials of the LIB cathodes.

After the oxidation process, the spherical shape of CN-2 was turned to OCN with graphene multilayers, which is obviously seen in Figure 2a,b. After the reduction process of OCN with graphene multilayers, which is obviously the LIB cathodes.

The functional groups of the samples characterized by Fourier transform infrared (FTIR) spectroscopy are shown in Figure 3b. A peak at 1724 cm$^{-1}$ is due to the stretching vibrational mode of the carbonyl group (C=O). The C=O stretching vibration is from the alcoholic and carboxylic groups at ca. 1323 cm$^{-1}$. The peaks at 2660 and 1620 cm$^{-1}$ indicate the C=H and C=O groups, respectively. The FTIR results here confirm that the acid oxidation process can introduce the oxygen-containing functional groups, mainly the carboxylic group on the OCN surface. Consequently, the oxygen-functional peaks of HCN reduced and disappeared after the reduction process. Without oxygen-containing groups, HCN is an ideal conductive additive, not leading to the parasitic reactions when cycling the LIBs.

Figure 3c shows the X-ray diffraction (XRD) patterns of the samples, exhibiting the diffraction peaks at 2θ of ca. 25° and 44° assigned to the (002) and (100) planes of the graphitic carbon, respectively. The average stacking heights ($L_c$) of CN-1, OCN, and HCN calculated by the Scherrer equation are 1.39, 0.94, 1.00, 0.94, 1.27, and 1.10, respectively. The average lateral sizes ($L_a$) of the layer structures in the samples calculated from Raman spectra ranged from 3.42 to 4.65 nm, as listed in Table 1.

From high-resolution transmission electron microscopy (HR-TEM) images, the curvature graphene layers are clearly observed for both OCN and HCN samples (see the inset images in Figure 2b,d). Notably, the electrical conductivity of carbon conductive additives is due to electron delocalization in the graphene sheets. The resistance of LiMn$_2$O$_4$/HCN/PVDF (8:1:1 wt %) measured by a four-point probe (Jandel) is 1.07 Ω cm$^{-2}$, which is lower than 1.80 Ω cm$^{-2}$ of LiMn$_2$O$_4$/CN-2/PVDF (8:1:1 wt %) (see Table S1 and Figure S1 of Supporting Information). This result indicates the high electrical conductivity of HCN over CN-2.

Raman spectra in Figure 3a display two main peaks of D and G bands at ca. 1350 and 1587 cm$^{-1}$, respectively. Theoretically, the G band is attributed to the stretching mode of the C=C bond in a benzene ring. The G band is related to the vibrational mode of sp$^3$ carbon atom from the disordered structure. The amount of disordered carbon structures can be estimated by a peak intensity ratio between D and G bands ($I_D/I_G$). The $I_D/I_G$ values of CN-1, CN-2, CN-3, CN-4, OCN, and HCN are 1.07, 0.94, 1.00, 0.94, 1.27, and 1.10, respectively. The average lateral sizes ($L_a$) of the layer structures in the samples calculated from Raman spectra ranged from 3.42 to 4.65 nm, as listed in Table 1.

The N$_2$ adsorption and desorption were characterized to investigate the specific surface area and porous characteristics of the samples (Figure 3d). The gas adsorption isotherm of the HCN sample relates to the type IV isotherm, according to the IUPAC classification. The carbon black samples exhibit the mesoporous characteristics, which are found in the range of 2–50 nm, according to the pore size distributions (the inset image of Figure 3d). The Brunauer–Emmett–Teller (BET) equation was used to calculate the BET specific surface areas of all samples, which are 168.16–723.47 m$^2$ g$^{-1}$, as listed in Table 1. The HCN shows higher specific surface area than that of CN-2 (Super P), the material precursor.
Figure 4a shows a field-emission scanning electron microscopy (FE-SEM) image of the crystalline LiMn$_2$O$_4$ that has a hexahedron shape. Figure 4b–f shows the morphology of the LiMn$_2$O$_4$ cathode mixed with conductive additive and PVDF (80:10:10 wt % ratio) before and after being charged/discharged for 1, 25, 50, and 100 cycles. The results clearly illustrate that the morphology of the tested LiMn$_2$O$_4$ remains almost the same as that tested before. This indicates the high stability of LiMn$_2$O$_4$.

**Electrochemical Property.** To further understand the electrochemical property of the HCN, the cyclic voltammograms (CVs) of HCN and its composite with 80 wt % active material LiMn$_2$O$_4$ and 10 wt % polymer binder PVDF versus a standard redox mediator (ferrocenemethanol, FcOH) with one electron-transfer reversible process were investigated. For comparison, the CVs of LiMn$_2$O$_4$ and CN as well as their composites coated on glassy carbon (GC) electrodes are also shown in Figure 5. Figure 5a shows a control experiment for which the CVs of bare GC in 1.6 mM FcOH in 0.1 M KCl at different scan rates have a reversible feature, indicating a...
The CVs of bare LiMn$_2$O$_4$ coated on GC shown in Figure 5b with lower currents indicate that an insulating LiMn$_2$O$_4$ layer can block the redox reaction of FcOH at the GC electrode. This is because LiMn$_2$O$_4$ occupies an active surface area of GC. On the other hand, the CN layer clearly shows an adsorption effect, preconcentrating FcOH (Fe$^{2+}$) mediator, leading to a significant enhancement in the anodic current (see Figure 5c). However, the CN layer on the GC surface has an irreversible feature with a lower cathodic current when compared to the anodic current. Interestingly, the HCN layer can provide both higher anodic and cathodic currents when compared with those of the bare LiMn$_2$O$_4$-coated GC. In addition, it has a reversible redox reaction characteristic and high capacitive current, which is good for the energy storage application. Also, the diffusion limit of FcOH through the HCN layer is not so high when compared with those of other systems. When CN and HCN were mixed with LiMn$_2$O$_4$ and PVDF at a ratio of 10:80:10 wt % and coated on the GC electrodes, the CVs in Figure 5d,e clearly show that CN and HCN are great in terms of electrical conductivity, providing a reversible redox reaction of FcOH (Fe$^{2+/3+}$) and significantly enhancing both anodic and cathodic currents when compared with those of the bare LiMn$_2$O$_4$-coated GC. In addition, the reversible behavior was quantitatively measured by the ratio of the anodic/cathodic peak current ($i_{pa}/i_{pc}$), as listed in Table 2. The GC shows a reversible behavior with $i_{pa}/i_{pc}$ equal to 1.00 at all scan rates. Also, LiMn$_2$O$_4$/GC has the reversible characteristics with an $i_{pa}/i_{pc}$ ratio of 0.98−1.0 for different scan rates. Surprisingly, CN-2, which is widely used as a conductive additive in commercial LIBs, and its composite with LiMn$_2$O$_4$ and PVDF provide rather high $i_{pa}/i_{pc}$ values (2.2−4.2), which are very much higher than 1.0, a theoretical value of an ideal reversible process (see Table 2). By contrast, HCN provides desirable $i_{pa}/i_{pc}$ values that are closer to 1.0. Note that a reversible process is needed for an ideal energy storage material because it can provide high Coulombic efficiency.

![Figure 5. CVs of (a) bare GC electrode, (b) LiMn$_2$O$_4$, (c) CN, (d) HCN, (e) CN/LiMn$_2$O$_4$, and (f) HCN/LiMn$_2$O$_4$ using 1.6 mM FcOH as a redox mediator in 0.1 M KCl with scan rates of 10−100 mV s$^{-1}$.](image)

Table 2. Ratio of Anodic and Cathodic Current ($i_{pa}/i_{pc}$) Values of Bare GC Electrode and Coated Materials Using 1.6 mM FcOH as a Redox Mediator in 0.1 M KCl with Different Scan Rates

| scan rate (mV s$^{-1}$) | GC  | LiMn$_2$O$_4$ | CN-2 | HCN   | CN-2/LiMn$_2$O$_4$ | HCN/LiMn$_2$O$_4$ |
|------------------------|-----|--------------|------|--------|-------------------|-------------------|
| 10                     | 1.00| 0.99         | 4.16 | 0.96   | 0.89              | 1.02              |
| 25                     | 1.00| 1.00         | 3.00 | 0.82   | 0.73              | 0.99              |
| 50                     | 1.00| 0.99         | 2.56 | 0.88   | 0.67              | 1.03              |
| 75                     | 1.00| 0.98         | 2.28 | 0.86   | 0.73              | 0.96              |
| 100                    | 1.00| 1.00         | 2.21 | 0.87   | 0.66              | 0.99              |
Figure 6 shows the Nyquist plots of (a) bare GC rotating disc electrode (GC RDE), (b) LiMn$_2$O$_4$, (c) CN, (d) HCN, (e) CN/LiMn$_2$O$_4$, and (f) HCN/LiMn$_2$O$_4$ coated on GC RDEs in 1.6 mM FcOH in 0.1 M KCl with different rotation rates. The experiments were carried out at 0.1 Hz–10 kHz, an amplitude of 0.01 V, and with 50 harmonic frequencies data.

Table 3. Standard Heterogeneous Rate Constant of FcOH (Fe$^{2+}$/Fe$^{3+}$) at GC RDE and CN, HCN, CN/LiMn$_2$O$_4$, and HCN/LiMn$_2$O$_4$ Coated on GC RDEs at Different Rotation Rates

| rotation rates (rpm) | GC  | LiMn$_2$O$_4$ | CN  | HCN | CN/LiMn$_2$O$_4$ | HCN/LiMn$_2$O$_4$ |
|----------------------|-----|---------------|-----|-----|------------------|------------------|
| 0                    | 49.13 | 20.83       | 30.68 | 38.96 | 23.07          | 27.92          |
| 500                  | 52.65 | 21.40       | 32.19 | 41.51 | 24.06          | 28.98          |
| 1000                 | 56.03 | 22.41       | 33.86 | 43.10 | 24.82          | 30.02          |
| 2000                 | 58.40 | 23.30       | 35.34 | 46.24 | 25.80          | 31.30          |
| 3000                 | 60.66 | 24.01       | 37.18 | 48.72 | 26.62          | 32.19          |
| 4000                 | 63.95 | 25.86       | 38.52 | 50.94 | 27.62          | 33.43          |
| 5000                 | 70.88 | 26.50       | 40.37 | 53.00 | 28.18          | 35.02          |

Figure 6 shows the Nyquist plots of the samples with different rotation speed rates of GC rotating disc electrode (RDE) from 0 to 5000 rpm. The Nyquist plot of LiMn$_2$O$_4$ exhibits the highest resistance of charge transfer because of the kinetically sluggish of the insulating material. When the conductive additives CN and HCN were mixed with the active material, it can be clearly observed that HCN possesses lower charge-transfer resistance. The equivalent circuit (the inset image of Figure 6a) was used to fit the experimental data, where $R_s$ is the resistance in solution, $R_{ct}$ is the charge-transfer resistance, $C_{dl}$ is the double-layer capacitance, and $W$ is the Warburg impedance, which represents the interfacial diffusive resistance. The standard heterogeneous rate constant of electron transfer ($k^0$, cm s$^{-1}$) was calculated from eq 1. The $k^0$ values of all materials with different rotation rates as listed in Table 3 indicate that when HCN was used, the rate of charge transfer was increased, which is an ideal property for the conductive additive.

$$k^0 = \frac{RT}{nF^2AC_{R_{ct}}}$$

Charge Storage Performance. For the charge storage capacity, the as-fabricated LiMn$_2$O$_4$ electrode was electrochemically evaluated using a galvanostatic charge/discharge (GCD) technique. The specific capacity of the first charge/discharge profiles at 0.1 C from 3.0 to 4.3 V versus Li$^+$/Li is shown in Figure 7a. The results indicate that the battery using HCN as the conductive additive exhibits a specific capacity of ca. 125 mA h g$^{-1}$, which is ca. 3.85-fold higher than those of the batteries using the pristine CN-2 (Super P) at 0.1 C. Note that
Table 4 also compares the charge storage performances of the LiMn2O4-based batteries for which the as-fabricated battery here in this work provides significantly higher specific discharge capacity than that in other previous reports.

Figure 7b also clearly shows that the LiMn2O4/HCN/PVDF (8:1:1 wt %) cathode has the highest discharge specific capacity for all applied C rates (0.1–4 C). The stability of the as-fabricated LiMn2O4/HCN/PVDF cathode was eventually evaluated over 800 cycles at 1 C. Its capacity retention remains over 95% with a Coulombic efficiency of 100% (see Figure 7c).

To further investigate the advantages of using HCN as the conductive additive in LIBs, other cathode materials of the present LIBs, such as LiCoO2, LiNiMnCoO2, and LiFePO4, were also employed, and their charge storage performances are shown in Figure 7d–f. The LiCoO2 (Figure 7d), LiNiMnCoO2 (Figure 7e), and LiFePO4 (Figure 7f) batteries using HCN exhibit significantly higher discharge specific capacities at 0.1 C when compared with those using CN (see their charge/discharge profiles in Figure S2 of Supporting Information). The specific capacities of LiCoO2, LiNiMnCoO2, and LiFePO4 are ca. 106, 124, and 169 mA h g−1, respectively, which are also higher than those in other reports. As a result, it can be concluded here that including 10 wt % HCN to the cathodes of the present LIBs can significantly improve the overall charge storage performance of the cathodes of LIBs.

The Mn K-edge X-ray absorption near-edge structure (XANES) spectra of the LiMn2O4 cathodes before and after

**Table 4. Charge Storage Performances of the LiMn2O4-Based Batteries**

| cathode materials (wt %)                  | specific discharge capacities (mA h g⁻¹) | ref |
|-------------------------------------------|-----------------------------------------|-----|
| LiMn2O4/carbon black/PVDF (9:0.5:0.5)     | 92.76                                   | 35  |
| LiMn2O4/carbon black/PVDF (9:0.5:0.5)     | 88                                      | 36  |
| LiMn2O4 NWs/carbon black/PVDF (8:1:1)     | 94.7                                    | 20  |
| LiMn2O4/carbon black/PVDF (8:1:1)         | 82.6                                    | 18  |
| LiMn2O4 NWs/carbon black/PTFE (8:1:1)     | 96.8                                    | 19  |
| LiMn2O4/carbon black/PVDF (8:5:0.75:0.75)| 87.5                                    | 37  |
| LiMn2O4 with graphite/PVDF (9:9:0.1)      | 96                                      | 38  |
| LiMn2O4 thin film                         | 85                                      | 39  |
| LiMn2O4/carbon black/PVDF (7:1:2)         | 96.19                                   | 40  |
| LiMn2O4/carbon black/PVDF (7:5:2:0.5)     | 87                                      | 41  |
| LiMn2O4/carbon black/PVDF (7:2:1)         | 93.7                                    | 42  |
| LiMn2O4/HCN/PVDF (8:1:1)                 | 125                                     | this work |

**Figure 7.** (a) GCD curves of LiMn2O4 LIBs with the potential ranging from 3.0 to 4.3 V vs Li+/Li at 0.1 C; (b) specific discharge capacity of LiMn2O4 LIBs as a function of cycle number; (c) specific capacity retention and Coulombic efficiency of LiMn2O4 LIBs at 1 C for 800 cycles; and specific discharge capacities as a function of cycle number of (d) LiCoO2 (LCO), (e) LiNiMnCoO2 (NMC), and (f) LiFePO4 (LFP) using Super P (CN-2) and HCN as the conductive additives.
being electrochemically tested by the GCD are shown in Figure 8a. The average oxidation number of Mn in the LiMn$_2$O$_4$ cathode before being charged is +3.45. The average oxidation numbers of Mn after being tested for 25, 50, and 100 cycles are close to +3.45 (see Figure 8b). This result indicates that the Li ions intercalate/deintercalate through the LiMn$_2$O$_4$ structure via a reversible reaction process without a parasitic reaction.

### CONCLUSIONS

The commercial spherical CNs such as EC300J (CN-1), Super P (CN-2), Denka (CN-3), and ENSACO (CN-4) as well as OCN and HCN were used as the conductive additives in the cathodes of the commercial LIBs, such as LiMn$_2$O$_4$, LiCoO$_2$, LiNiMnCoO$_2$, and LiFePO$_4$. For example, the as-fabricated LiMn$_2$O$_4$ cathode using 10 wt % HCN as the conductive additive exhibits a specific capacity of 125 mA h g$^{-1}$, which is 3.85-fold higher than that of the battery using CN at 0.1 C with a potential ranging from 3.0 to 4.3 V versus Li$^+$/Li. The capacity retention is over 95% after 800 cycles with 100% Coulombic efficiency at 1 C. In addition, the HCN can significantly improve the charge storage performances of other commercially available LIB cathodes such as LiCoO$_2$, LiNiMnCoO$_2$, and LiFePO$_4$ because of its high surface area and high ionic conductivity. This work indicates the influence of the superior conductive additive HCN to the charge storage performance of the LIB cathodes. The HCN in this work may be one of the best choices to increase the charge storage performance of LIBs for high-energy applications.

### EXPERIMENTAL SECTION

#### Chemicals and Materials.
Spherical CNs including EC300J (Lion, Japan), Super P (Timcal), Denka (Japan), and ENSACO (Timcal), lithium manganese oxide, lithium cobalt oxide, lithium nickel manganese cobalt oxide, lithium iron phosphate (Gelon, Hong Kong), sulfuric acid (H$_2$SO$_4$, 98%, QRec), nitric acid (HNO$_3$, 65%, QRec), PVDF (Sigma-Aldrich), ferrocenemethanol (97%, Sigma-Aldrich), hydrazine hydrate (99%, Loba Chemie), N-methylpyrrolidone (NMP, 99.5%, QRec), and 1 M lithium hexafluorophosphate (LiPF$_6$, Sigma-Aldrich) in the mixture of ethylene carbonate (EC), ethyl methyl carbonate (EMC, Sigma-Aldrich), and dimethyl carbonate (DMC, Sigma-Aldrich) (1:1:1 v/v/v) (Gelon) were of analytical grade and used without further purification. Carbon fiber paper (CFP) (SGL Carbon SE, Germany) was used as a current collector. Deionized water was purified by using the Milli-Q system (>18 MΩ·cm, Millipore). Teflon-mounted GC electrode with 3.0 mm in diameter was from Metrohm Siam Co., Ltd.

#### Synthesis of OCNs.
OCN was prepared via an oxidizing process. Briefly, CN-2 (5 g, Super P) and HNO$_3$ (400 mL) were mixed together in a round-bottom flask and heated to 100 °C for 96 h by a reflux condenser process. The obtained suspension was washed several times with deionized water and then centrifuged at 6000 rpm for 30 min until neutral (pH 7). Afterward, OCN was collected by a vacuum filtration process and dried at 60 °C overnight.

#### Synthesis of HCNs.
HCN was synthesized by reducing OCN with hydrazine. First, OCN (100 mg) was mixed with deionized water (100 mL) and sonicated for 1 h. Then, 1 mL of 1 M hydrazine hydrate was added into the dispersion and heated by a reflux condenser process at 100 °C for 36 h. The suspension was centrifuged at 12,000 rpm for 30 min with deionized water (500 mL) and methanol (500 mL) until pH 7. The product was collected after being dried at 60 °C overnight.

#### Characterizations.
The morphology of the as-synthesized samples was characterized using FE-SEM and TEM. The structural properties were characterized using Raman spectra (Senterra dispersive Raman microscope, Bruker) and XRD (PANalytical with Cu Kα radiation, λ = 1.54056 Å) techniques. The functional groups on the surfaces of the as-synthesized materials were determined by an FTIR spectrometer (Frontier FT-IR, PerkinElmer). The surface area and porous structures of the samples were measured by an N$_2$ adsorption/desorption technique (Autosorb 1 MP, Quantachrome). The BET model was used to calculate the specific surface area of the sample.

#### Charge Storage Evaluation.
The cathode of the LIBs was fabricated by mixing 80 wt % active materials, such as LiMn$_2$O$_4$, LiCoO$_2$, NMC, and LiFePO$_4$, 10 wt % conductive additives, such as CN-1, CN-2, CN-3, CN-4, OCN, and HCN, and 10 wt % PVDF adhesive binder in an NMP solvent. The mixture was stirred for 24 h. The as-prepared slurry was casted on the CFP substrate with hydrophilic surface using a casting machine (GN-AFA-III, Gelon). The as-coated CFP was vacuum-dried at 60 °C overnight. Afterward, the samples were measured by an N$_2$ adsorption/desorption technique (Autosorb 1 MP, Quantachrome). The BET model was used to calculate the specific surface area of the sample.

#### References.

- LiNiMnCoO$_2$, and LiFePO$_4$ because of its high surface area and high ionic conductivity. This work indicates the influence of the superior conductive additive HCN to the charge storage performance of the LIB cathodes. The HCN in this work may be one of the best choices to increase the charge storage performance of LIBs for high-energy applications.

Figure 8. (a) Mn K-edge XANES spectra and (b) oxidation states of the LiMn$_2$O$_4$ cathodes before and after being tested by a GCD technique with different cycles. Note that the results were compared with the Mn standard compounds.
ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00763.

Resistivity of the cathodes using different conductive additives, digital photo of four-point probe equipment for measuring the resistivity of the as-prepared electrodes, and galvanostatic charge/discharge profiles of LiCoO₂, LiNiMnCoO₂, and LiFePO₄ batteries (PDF)

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ACKNOWLEDGMENTS

This work was financially supported by the Thailand Research Fund and Vidyasirimedhi Institute of Science and Technology (RSA5880043). Synchrotron Light Research Institute (Public Organization), Thailand for XANES facilities, and the Frontier Research Centre at VISTEC are acknowledged.

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