Natural Organic Phytate Modified Graphene Hydrogel for Flexible Supercapacitor Electrodes

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A simple and template-free method for fabrication of a modified porous graphene hydrogel electrode was developed. The method involved adding natural organic phytate in the pure graphene hydrogels. Benefitting from the introduced phosphate groups and positively charged metal ions, the flexible magnesium phytate/graphene (Mg-P/G) hydrogel electrode showed large specific capacitance of 281 F/g with a small charge transfer resistance of 0.3 Ω. Furthermore, the flexible supercapacitor showed prominent cycling stability (about 100% retention in capacitance over 10000 cycles) and excellent mechanical flexibility (about 97.5% of its original capacitance after 500 bending cycles).

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Graphene materials have gained considerable interest in flexible energy devices because of their unique and fascinating characteristics, especially for chemically modified graphenes (such as graphene oxide (GO) and reduced graphene oxide (rGO)). These graphene sheets also frequently have higher conductivities, much larger specific surface areas, and can be used as electrodes/active materials for flexible supercapacitor (SC). However, owing to its strong π-π stacking, rGO sheets tend to cause irreversible agglomeration or even restack to form graphite. Thus, the assembly and regulation of GO is a crucial factor in electrochemistry. Most research has focused on graphene-based composites with polymers, inorganic nanoparticles, or other carbon materials including activated carbon and carbon nanotubes to extend their functions. 3D architectures of graphene (such as graphene aerogels and hydrogels) have been frequently designed. Yet a few obstacles still need to be overcome for commercialization. For example, further improving graphene-based electrodes’ mechanical flexibility, cycle stability, and searching for a safe, low-cost, renewable, and environment-friendly nanomaterials to modify 3D porous graphene structures.

Natural organic phytate, derived from legume seeds, cereal grains, and corn, is a nontoxic, eco-friendly, abundant, and readily available resource. Phytate has six phosphate groups located symmetrically on a cyclohexane ring, which is viable for interacting with positively charged metal ions (such as Ca2+, Mg2+, Zn2+, etc.) and can attach to the surface of GO sheets to form a network structure through hydrogen-bond interaction. Based on these properties, we chose one of these positively charged metal ions (Mg2+) to prepare aperated magnesium phytate (Mg-P). The oxygen atoms in the phosphate groups and GO sheets can act as coordination atoms to chelate with metal ions (Mg2+). Mg-P molecules can provide a variety of viable cross-linking sites through π-π and hydrogen-bond interaction that may “stitch” two or more GO sheets to form 3D assemblies.

A major challenge in the regulation of 3D porous magnesium phytate/graphene (Mg-P/G) hydrogel requires a certain concentration and proportion of Mg-P to GO that form a stable network. Herein, we report a simple method for modifying graphene hydrogel. As expected, trace amounts of Mg-P molecules can produce a remarkable effect on electrochemical performances, especially for the charge transfer resistance and cycling stability of the modified electrodes. The microscopic regulation of 3D Mg-P/G hydrogels by natural organic phytates have a guiding significance for the graphene-based composites.

Experimental

Synthesis and regulation of 3D Mg-P/G hydrogel.—The preparation of 3D Mg-P/G hydrogels were outlined in Scheme 1. In a typical procedure, 0.4 mM of sodium phytate (30 mL) was heated to boiling, then 30 mL of magnesium chloride was slowly added. Subsequently, the solution was put in a water bath (~80°C) for 1 h, forming a 0.2 mM Mg-P. GO was obtained by chemical treatment of exfoliated natural graphite powders according to the modified Hummers’ method. Specifically, the obtained GO solution was carefully diluted into 2 mg/mL using deionized water. 30 mL of GO was mixed with the obtained Mg-P solution evenly and treated under ultrasonic condition for 30 min. Then, the mixture was sealed in a hydrothermal reactor (100 mL capacity) and maintained at 180°C for 12 h in an oven. After the reactor cooled to room temperature, a black Mg-P/G hydrogel was dialyzed overnight in deionized water. Different concentrations of Mg-P/G and pure G hydrogels were treated in the same procedure for comparisons.

The main reaction mechanism was proposed. As shown in Scheme 1, the phosphate group and positive Mg2+ ions were used in the scheme for higher activity. In hydrothermal reaction process, the hydroxyls on the graphene sheets could produce dehydrogenation reaction and form chelates with Mg2+ ions in Mg-P molecules though a chemical bonding. Meanwhile, the six phosphate groups were readily connected with graphene sheets by hydrogen-bond interactions, generating a stable and interlaced network structure.

The as-prepared Mg-P/G hydrogel was cut into small cylindrical blocks (with a thickness of ~2 mm). Then the Mg-P/G block was placed on a piece of 316L stainless steel fabric (SSF) (2.0 × 1.0 cm), and the sample was kept under 6 MPa for 10 min using infrared tablet press to form well-adhered Mg-P/G film on the SSF. The efficient electrode mass is about 6 to 8 mg. Finally, the sample was immersed in 1.0 M H2SO4 aqueous for 12 h for subsequent use.

Characterizations.—The microscopic morphologies of the samples were characterized by transmission electron microscopy (TEM, JEOL 2100F) and field-emission scanning electron microscopy (FE-SEM, JSM-7001F) equipped with energy dispersive spectrometer (EDS). Raman spectra were collected with a LabRAM HR Evolution Raman spectroscope using a 532 nm laser source. X-ray photoelectron spectroscopy (XPS) characterizations were conducted using an Axis Ultra DLD X-ray photoelectron spectroscopy. All electrochemical performances were evaluated by a CHI 660D electrochemical workstation using a three-electrode system, in which platinum plate electrode and saturated calomel electrode were used as counter electrode and reference electrode respectively in an 1.0 M H2SO4 aqueous electrolyte. Cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) tests were set in the range from 0–1.0 V. Electrochemical impedance spectroscopy (EIS) curves were detected at a frequency range of 10 mHz to 100 kHz. Moreover, the specific capacitance (C_s) values were calculated from CV and GCD curves using the following:  

\[ C_s = \frac{\text{It}}{\Delta V \times \text{m}} \]

where I is the charge/discharge current, t is the discharge time, ΔV is the potential window, and m is the mass of active material.

Experimental

To fabricate the hydrogel, a mixture of phytate, GO, and MgCl2 was heated to boiling under ultrasonic irradiation, forming a stable hydrogel. The hydrogel was then pressed onto a stainless steel fabric to form a stable film, which was used as an electrode in supercapacitor tests. The performance of the supercapacitor was evaluated using cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) methods.

\[ C_s = \frac{\text{It}}{\Delta V \times \text{m}} \]

where C_s is the specific capacitance, I is the current, t is the discharge time, ΔV is the potential window, and m is the mass of active material.
Scheme 1. Synthesis method and proposed mechanism of the 3D Mg-P/G hydrogel.

equations, respectively.23–25

\[ C_s = \frac{\int I(V) dV}{m v \Delta V} \quad [1] \]

\[ C_s = \frac{I \Delta t}{m \Delta V} \quad [2] \]

where \( I \) (A) is instantaneous current, \( \Delta V \) (V) is the applied voltage, \( v \) (mV/s) is the scan rate, \( \Delta t \) (s) is the discharge time, \( m \) (g) is the effective mass of electrode material.

Results and Discussion

The microscopic morphologies of the G and Mg-P/G hydrogel electrodes were characterized by TEM and SEM. The TEM image in Fig. 1a indicates that GO sheets were ultrathin with large lateral size. During the hydrothermal reduction process, GO sheets could be readily reduced to rGO with partial restoration of the conjugated structure. Figure 1b shows SEM images of the freeze-dried G hydrogels. There were many interconnected channels that made a lot of pores to facilitate the transmission of electrolyte ions, demonstrating G hydrogel is a suitable electrode material for supercapacitors.26 The modified Mg-P/G hydrogels are shown in Fig. 1c. Mg-P molecules were viable for capturing the negatively charged GO sheets because of the positively charged metal ions (Mg\(^{2+}\)) and six phosphate groups locating on either side of the cyclohexane ring. However, the interactions between GO sheets and Mg-P molecules were complex. It can be seen from Fig. 1c that the Mg-P molecules dispersed the twisted GO sheets to some extent, forming an intricate 3D porous network with good structural stability. The 3D Mg-P/G hydrogels showed a satisfactory stiffness and two of them could support a balancing weight of 100 g without any deformation (Fig. 1d). Each Mg-P molecule can interact with several rGO sheets to form a branched microstructure due to the introduced functional groups (such as inositol triphosphate and magnesium phosphate), which can act as hydrophilic functional groups. The Mg-P/G hydrogel electrode was hydrophilic with the initial contact angle of 81.5° (Fig. 1e). As a result, Mg-P/G hydrogel formed a much rougher network with interpenetrated nano- and micropores, which was beneficial to facilitate ion transport within the hydrogel electrode. In addition, EDS was conducted to provide element mapping images of Mg-P/G hydrogel (Figs. 1f–1j), confirming the existence of C, O, Mg and P elements, and trace amounts of Mg-P molecules were evenly distributed in hydrogels.

The XPS spectra of Mg-P/G hydrogel in Fig. 2a revealed a strong graphitic C1s peak at around 285 eV and an obvious O1s peak at around 533 eV, confirming the existence of oxygen-containing groups, such as hydroxy/epoxy groups.27–29 XPS also showed the characteristic P2p peak and Mg1s peak at around 131 eV and 1230 eV, respectively, thereby providing evidence for the successful integration of Mg-P. High-resolution XPS of C1s and their deconvolution are shown in Figs. 2b–2d. As compared with C1s peaks of GO sheets (Fig. 2b), the C-O (~286 eV) and C=O (~289 eV) peak intensities of G hydrogel decreased dramatically because of the hydrothermal reduction reaction (Fig. 2c). Notably, the intensities of the C-O/C=O peaks in XPS spectra of Mg-P/G hydrogel increased significantly due to multiple oxygen contained groups in Mg-P molecules (Fig. 2d). Raman spectra of G and Mg-P/G hydrogels were showed in Fig. 2e. Typically, the two first-order bands D and G were focused at the wave number of ~1330 and ~1590 cm\(^{-1}\), respectively. The intensity ratio

Figure 1. a. TEM image of GO sheets; b. SEM images of G hydrogel; c. SEM images of Mg-P/G hydrogel; d. Photograph of 3D Mg-P/G hydrogels; e. Contact angle test of a droplet of water on the Mg-P/G electrode surface; f-j. EDS element mapping images of Mg-P/G hydrogel.
Figure 2. a. XPS spectrum of Mg-P/G hydrogels; High-resolution XPS spectra of C1s peaks for b. GO sheets, c. G hydrogel and d. Mg-P/G hydrogel; e. Raman spectra of G and Mg-P/G hydrogels.

To evaluate the effects of Mg-P on electrochemical properties of graphene hydrogel, different concentrations of Mg-P were prepared to explore the optimal proportion. Figure 3a shows the morphology of the resulting hydrogels containing 60 mg of GO but varying proportions of Mg-P. The volume of hydrogels increased as the concentrations of Mg-P increased. When adding 0.3 mM of Mg-P solution, the obtained Mg-P/G hydrogel became softer and could not form a relatively stable structure. The high concentration of Mg-P might reduce the number of sites for cross-linking between GO sheets. The corresponding GCD
curves are shown in Fig. 3b, the formed Mg-P/G hydrogel by 0.2 mM of Mg-P had the longest time span (the specific capacitance was about 264 F/g) at a current density of 1 A/g. The following Mg-P/G hydrogels referred to ones fabricated using 0.2 mM of Mg-P unless otherwise specified.

Figure 3c shows CV curves of the 3D Mg-P/G hydrogel electrode in the potential of 0–1.0 V at different scan rates ranging from 5 to 100 mV/s. The CV curves had slightly deformed rectangle shapes, giving rise to a “capacitive like” behavior. Such behavior was “extrinsic” pseudocapacitance due to the electrode design or architecture,34 which could be ascribed to the hydrogen bonds between phosphate groups of Mg-P molecules and hydroxyl groups of graphene sheets. However, there was no obvious redox peaks to be found, indicating that the pseudocapacitance did not take a major role in the modified Mg-P/G hydrogel electrodes. Moreover, the GCD curves of Mg-P/G hydrogel electrode at different current densities are shown in Fig. 3d. All of GCD curves exhibited the nearly triangular shape, confirming a good capacitive behavior and reversible faradaic reaction.35 From CV and GCD curves, the specific capacitances of Mg-P/G and G hydrogel electrodes can be calculated based on Equations 1 and 2. As shown
in Fig. 3e, it can be found that the specific capacitances of Mg-P/G electrode was significantly higher than the pure G electrode. At different current densities of 0.5, 1, 3, 5, 10, 20 A/g, the corresponding specific capacitances of Mg-P/G electrode (G electrode) were 281 (204), 264 (195), 227 (141), 205 (95), 163 F/g (48 F/g), respectively. Note that even at higher current density of 20 A/g, the specific capacitance of Mg-P/G electrode can still maintained at 58% of its highest value (281 F/g), and more than three times higher than G electrode’s, indicating that the Mg-P/G hydrogel electrode had a high rate performance. In contrast, there was only 23.5% retention in capacitance of G electrode at higher current density, much lower than the values of Mg-P/G electrode. Similarly, these results also can be obtained from CV curves at different scan rates, well demonstrating that the addition of trace amounts of Mg-P molecules had a positive effect on the graphene hydrogel electrodes.

The electrochemical impedance spectroscopy (EIS) analysis was used to explore electrochemical transfer property of the supercapacitor electrode materials. The resulting Nyquist plots (Fig. 3f) consists of semicircle arcs at the high-frequency region (the below inset of Fig. 3f) and nearly straight lines at the low-frequency region, and the measured impedance spectra were analyzed by fitting the impedance data with the equivalent circuit (the above inset of Fig. 3f). The relevant equivalent electrical circuit consisted of an ionic resistance (R_s), connected in series with a parallel combination of a charge transfer resistance (R_{ct}) and a Warburg resistance (Z_w) with a double layer capacitance (C_{dl}), in which the ionic resistance (R_s) depended upon the characteristics of the electrolyte solution, and the charge transfer resistance (R_{ct}) represented the resistance involved in the electron transfer process of the electrode materials. The constant phase elements C_{dl} and Z_w were added in the equivalent circuit representing double layer and pseudocapacitance due to the non-ideal behavior of the electrodes. The Nyquist plot of Mg-P/G electrode started from the Z’-axis and progressed almost vertically to the Z”-axis at low frequency, indicating a better capacitive characteristics than G electrode. The R_{ct} values for the Mg-P/G and G electrodes were 0.78 and 0.71 Ω, respectively, indicating a higher charge transfer rate between the electrode material and electrolyte due to Mg-P assisted enhancement of electron transportation among graphene sheets. Compared to G electrode, the Mg-P/G electrode revealed a nearly ideal capacitive behavior.

Furthermore, symmetric supercapacitors were assembled by fixing two Mg-P/G hydrogel electrodes in parallel with PVA/H_2SO_4 electrolyte (see the inset of Fig. 4a), and a two-electrode cell configuration was used to evaluate the electrochemical performances. As shown in Fig. 4a, GCD curves were nearly overlapped under different bending angles of 0°, 90° and 180° at a current density of 1 A/g. Almost no performance fading can be found. In addition, the corresponding specific capacitances at different bending angles were calculated by GCD curves and plotted in Fig. 4b. There was only about 1.0% fading for the capacitance when bended to 180°, indicating an excellent mechanical flexibility. Even after 500 bending cycles, the device also exhibited a high capacitance retention of 97.5% (Fig. 4c). This result demonstrates that the Mg-P/G hydrogel electrode with a stable network structure could be folded or bent arbitrarily and had negligible
Table I. Literature on graphene-based flexible electrodes.

| Flexible electrodes | Specific capacitance (F/g) | Cycling capability | Ref. |
|---------------------|----------------------------|--------------------|------|
| TiO₂/graphene hydrogel | 206.7 (0.5 A/g) | 96.4% after 2000 | 41 |
| MnO₂/graphene hydrogel | 242 (1 A/g) | 89.4% after 1000 | 42 |
| rGO/POPpy | 163 (0.5 A/g) | 78% after 1000 | 43 |
| Graphite/PEDOT/MnO₂ | 195.7 (0.5 A/g) | 81.1% after 2000 | 44 |
| PPy/RGO/BC | 235.2 (2 mA/cm²) | 64.7% after 5000 | 45 |
| Graphene-cellulose paper | 120 (1 mV/s) | 99.1% after 1000 | 46 |
| Carbon nanotube/graphene | 245.5 (2 A/g) | 97% after 2000 | 47 |
| Mg-P/G | 281 (0.5 A/g) | 99.3% after 1000 | This work |

Conclusions

In summary, we have modified graphene hydrogels with trace amounts of Mg-P to prepare a flexible supercapacitor electrode by a simple hydrothermal method. Because of the introduced phosphate groups and positively charged metal ions (Mg²⁺), the Mg-P molecules were evenly distributed in the graphene hydrogels and formed an intricate 3D porous network with good structural stability. In addition, other positively charged metal ions (such as Ca²⁺ and Zn²⁺, etc.) need to be synthesized and discussed in the future work. In this study, the modified Mg-P/G hydrogel electrode demonstrated the impressive electrochemical performance with a low charge transfer resistance of 0.3 Q. More importantly, the as-assembled symmetric supercapacitors displayed extraordinary cycle stability and mechanical flexibility. Even after 10000 charge/discharge cycles, its capacitance retention was about 100%, and after 500 bending cycles, the capacitance of the device remained 97.5% of the original value. Based on these superior properties, the Mg-P/G hydrogel electrode represents a promising direction for building future generation high-life, flexible and stable energy storage devices as innovative graphene-based materials for portable and wearable electronics.

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References

1. X. Wang and G. Shi, Energy & Environmental Science, 8, 790 (2015).
2. H. Dai, N. Wang, D. Wang, H. Ma, and M. Lin, Chemical Engineering Journal, 299, 150 (2016).
3. K. Yang, H. Lee, H. Lee, Y. Shin, Y. Yoon, D. Kim, and H. Lee, Nano Energy, 26, 746 (2016).
4. C. Xu, B. Xu, Y. Gu, Z. Xiong, J. Sun, and X. Zhao, Energy & Environmental Science, 6, 1388 (2013).
5. M. F. El-Kady, V. Strong, S. Dubin, and R. B. Kaner, Science, 335, 1326 (2012).
6. M. D. Stoller, S. Park, Y. Zhu, J. An, and R. S. Ruoff, Nano letters, 8, 3498 (2008).
7. X. Song, Y. Chen, M. Rong, Z. Xie, T. Zhao, Y. Wang, X. Chen, and O. S. Wolfbeis, Angewandte Chemie International Edition, 55, 3936 (2016).
8. H. Sun, P. She, K. Xu, Y. Shang, S. Yin, and Z. Lin, Synthetic Metals, 209, 68 (2015).
9. C. Yang, L. Zhang, N. Hu, Z. Yang, H. Wei, Y. Wang, and Y. Zhang, Applied Surface Science, 387, 666 (2016).
10. K. Vijaya Santhar and R. Kailai Selvan, Electrochimica Acta, 213, 469 (2016).
11. A. Sumboja, C. Y. Foo, X. Wang, and P. S. Lee, Advanced materials, 25, 2809 (2013).
12. Y. Liu, X. Miao, J. Fang, X. Zhang, S. Chen, W. Li, W. Feng, Y. Chen, W. Wang, and Y. Zhang, ACS applied materials & interfaces, 8, 5251 (2016).
13. Y. R. Chen, K. F. Chiu, H. C. Lin, C. L. Chen, C. Y. Hsieh, C. B. Tsai, and B. T. T. Chu, Solid State Sciences, 37, 80 (2014).
14. Z. Zhou and H.-J. Zhao, Organic Electronics, 37, 197 (2016).
15. H. Zhou, H.-J. Zhao, and G. Han, Journal of Power Sources, 323, 125 (2016).
16. Y. Xu, Z. Lin, X. Huang, Y. Liu, Y. Huang, and X. Duan, ACS nano, 7, 4042 (2013).
17. J. Chen, K. Sheng, P. Luo, C. Li, and G. Shi, Advanced materials, 24, 4569 (2012).
18. L. Zhang and G. Shi, Journal of Physical Chemistry C, 115, 17206 (2011).
19. K. X. Sheng, X. X. Yu-Xi, L. I. Chun, and G. Q. Shi, New Carbon Materials, 26, 9 (2011).
20. Y. Xu, K. Sheng, C. Li, and G. Shi, ACS nano, 4, 4324 (2010).
21. D. Wang, H. Yu, J. Hu, and M. Lin, Materials science & engineering, C, Materials for biological applications, 71, 1066 (2017).
22. W. S. Hammers Jr and R. E. Offeman, Journal of the American Chemical Society, 80, 1339 (1958).
23. S. Li, K. Zhou, Z. Song, B. Li, Z. Chen, T. Chen, Y. Guo, and G. Fang, Journal of Power Sources, 324, 325 (2016).
24. S. Li, J. Wen, X. Mo, H. Long, H. Wang, J. Wang, and G. Fang, Journal of Power Sources, 256, 206 (2014).
25. Z. Yu, B. Duong, D. Abbitt, and J. Thomas, Advanced materials, 25, 3302 (2013).
26. J. Yu, J. Wu, H. Wang, A. Zhou, C. Huang, H. Bai, and L. Li, ACS applied materials & interfaces, 8, 4724 (2016).
27. X. Wu, Q. Wang, W. Zhang, Y. Wang, and C. Chen, Electrochimica Acta, 211, 1066 (2016).
28. B. Guo, Q. Liu, E. Chen, H. Zhu, L. Fang, and J. R. Gong, Nano letters, 10, 4975 (2010).
29. P. Yu, Y. Li, X. Zhao, L. Wu, and Q. Zhang, Langmuir the Acs Journal of Surfaces & Colloids, 30, 5306 (2014).
30. A. C. Ferrari, J. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K. Novoselov, and S. Roth, Physical review letters, 97, 187401 (2006).
31. L. G. Cancado, K. Takai, T. Enoki, and M. Endo, Applied Physics Letters, 88, 163106 (2006).
32. H. C. Chang, S. H. Park, and S. I. Woo, ACS nano, 6, 7084 (2012).
33. X. Song, Y. Chen, M. Rong, Z. Xie, T. Zhao, Y. Wang, X. Chen, and O. S. Wolfbeis, Angewandte Chemie, 55, 3936 (2016).
34. T. Brousse, D. Belanger, and J. W. Long, Journal of the Electrochemical Society, 162, A5185 (2015).
35. J. Zhang, X. Zhao, Z. Huang, T. Xu, and Q. Zhang, Carbon, 107, 844 (2016).
36. Z. Pan, Y. Qiu, J. Yang, F. Ye, X. Yu, X. Zhang, M. Liu, and Y. Zhang, Nano Energy, 26, 610 (2016).
37. X. Zhang, J. Wang, J. Liu, J. Wu, H. Chen, and H. Bi, Carbon, 115, 134 (2017).
38. M. Rajesh, C. Raj, B. C. Kim, B.-B. Cho, J. M. Ko, and K. H. Yu, Electrochimica Acta, 220, 373 (2016).
39. D. Kampouris, X. Ji, E. Randviir, and C. Banks, Rsc Advances, 5, 12784 (2015).
40. P. T. Taberna, P. Simon, and J. F. Fauvarque, Journal of the Electrochemical Society, 150, A292 (2003).
41. D. K. Zhang, F. Xiao, Y. Guo, S. Wang, and Y. Liu, ACS applied materials & interfaces, 5, 2227 (2013).
42. K. Leitner, B. Gallus, M. Winter, and J. Besenhard, Electrochimica acta, 50, 199 (2004).
43. K. Shu, C. Wang, C. Zhao, Y. Ge, and G. G. Wallace, Electrochimica Acta, 212, 561 (2016).
44. P. Wang, L. Han, and L. Zhang, ACS applied materials & interfaces, 6, 10506 (2014).
45. L. Ma, R. Liu, H. Niu, M. Zhao, and Y. Huang, Composites Science & Technology, 137, 87 (2016).
46. W. Zhao, B. Yang, D. Wang, W. Feng, J. Du, and H. M. Cheng, Advanced Energy Materials, 1, 917 (2011).
47. Q. Shao, J. Tang, Y. Lin, J. Li, F. Qin, J. Yuan, and L. C. Qin, Journal of Power Sources, 278, 751 (2015).