Unlocking the energy capabilities of micron-sized LiFePO₄

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Utilization of LiFePO₄ as a cathode material for Li-ion batteries often requires size nanonization coupled with calcination-based carbon coating to improve its electrochemical performance, which, however, is usually at the expense of tap density and may be environmentally problematic. Here we report the utilization of micron-sized LiFePO₄, which has a higher tap density than its nano-sized siblings, by forming a conducting polymer coating on its surface with a greener diazonium chemistry. Specifically, micron-sized LiFePO₄ particles have been uniformly coated with a thin polyphenylene film via the spontaneous reaction between LiFePO₄ and an aromatic diazonium salt of benzenediazonium tetrafluoroborate. The coated micron-sized LiFePO₄, compared with its pristine counterpart, has shown improved electrical conductivity, high rate capability and excellent cyclability when used as a 'carbon additive free' cathode material for rechargeable Li-ion batteries. The bonding mechanism of polyphenylene to LiFePO₄/FePO₄ has been understood with density functional theory calculations.

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Li-ion battery, since its first commercialization in 1991, has drastically transformed and popularized portable electronic devices, and will continue to play a major role in the electrification of road transportation in the future. However, for the realization of the latter, better energy storage materials are needed. LiFePO4, an environmentally benign and relatively safe cathode material for rechargeable Li-ion batteries, has attracted a great deal of interest during the last few decades. Considerable efforts have been devoted to overcoming the intrinsically low electrical conductivity of LiFePO4, a drawback that hinders its direct use in Li-ion cells. Several strategies, such as doping with foreign metal ions, have been explored. However, the most common approach remains coating with carbon. Carbon coatings are usually formed during LiFePO4 synthesis, in which an organic precursor (the carbon source) and the inorganic raw materials are mixed together. The subsequent calcination of the mixture in an inert or reducing atmosphere produces conducting carbon and LiFePO4, simultaneously. Similarly, carbon coatings can also be introduced after LiFePO4 synthesis, in which an organic precursor and preformed LiFePO4 are mixed and then calcined. The calcination-based strategies are often energy intensive and can be environmentally unfriendly because of the emission of harmful volatile organic compounds from the thermal decomposition of organic precursors. Moreover, carbon coatings on LiFePO4 produced by heat treatment tend to be irregular, which does not provide a good connectivity for the particles and hence the expected performance for battery applications. To mitigate the negative environmental effects of calcination, conducting polymers have been employed to increase the electronic conductivity and thus improve the performance of LiFePO4. Several methods have been used to produce polymer/LiFePO4 composites, including electrochemical and chemical polymerization in the presence of LiFePO4 particles; rapid mixing of conducting polymer colloidal and LiFePO4 suspensions; and more recent spontaneous polymerization driven by the oxidation power of partially delithiated LiFePO4 (ref. 22).

It shall be noted here that the above mentioned carbon and conducting polymer-coating procedures work well mainly on nano-sized LiFePO4, ranging typically from 200 to 20 nm (ref. 3). The reason for using nano-sized LiFePO4 lies in that reducing particle size can shorten the solid-state diffusion distance within LiFePO4, which is beneficial to the high-power (or high rate) applications. However, one obvious drawback associated with nano-sized LiFePO4 is the decreased tap density (and the resultant lower volumetric energy density), which becomes critical when fitting LiFePO4-based batteries into the trunks of pure electric vehicles. Although the literatures on LiFePO4 are predominantly based on nano-sized materials, there are indeed some efforts of exploring submicron- and micron-sized LiFePO4. For instance, Dominiko et al. showed that a 0.5-μm carbon-free LiFePO4 has a specific capacity of 72 mAh g\(^{-1}\) at 1 C; McNeil et al. reported that a carbon-coated LiFePO4 (0.5–1.0 μm) exhibited a specific capacity of 129 mAh g\(^{-1}\) at 1 C; Wang et al. reported that 0.5 μm LiFePO4 could exhibit an initial capacity of 151 mAh g\(^{-1}\) at 1 C and 58 mAh g\(^{-1}\) at 10 C, but with limited cyclability; larger (>5 μm) LiFePO4 particles have been identified to have very poor performance even when coated with conducting carbon. So far, no facile procedure has been reported to make high-performance micron-sized LiFePO4, possibly due to the limited robustness of the coatings that cannot keep the integrity of the LiFePO4 particles during discharge and charging, particularly at high rates.

Here we report a room-temperature method that can spontaneously coat micron-sized (~1.01 μm) LiFePO4 uniformly with a thin conducting polymer of polyphenylene, as depicted in Fig. 1. The coated LiFePO4, compared with its pristine counterpart, has demonstrated enhanced electrical conductivity, high rate capability and excellent cyclability when used as a ‘carbon additive free’ cathode material for rechargeable Li-ion batteries. In addition, the bonding of polyphenylene to LiFePO4, Li1-xFePO4 and FePO4 has been explored by performing density functional theory (DFT) calculations for the adsorption of the phenyl radical on model surfaces of these compounds. It is concluded that phenyl preferentially forms a strong chemical bond to surface O sites under typical experimental and battery operational conditions, which could be disrupted in the unlikely event that the surface of LiFePO4 becomes completely lithiated.

**Results**

**Reaction of LiFePO4 and C6H5N2BF4.** It is known that when an aromatic diazonium salt (ArN2\(^{+}\) X\(^{-}\)) is subjected to electrochemical or chemical reduction or thermal decomposition, an aryl radical (Ar\(^{•}\)) will form, which is reactive and is an effective agent for surface functionalization of many kinds of substrates. The obtained organic layers strongly adhere to the substrates because a covalent bond is thought to form between the substrate surface and the aryl radicals. Although most of the organic layers reported in the literatures are insulating, a few of them are indeed conducting when certain diazonium precursors are used. One such diazonium salt is benzenediazonium tetrafluoroborate (C6H5N2\(^{+}\)BF4\(^{-}\)), which can be easily and economically prepared in a single-step synthesis (Supplementary Figs 1 and 2 for the nuclear magnetic resonance (NMR) and infrared (FTIR) characterizations (Supplementary Figs 3–5). It is known that when the diazonium cations are reduced to phenyl radicals by electrons from LiFePO4, the reactive phenyl radicals bond to the surface of Li1-xFePO4, forming conducting polyphenylene coatings.

![Figure 1 | Schematic illustration of the reaction of LiFePO4 and C6H5N2 BF4.](image-url)
Electroreduction of 1 mM C₆H₅N₂BF₄ at a 2-mm diameter Au electrode in a three-compartment cell thermostated at 21 °C. Supporting electrolyte is 0.1 M TBAClO₄-acetonitrile and scan rate is 0.1 V s⁻¹.

Figure 2 | Measurement of the reduction potential of C₆H₅N₂ BF₄⁻.
Electroreduction of 1 mM C₆H₅N₂BF₄ at a 2-mm diameter Au electrode in a three-compartment cell thermostated at 21 °C. Supporting electrolyte is 0.1 M TBAClO₄-acetonitrile and scan rate is 0.1 V s⁻¹.

Reference electrode because of its highly stable potential of 3.43 V versus Li⁺/Li35. Figure 2 shows the cyclic voltammograms for the first 1–5 cycles. One distinct feature of the I–E curves is that the successive peak currents corresponding to the electroreduction of C₆H₅N₂⁺ to C₆H₅⁻ radical does not decrease drastically, which is different from the insulating film-forming diazonium salts, such as 4-nitrobenzenediazonium tetrafluoroborate36, a benchmark compound for electrografting of diazonium salt. This observation is consistent with the conducting nature of the grafted polyphenyl layers on the electrode31. Although the reduction peak potential is located at −0.05 V, the onset potential of the electroreduction of C₆H₅N₂⁺ to C₆H₅⁻ is around 0.1 V, which is positive to the Li₁₋ₓFePO₄ reference. It should be noted that the open circuit potential of the pristine LiFePO₄ electrode against Li⁺/Li is in the range of 2.5–3.0 V, thus providing an even greater driving force for the reduction of C₆H₅N₂⁺ to C₆H₅⁻. Recently, Madec et al.37 have used nitrobenzenediazonium salts to functionalize pristine LiFePO₄ and limited reaction extent has been observed, which could be due to the insulating nature of the polymers formed from the nitrobenzenediazonium precursors.

Following the realization that LiFePO₄ can reduce C₆H₅N₂⁺ to C₆H₅⁻, three reactions were conducted with molar ratios of LiFePO₄:C₆H₅N₂ BF₄⁻ of 1:5, 1:1 and 1:0.05, respectively. The obtained products were subjected to structural and compositional analysis with the aim of understanding the extent and kinetics of the reaction. PXRD analysis (Fig. 3a) of the products after 12 h of reaction shows that the reaction, as expected, produces a new phase, that is, FePO₄, and that the amount of the FePO₄ increases with that of the added C₆H₅N₂⁺. However, the excess C₆H₅N₂⁺ cannot completely transform LiFePO₄ to FePO₄, which means the reaction could be a self-limiting process. At molar ratios of LiFePO₄:C₆H₅N₂⁺ of 1:5 and 1:1, around 48 and 44% of the pristine LiFePO₄ were oxidized to FePO₄, respectively, as determined by a Rietveld refinement procedure38 (Supplementary Fig. 6 and Table 1 for details). These two products contain a high ratio of FePO₄, which is not beneficial to the direct application as cathode material of Li-ion battery because of the severe Li⁺ ion loss. However, the reaction of LiFePO₄ and C₆H₅N₂⁺ with molar ratio of 1:0.05 shows a very small amount of FePO₄ is formed (4.3% as measured indirectly by element analysis and online mass spectrometry, instead of Rietveld refinement due to the very weak PXRD signal of FePO₄ phase, see Supplementary Fig. 6 and Table 1 for the fitting results) and thus much Li is extracted, as seen in Fig. 3a (blue curve). It is this reaction with less C₆H₅N₂⁺ that we will focus on.

First we conducted a quantitative online mass spectrometric investigation (the technical details may be found in refs 39,40) of the reaction of LiFePO₄ and C₆H₅N₂⁺. In a typical experiment, 0.162 g of LiFePO₄ was dispersed in acetonitrile in a reaction vial that was incorporated into the purging system of an online mass spectrometer. Before mixing with C₆H₅N₂⁺, the open circuit potential of the LiFePO₄ reference electrode was −0.41 V, which was positive to the Ar carrier gas signal. On addition of C₆H₅N₂⁺, the signal of N₂ increased abruptly and the reaction finished within 20 min. The evolved N₂ was quantified, according to a procedure published previously39,40, to be 1.03 ml (0.046 mmol), while the expected N₂ volume was 1.15 ml (0.051 mmol). This discrepancy may be due to the reaction of LiFePO₄ and C₆H₅N₂⁺. The symbol * highlights the evolution of FePO₄ phase.

Figure 3 | Characterizations of the reaction of LiFePO₄ and C₆H₅N₂ BF₄⁻.
(a) PXRD patterns of the reaction products of LiFePO₄ and C₆H₅N₂ BF₄⁻ at different molar ratios (1:5, 1:1 and 1:0.05), together with pure phase LiFePO₄ and FePO₄. The symbol * highlights the evolution of FePO₄ phase. (b) Quantitative online mass spectrometric analysis of N₂ gas evolution of the reaction of 0.162 g LiFePO₄ and 10 mg C₆H₅N₂ BF₄⁻. The symbol * highlights the evolution of FePO₄ phase. (c) FTIR of the reaction products of LiFePO₄ and C₆H₅N₂ BF₄⁻ with molar ratio of 1:0.05, together with the spectra of LiFePO₄ and C₆H₅N₂ BF₄⁻. The symbols *, + and # denote bands associated with LiFePO₄, FePO₄ and polyphenylene, respectively. (d) TEM of polyphenylene-coated LiFePO₄.
to minor side reactions that do not release $N_2$ gas. To verify the formation of the conducting polyphenyl polymers on LiFePO$_4$, the solid product was analysed with FTIR. Figure 3c shows the FTIR spectra of the LiFePO$_4$ after reaction, and also the pristine LiFePO$_4$ (associated bands are marked with *). The band at 1,375 cm$^{-1}$, corresponding to the stretching of $C=\equiv C$ bonds in aromatic rings, together with a stronger band at 686 cm$^{-1}$, has been observed for isolated particles. The formation of conducting polyphenyl polymers is further evidenced by the non-regiospecific attack of aryl radicals at those sites where the molecules are already attached to the surface, which has been found previously in the multilayers from diazonium reactions.

Figure 3d shows the TEM micrograph of the polyphenylene-coated LiFePO$_4$, in which a coating with a thickness of 2–4 nm has been observed for isolated particles. The formation of the polymer coating has also been proved by a high-angle annular bright-field scanning TEM. We also noticed that the extended exposure of the polymer under electron beam causes degradation. Similar phenomena have been observed previously for polyaniline-coated noble metal particles. The weight percentage of polyphenylene in the composite was determined by elemental analysis to be 2.0% (wt%), which is consistent with the value measured by online mass spectrometry 2.1% (wt%). The latter is transformed from a 4.3% (mol%) of LiFePO$_4$ that is oxidized to FePO$_4$, by taking into account that the reaction occurs according to LiFePO$_4$ + $N_2$ + $C_6H_5N_2$BF$_4$ → FePO$_4$ + $C_6H_5N_2$ + $N_2$ + BF$_4$. The formation of conducting polymer was further evidenced by the conductivity measurement of pressed powders, in which the polyphenylene coating, particularly at higher rates. The Li$^{+}$ ion diffusion within the micron-sized LiFePO$_4$ has also been measured with the electrochemical impedance spectroscopy, and diffusion coefficients in the range of $10^{-16}$ to $10^{-14}$ cm$^2$s$^{-1}$ comparable to that of nano-LiFePO$_4$ have been obtained (Supplementary Fig. 11 and Table 2).

**Electrochemical performance.**

The obtained polymer/LiFePO$_4$ composite had a tap density of 2.02 g cm$^{-3}$ that was higher than the values reported for nano-sized LiFePO$_4$ (typically in the range of 1.0–1.5 g cm$^{-3}$), and were mixed with polyvinylidene difluoride (PVDF) binder (9:1 wt/wt) and cast on an Al foil current collector to make a cathode (mass loading in the range of 2–3 mg cm$^{-2}$) for Li-ion cells. It is worth noting that the cathode does not contain any conducting carbon such as Super P, an additive that is extensively used in the practical cathode fabrication to ensure electronic conductivity throughout the electrode. When tested at a lower rate of 0.1 C, a capacity of 165 mAh g$^{-1}$ (the capacity is normalized to the expected mass of the active material of the cathode after complete lithiation) was achieved, as seen in Fig. 4a,b. This value is close to the theoretical capacity of LiFePO$_4$ (170 mAh g$^{-1}$), while very limited capacity is obtained for LiFePO$_4$ treated in the absence of $C_6H_5N_2$BF$_4$ (Supplementary Fig. 9). When the carbon additive of Super P was used, improved electrochemical performance, relative to that of pristine LiFePO$_4$, has been obtained (Supplementary Fig. 10), which was, however, still inferior to the performance of the polyphenylene coating, particularly at higher rates. Electrochemical impedance spectroscopy has been used to probe the interfacial reaction kinetics, and smaller interfacial reaction resistance has been identified for polyphenylene-coated LiFePO$_4$ (Supplementary Fig. 11), which could account for the improved performance at higher rates. The Li$^{+}$ ion diffusion within the micron-sized LiFePO$_4$ has also been measured with the electrochemical impedance spectroscopy, and diffusion coefficients in the range of $10^{-16}$ to $10^{-14}$ cm$^2$s$^{-1}$ comparable to that of nano-LiFePO$_4$ have been obtained (Supplementary Fig. 11 and Table 2). The performance of polyphenylene-coated LiFePO$_4$ is significant since the prepared cathode contains no conducting carbon additive, and it shall be emphasized here that conducting carbon additive is not electrochemically active and therefore
diminishes the practical energy density of the electrode. The ability to replace carbon with a conducting polyphenylene coating is for these reasons highly advantageous. Cycling at a higher rate of 20°C for 1,000 cycles confirms the stability of the coating in the lithium-ion battery environment (Fig. 4c). Performances of the polyphenylene-coated LiFePO₄ at different temperatures have also been tested, and the results at 0°C demonstrated comparable performance at rates < 8°C and somewhat degraded performance rates > 12°C (Supplementary Fig. 12). The high rate capability of the micron-sized LiFePO₄ can be attributed to the formation of a metastable phase that can effectively decrease the energy barrier of nucleation and growth of a new phase, even the intrinsic Li⁺ bulk diffusion coefficient of LiFePO₄ is small.

The interaction between LiFePO₄/FePO₄ and phenyl radicals. To address the issue of how polyphenylene is bonded to LiFePO₄, we have performed DFT calculations using the phenyl radical as the probe molecule. As noted above, the initial reaction between LiFePO₄ and the phenyl radical results in the formation of an exothermic adsorption of phenyl on LiFePO₄ with Li vacancies. The stoichiometric, fully lithiated LiFePO₄ is included below for comparison purposes. The (010) termination is chosen because it is the dominant facet based on Wulff constructions for both LiFePO₄ and FePO₄ (ref. 53).

On FePO₄(010), phenyl is most stable on the O₁ site (Fig. 5a) with a C–O bond length (dC–O) of 1.420 Å, which is consistent with covalent C–O single bonds. The adsorption energy (ΔE_{ads}) is −2.80 eV, indicating the bond to be chemical in nature. We have not located any previous report of the phenyl adsorption energy on metal oxides for comparison. DFT-calculated ΔE_{ads} of phenyl on transition metal surfaces range widely from −1.04 (on Au(111)) to −2.81 (on Ti(0001)) eV. Van der Waals forces may further stabilize phenyl adsorption, but are not expected to change the site preference of phenyl on these surfaces. Phenyl adsorption on LiFePO₄(010) with a Li vacancy is weaker than on FePO₄(010), although phenyl still preferentially binds to an O site (Fig. 5b) with a considerably exothermic ΔE_{ads} of −1.55 eV and dC–O = 1.414 Å. For comparison, phenyl adsorption on stoichiometric LiFePO₄(010) has a ΔE_{ads} of only −0.18 eV (most stable O site is O₂, Fig. 5c) with dC–O = 1.410 Å.

In contrast, the adsorption of phenyl on Fe sites varies much less across the three model surfaces. Phenyl on the best Fe site (Fe₁, Fig. 5a) has dC–Fe = 2.239 Å and ΔE_{ads} = −0.59 eV on FePO₄(010); 2.113 Å and −0.84 eV on LiFePO₄(010) with a Li vacancy (Fe₂, Fig. 5b), and 2.136 Å and −0.94 eV, respectively, on stoichiometric LiFePO₄(010) (Fe₁, Fig. 5c).

Our DFT results suggest that the phenyl radical (and thus the polyphenylene coating) is most likely attached to the LiFePO₄ surface via O sites. Although the strength of the phenyl–O bond varies with the extent of surface lithiation, a strong chemical bond is expected under typical experimental and operational conditions as the surface is expected to be always deficient in Li in some extent. However, if the surface were to be completely lithiated, that is, by over-discharging a battery, the bonding of the coating to the surface could be disrupted because the bond strength would be weakened considerably and the preferred bonding site would shift from O to Fe.

Discussion

It has long been desirable to obtain high-performance LiFePO₄ particles with sizes approaching micrometres. In this way, a high volumetric energy density of the Li-ion batteries resulted from a high tap density of micron-sized LiFePO₄ particles can be achieved, which is critically important for electric vehicle applications. Practically, it has been difficult to coat large LiFePO₄ particles with uniform carbon coatings by calcination of carbon sources (usually organic small or macro molecules) and the preformed LiFePO₄ particles, possibly because of the inhomogeneous mixing of carbon sources and the large LiFePO₄ particles, which frequently results in phase-separated mixture of carbon and LiFePO₄. On the other hand, simultaneous calcination of carbon sources and LiFePO₄ precursors often produces only nano-sized carbon-coated LiFePO₄ particles, because the formation of carbon phase inhibits the further growth of the LiFePO₄ phase, which has been proved in numerous literatures on the synthesis of nano-LiFePO₄ (refs. 3, 4). Furthermore, as pointed out by Zhou and co-workers, carbon coatings on LiFePO₄ produced by heat treatment tend to be irregular and not well connected to the particles, particularly for large LiFePO₄ particles, and hence do not fully deliver the expected performance for battery applications. Actually, the difficulty encountered when coating large LiFePO₄ particles with a uniform carbon coating by calcination has motivated us to find alternatives to coat large LiFePO₄ particles with other conducting materials in the first place, as exemplified in this work.

To demonstrate the importance of the conductive coatings (either carbon or polymer coatings) on large LiFePO₄, we have tested the electrochemical performance (Supplementary Fig. 9) of bare LiFePO₄ by preparing cathode of binder + LiFePO₄ (1.9 wt/wt).
To compare the performances between polyphenylene- and carbon-coated LiFePO₄, we prepared and tested the cathode of binder + polyphenylene-coated LiFePO₄ (1.9 wt/wt), and the cathode of binder + carbon additive + LiFePO₄ (1:1:8 wt/wt) (Fig; Supplementary Fig. 10). These results highlight the importance of the high-quality conducting coatings on the electrochemical performance of large pristine LiFePO₄ particles, and that for improving the performance of micron-sized LiFePO₄ particles, polyphenylene clearly outperforms the typical conducting carbon.

On the basis of the electrochemical measurement results of pristine, carbon-coated and polymer-coated LiFePO₄ (Fig. 4; Supplementary Figs 9 and 10), and particularly on the fact that large LiFePO₄ usually could not be easily coated with high-quality carbon coatings and therefore could only exhibit limited performance even in the presence of conducting carbon, we attributed the improved electrochemical performance of polymer-coated large LiFePO₄ particles to the intimate bonding between LiFePO₄ and polyphenylene, a result of the surface-initiated electrografting of a diazonium salt, which is also supported by the DFT calculation. Another factor that might attribute to the improved performance of polymer-coated LiFePO₄ is that Li⁺ diffusion coefficient in polyphenylene (∼1.32 × 10⁻⁸ cm² s⁻¹) is higher than in amorphous carbon coatings (∼9.0 × 10⁻¹⁰ cm² s⁻¹). At higher rates, the Li⁺ diffusion within the coatings that separate the LiFePO₄ particles and Li⁺ containing electrolytes become crucially important, because better Li⁺ ion conducting coatings can ensure a rapid exchange of Li⁺ ions between the LiFePO₄ phase and the liquid Li⁺ electrolyte.

In summary, the energy capabilities of micron-sized LiFePO₄ have been unlocked in this work. Using the intrinsic reducing power of LiFePO₄ towards a diazonium salt of C₆H₅N₂BF₄, a covalently bonded conducting polymer coating of polyphenylene can spontaneously form on pristine LiFePO₄. The reaction mechanism has been studied in a detailed way by a range of complementary techniques coupled with theoretical calculations. More importantly, we have shown that the standard carbon coating generated by pyrolysis reaction can be substituted by the polymer coatings without emission of volatile organic compounds. Moreover, the polymer-coated LiFePO₄ can be used directly as ‘carbon additive free’ electrodes with desired electrochemical performance for rechargeable Li-ion batteries. Combined, the method reported here represents a potential replacement of the industrial standard of carbon coating LiFePO₄ with the spontaneous formation of conducting polymers from diazonium salt reactions.

Characterization. Electroreduction of C₆H₅N₂⁺BF₄⁻ was conducted in an air-tight, three-compartment glass cell with valves to control the gas inlet and outlet. A polyvinylidene fluoride (PVDF) film (12 μm, AV Carbone) was used as the working electrode and was polished with 0.05 μm alumina slurry before use. A partially delithiated Li₂FePO₄ (x = 0.10) coated on stainless steel mesh (Li₂FePO₄/Aluminum mesh) was used as the reference electrode. All electrochemical measurements were carried out using a Biologic VMP3 electrochemical workstation. The conductivity of the coated material measured in a D41–11C/2M four-probe resistivity tester. The chemical structure of C₆H₅N₂⁺BF₄⁻ was checked by 1H NMR (Avance III 400, Bruker) and ESI-MS (Quattro Premier XE system, Waters). PXRD was carried out using a STOE STADI/P diffractometer operating in transmission mode with a primary beam monochromator and position-sensitive detector. Fe Kα1 radiation (λ = 1.936 Å) was employed. The details of online mass spectrometry were reported elsewhere. The FTIR analysis was carried out with a Nicolet 6700 FTIR in transmission mode. Elemental analyses were performed using a Vario EL analyser. TEM images were recorded with JEOL, JEM-2100F TEM operating at 200 kV. The electrochemically generated 500 eV area at high-angle annular dark-field scanning TEM for LiFePO₄ were reported elsewhere.

Theoretical calculations. Periodic DFT calculations were performed using the Perdew-Burke-Ernzerhof functional and the projected augmented wave method as implemented in the Vienna Ab initio Simulation Package (version 5.3). The Kohn-Sham valence states (Fe(3d4s), Li(2p2p), O(2p3p), C(2p2p) and H(1s)) were expanded in a plane wave basis up to a kinetic energy of 400 eV. As the electronic structures of both LiFePO₄ and FePO₄ are sensitive to electron correlation effects, the DFT + U approach was used. The optimized U-values and lattice parameters for the bulk LiFePO₄ and FePO₄ were taken from Zhou et al. The electronic energies of LiFePO₄ and FePO₄ depend strongly on the magnetic state of the Fe atoms. In accord with previous investigations, we found DFT + U of high-spin ferromagnetic/high-spin antiferromagnetic ordering of the Fe ions, we report here results for high-spin ferromagnetic states, where the site projected atomic magnetic moments of Fe remain essentially identical to their computed bulk values (4.3 and 3.7 μB for FePO₄ and LiFePO₄ respectively). Following relaxation of the bulk atomic positions, symmetric (010) slabs were constructed according to the procedure outlined in ref. 51. The dimensions of each slab correspond to a × b × c of the bulk lattice vectors, where a = 12.9, b = 12.9 and c = 5.75 Å for LiFePO₄ and a = 5.88 and c = 5.87 Å for FePO₄, yielding 16 formula units per unit cell. Vacuum space (13 Å) was added along the b direction. The surface Brillouin zone was sampled with a k-point mesh of 3 × 1 × 3 k-point mesh, which was confirmed to converge the total energies of both surfaces to within 3 meV per formula unit. For FePO₄(010), the atomic positions of the top layer of Fe and P atoms along with all the O atoms coordinated to them (including subsurface O atoms) were relaxed, while holding the coordinates of the remaining atoms frozen in their bulk positions. For LiFePO₄(010), the same layer of Fe, P and O atoms as in FePO₄(010) was relaxed, as well as the two top layers of Li atoms. The vacancy model was created by removing one of the two top-layer Li atoms in the surface unit cell that we used for FePO₄(010), with the surface relaxation value was added for 20-min relaxation. The surface was fully relaxed. All geometry relaxations were considered converged once the force in each relaxed degree of freedom fell below 0.03 eV Å⁻¹. The adsorption energy of phenyl was calculated as ΔEads = Eads − Esurf − Eads − Esurf. Including the semi-core states of Fe and Li in the valence (Fe(3s3p3d4s), Li(1s2s2p)) and increasing the kinetic cutoff energy to 500 eV we verified to changed adsorption energies by <0.1 eV on all three surfaces.

Methods

Procedure. Carbon-free LiFePO₄ powder was prepared according to a published procedure. In brief, the stoichiometric amount of precursors of FePO₄ (H₂O)₂ and LiOH were thoroughly mixed together in isopropanol. After drying, the obtained precursors were dissolved in 50 ml solution of 0.1 M of HCl. After cooling the solution at 0 °C for 30 min, acetonitrile. After reaction, the obtained products were subjected to a centrifugation also in acetonitrile. The supernatant after centrifuge was collected and examined by ultraviolet-visible to ensure the complete removal of the possible non-surface-confined polymer and the starting material. The electrochemical properties of polyphenylene-LiFePO₄ were determined with CR2032-type coin cells using metallic lithium as the anode. The cathode was made by coating polyphenylene-LiFePO₄ and a solution of PVDF (Kynar 2801; 90:10 wt/wt) in N-methylpyrroldione onto Al foil.

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