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Jiangtao Hu, Wen Li, Yandong Duan, Suihan Cui, Xiaohe Song, Yidong Liu, Jiaxin Zheng, Yuan Lin, and Feng Pan**

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1. n

T i e %he a% e f a ce f $LiFePO_4$, a i % % c e cia ca%a de a% ia f echa geab e i%ai i ba% %ie (LIB), ch eff %ha bee de %d % de % di g i% e ec% che ica e %e , ch a %he h g di- f i g, ca b a d i ic c a% g, e% d i g, i%i i %- ca a% a d ha e %a f a% , a d i e ce f defec% i %he % c% e.[1] H e e, % f %he e %e a e c- ec%d ba ed a ea i %c %hic ba%% e ec% de, i hich a a a %c e i%a a b ad di %ib % f a %c e ie a e b e. Rece %e e i e % %die h %a%%he e i a i ic %a %be% ee ad ace %c % i% %a% e % f %hei ed % %a diffe e ce d i g %he de i%ia% ,[2] hich i a i igi a% f %he de e de ce %he d a ic e %e a %c e i e.[3] The beha i f e i g %he ac% e a% ia i % %hic ice a e b i g % f ba%% ca a ead % %he c i g f %e i%a i%ai che ica % %a d i g %he i%ia% de i%ia% ce a d i % d ce %he c- ce %a% a i a% , e ec% che ica a i a% , a d %he i % a i % fe- e ce i%ai %he e ec% de.[2,4] A a e % %he b%i ed da% ba ed %hic ba%% e ec% de ai e ec%%he e %e f %he c ec% e a %c e i%a % a i a- % effec%.

Rece %, e e ed 3D i % g % fab ica% %hi LiM $_{0.21}Fe_{0.79}PO_4$ LIB e ec% de , hich h i e i e e ec- % che ica e f a ce: a ca aci% f 108.45 A h g^{-1} a%100 C a d a e e ib e ca aci% f 150.21 A h g^{-1} a%10 C af% 1000 c c e .[5] We %he de %a%d %ha% e ce %f %he b Li-i diff i i ca%a de a a %c e a d a %c e i %- facia eac% , %he % i %i ic dif- f i c ef cie % ef cie c i%, a d e ec% de %hic e c d a d i a% high a% e f a ce f %he ca%a de. H e e, %he %a%i e ec% de a e % c ed f a e- b ed LiM $_{0.21}Fe_{0.79}PO_4$ a c % a d ca % e ec% %he i %i ic e %e f a i g e a a %c e, hich d ha e dee i igh%% h % f %he i e %he e f a ce f e ec- % de a% ia . Th , % ge%%he i %i ic e %e f i g e a c % i% bec e % ge% %hi .

Ne % % g e%a d %hi b ec% h d be de e ed %Rece % g e e ab %%hi ha e bee ade % %d %he i % ca a% echa i f $LiFePO_4$ a c % i% . Ch eh e%a . i aged ≈450 i di id a $LiFePO_4$ a %c e % c %he a %c e-b - a %c e a%a a d i g i % ca a% .[6] B e%% e% a . ed ece i e ec% diff ac% % b%i $LiFePO_4$ a d $FePO_4$ ha e a i g a%%he ca e f a a %c e a d ed %he d i -ca cade de a%%he a ca e e e.[7] Li e%a . %ac %he ig a% f Li i $LiFePO_4$ e ec% de i%a i g e a %c e e- i% i% b i g e a d e ce ce- ie d X- a ic c a% .[8] U i g %a i i e ec% ic c a d b %he e e ec% f a d ca%% i g diff ac% %ch i e, R be %e% a . a big h %a%%he a a %c e de i%ia% % b %he %% %ca a a i f 64000 $LiFePO_4$ a %c e .[9] U i g

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a e a d X-a ic c a% , Li e%a . a ed %he d a ic f %he Li c i% a d i e % a% i%hi i- a $LiFePO_4$ a %c e .[10] The e e%h d ha e he f i igh% i % %he Li i % ca a% /dei % ca a% i e%c i%hi $LiFePO_4$ a %c e , b %%he e%h d % % %%he i %i ic e ec% che ica e %e f i ge $LiFePO_4$ a c %o i % ac i g.

C c ic %o e% (CV) i a e i%e a d i a ide ed %ch i e f %he i e %ga% f e ec% che ica i e%c . Gi e %ha% Ga a %o%c I % i%o % Ti%a% Tech i e (GITT) a d E ec% che ica I eda ce S ec% c (EIS) a e a icab e % id- % eac% % a d ca % be a icab e % $LiFePO_4$ d e % i% a%di cha ge a% ,[11] a d PITT ea e e %i e a%e % c e , CV e%h d d be a e a ia% e%h d % %d %he i e%c f e ec% che ica e f a ce f $LiFePO_4$. M % f %die i g %hi e%h d a e i %o i gad a %ge f %he e a- % [11] $I = 2.69\times10^5 n^{\frac{1}{2}} A(D_{Li})^{\frac{1}{2}} v^{\frac{1}{2}} \Delta c_0$ (I: ea c e %n: %he e ec- % ic be a %ci a% g i %he eac% ; A: %he e ec% de a ea i e ed i % ; D_{Li}: Li-i diff i c ef cie %v: ca eed; C_0: c ce %a% a ia% bef e a d af% %he eac%) % e a a% diff i c ef cie %[2] e ec% che ica i d [13] a d ea e ca aci% ce c %ib % .[14] We ha e e ed CV %o g % b%i %he e a% e a a e% % de- %a% %he ea h $LiFePO_4$ ha %ahigh a% e f- a ce i a e e ec% % .[15] He %idge' g [16] de i e a e e%h d f %he di ec%e %ac% f i e%c da% f e e i e %o CV b e ica i a% , ba ed %he B %e V e (BV) f c% a d %he Fic ' diff i a . F %he- e, %he i % d ce %he a e%ic Ma c H h Chid e (MHC) %he % %he %d f face-b d ed c e i CV c e a d ge%%he a %% f %he e ga i a% e e g a d %he a e% a a e% Tafe %. H e e, a % a CV da%i e i i% a% e a e c ec%d b %o % %hic e ec% de f ba%% % e ec%%he e a cha ac% i %c f %he i g e ec% de.[17] Th gh %he e di g a e ef a d ci- e % ca ea i gf % %he ac%ca %i a% f %he ba%% , % ge%acc a% a d a %%% e i f a% f %he CV %o % f a i ge a c %o d a be f f da e %o i %o e % a d i %o %f %he ac%ca %i a% .

I %hi , e de e ed a e e%h d % f %a%hi i g e- a %c e (SP) e ec% de f $LiFePO_4$, i hich $LiFePO_4$ a a %c e c d be f ca%% ed a d di %ib %d % c- %c% i%h %he c d c% e e% f ca b a %be (CNT) (c d c% e ca b e%). The ha e %CV ea f %he SP e ec% de a b%i ied % %d %he i %i ic e ec% che ica e %e f $LiFePO_4$ a c %o . We a de e ed a e SP- de f $LiFePO_4$ i%h %he e % %a%i%ca de c ibe %he e a% hi be% ee eac% a% a d %ge eci e b i g da%a f %he e e i e %o % %a -ca aci% (a- i ed a %ge %o% f cha ge (SOC)) c e f $LiFePO_4$ % e ace %he Ne %e a% . B i g %hi SP- de % %%he e e i e %o CV c e f SP e ec% de f $LiFePO_4$, e a ge%%he diff i c ef cie % a d face eac% c ef cie % f $LiFePO_4$ a c %o i %he a e a d ga ic e ec% % a%diffe e %%% e a% e . The e % a %%a% e h %ha% %he i %i ic Li-i diff i c ef cie % f $LiFePO_4$ a e ea %he a e i a% a d ga ic e ec% %o , b %%he i % facia a% c %o %i a% e ec% % i e de highe %ha %a% i ga ic e ec% %o, hich ca be %he deci i e fac% f %he e ce e % a% e f a ce i a e e ec% % f $LiFePO_4$. B i e %ga% g %he % e a% e effec% f i % facia a% c- % %%he i igh% f e-e e %a fac% a d %he ac% e e e g f %he i % facia eac% e a% ca be de % d f %he %%% e, hich a e e a%d i%h de a% / a% ce a d id i id i % face % c% e f $LiFePO_4$, e ec% e .

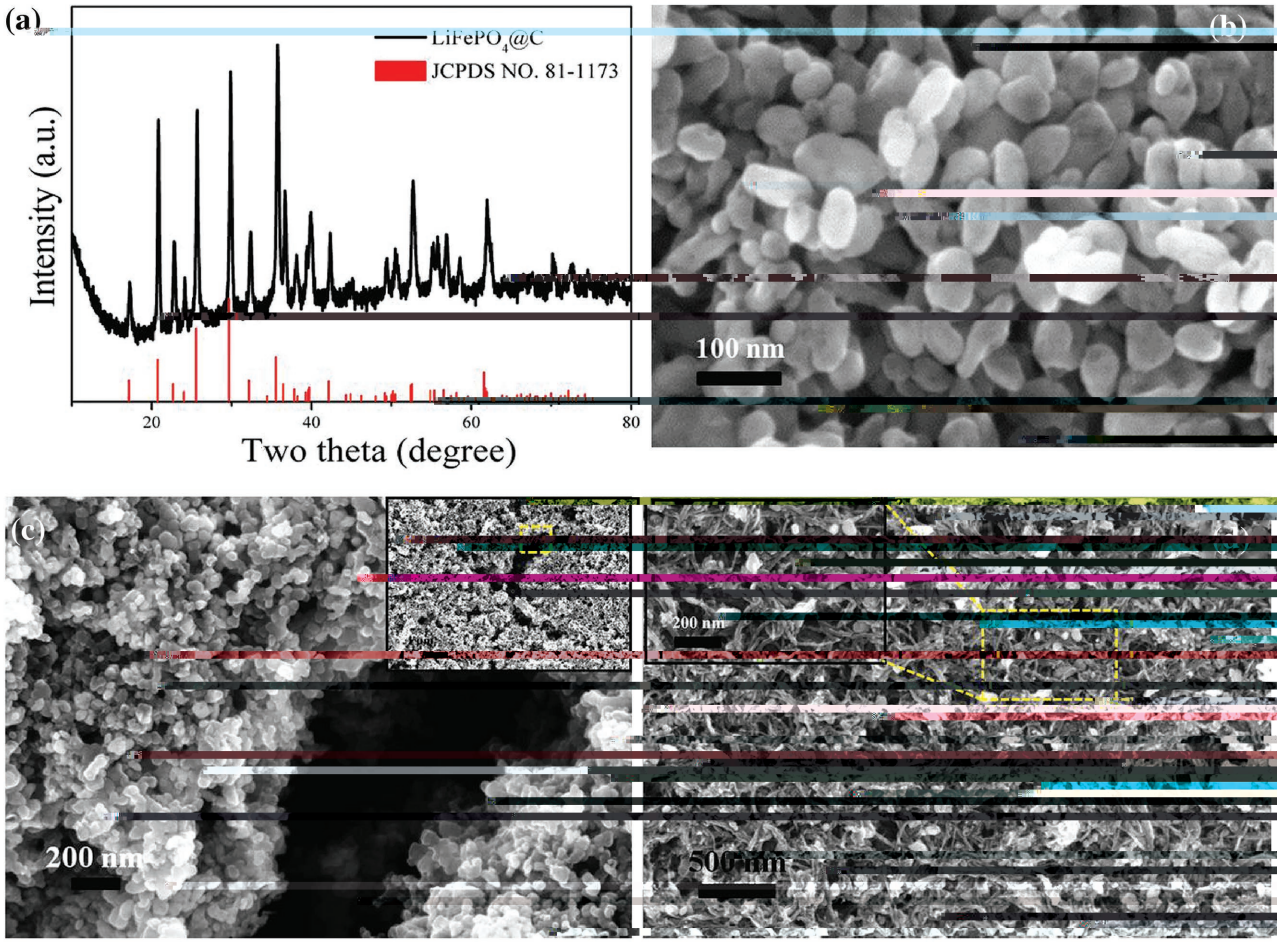
2. n D n

2.1. n E

Figure 1a h %he c %o % c% e f %he %he i ed $LiFePO_4$@C d c%, hich e hibi% a i g e- ha e i i e-% e % c% e i%h P a ace g (JCPDS NO. 81-1173). Rei%e d e e e % f X-a diff ac% (XRD) da%a i c d c%d % ide- %f %he a%%ce c %o % a d c %ha%%he e a e i i% ha e (Fig e S1, S %o g I f a%). The ca i g e ec- % ic c (SEM) ic% e f $LiFePO_4$@C e e h i Fig e 1b, a d %he ea a %c e i e f $LiFePO_4$ i ab %40 .

T e a e %he SP $LiFePO_4$ e ec% de, e e fac% , ch a %he % e- ca e f %he %a ic di e i f a a %c e i a d %he %ic e f %he e ec% de % achie e SP e- f a ce, e e %i e %ga%d. We de ed %ha%%he %hi e ec% de i%h e ha CV ea h e e ec% de a%- ia ha e fec% a %c e di e i i%h g %a ic % e a SP e ec% de. D i g e e i e %, e did CV %o % i b %h a e a d ga ic e ec% % i g %a%hi e ec- % de i%h %he a e de diffe e % %a ic % e (Fig e S2 a d S3, S %o g I f a%). Ob i , %he CV ea cha ge ha e i%h %he ge %a ic % e, a d %he ha f- id%h ea e ai c % %af% 50 i %a ic. The e d be % f agg e a% i%h h % %a ic % e, a h i Fig e S4 a d S5 f %he S %o g I f a% . We a did E e g Di e i e S ec% c (EDS) ea e- e % f a% ia i%h 70 a d 5 i %a ic % e, a h i Fig e S6 f %he S %o g I f a% , hich did %h di % g i hed diffe e ce f e e e %di %ib % d e % %he e % i i%The e %o e %he 70 i %a ic a% ia f f %he % %, hich d be di e ed e gh % f SP e ec% de . The % i ed a % f c d c%o e ca b i %he c ea% c d c%o e e% % ed ce %he e i % ce f e ec% de a d % e a a% $LiFePO_4$ a c % a i ge- a %c e e bedded i c d c%e ca b e% . I de % % %%he %hic e f e ec% de , e d ed %he (af% %a ic f 70 i) a % i% c %o i%h %he %a%hi (a ca e, ab %100 200 %hic , Fig e S7, S- %o g I f a%) a d i%h a %hic (ic e% i e, ab %7 µ , Fig e S8 f %he S %o g I f a% a d Fig e 1c) e ec% de , e ec% e . The CV e f a ce f %a%hi e ec% de f ed i%h %he dee -di e ed (af% %a ic f 70 i) e % ha e %%h ch % e f e ec% de c d be ca ed a SP e ec% de i %hi %d . He ce, % e a e %he SP e ec% de, e h d %o e ca e f % e fac% : % f a %hi e ec% de (e i i a% %he c ce %a% a i a% f e ec% de) a d % % e g %a d % e f di e i g % dec ea e agg e a% .

Fig e S7a a d S8a f %he S %o g I f a% h %he di- %ib % f %he e a ed SP e ec% de a d %hic e ec% de d ed



F 1. a,b) XRD and SEM data of $LiFePO_4$@C. c) The 3D confocal images of thick electrode dropped on quartz monitor crystals. d) The spatial structure of SP electrode using CNT.

a % i% c % b 3D c f ca , a d %he heigh% f %he %i a d %ic e ec% de a e a ca e a d ic e% i e, e ec- %e . Fig e 1c a d Fig e S7 ba d S9 (S %g I f a%) h %he a%a % c% e a d h ica a f %he % i d f e ec% de . Ob i , %he SP e ec% de h c %c%d a - a %c e (LiFePO4 a c % i%a ea i e f ab %40) e bedded i c d c% e ca b a a %c e (a ab %40) % a ea e% i%a e (10 20) a d ac (100 500), hich ca ead % each LiFePO4 a c % c e % c %c% i%a c d c% e e% f ed b c d c% e-ca b a a %c e a d e ec% % f e ec% ic a d Li-i c d c% f cie %, e ec% e . Th , %he SP e ec% de c d i i i e %he c ce %a% a i a% , e ec% che ica a i a% , a d %he i % a i % fe e ce % be e %f % % g %he i %i ic e ec- % che ica e %c f LiFePO4 i ge a %c e . Fig e S10 f %he S %g I f a% di a %he heigh%di %ib % f e ec- % de a% ia c a% g a % i% c % b % e. B c %a %%he %ic e ec% de h a c e c %c%d a - %c e- e% i%a e a d ac , hich d ea i ge e a% c ce %a% a i a% a g %he %ic -di ec% f a e ec% de d i g %he cha gi g di cha gi g ce f LIB .

Si i a , e cha ged %he ca b b ac % CNT i%a %he %a ic % e f 70 i . I%ca be ee %a%%he LiFePO4 a a %c e c d be ca%% ed a d di %ib %d % c %c% i%a %he CNT- e% e e , a h i Fig e 1d. Addi% a , e ad %d %he % f LiFePO4 a c % a d ca b b ac % ea i e a ab % i g e- a %c e e ec% de. N % %a% he e i c ea ed %he a% f ca b b ac % LiFePO4 a c - % % e %a 1:1 i eigh% %he CV c e e e ed e ca aci% ce i f a% (Fig e S11, S %g I f a%). A % i ed a % f c d c% e ca b b ac i % ed ce %he e i % ce be% ee %he a %c e a d %he e iece, b %a ca e a a% %he LiFePO4 a %c e a d ed ce %he i % a %c e i ic e ec% ic %a %i i%% . Th , c - d c% e ca b a a %c e ca c ea% %he c d c% e e% , hich a i ia e a CNT , % f ca%% a d di %ib % LiFePO4 a a %c e % c %c% i%a %he c d c% e e% , e % g i %a%b % e f SP e ec% de e hibi%%he ha e % CV c e .

2.2. E m

CV % % e e c d c%d %he e % i d f %ic (a c i ce) a d SP e ec% de i diffe e %e ec% % ci c - % ce . A %he ad f ac% e a% ia a %e ac% %he a e,

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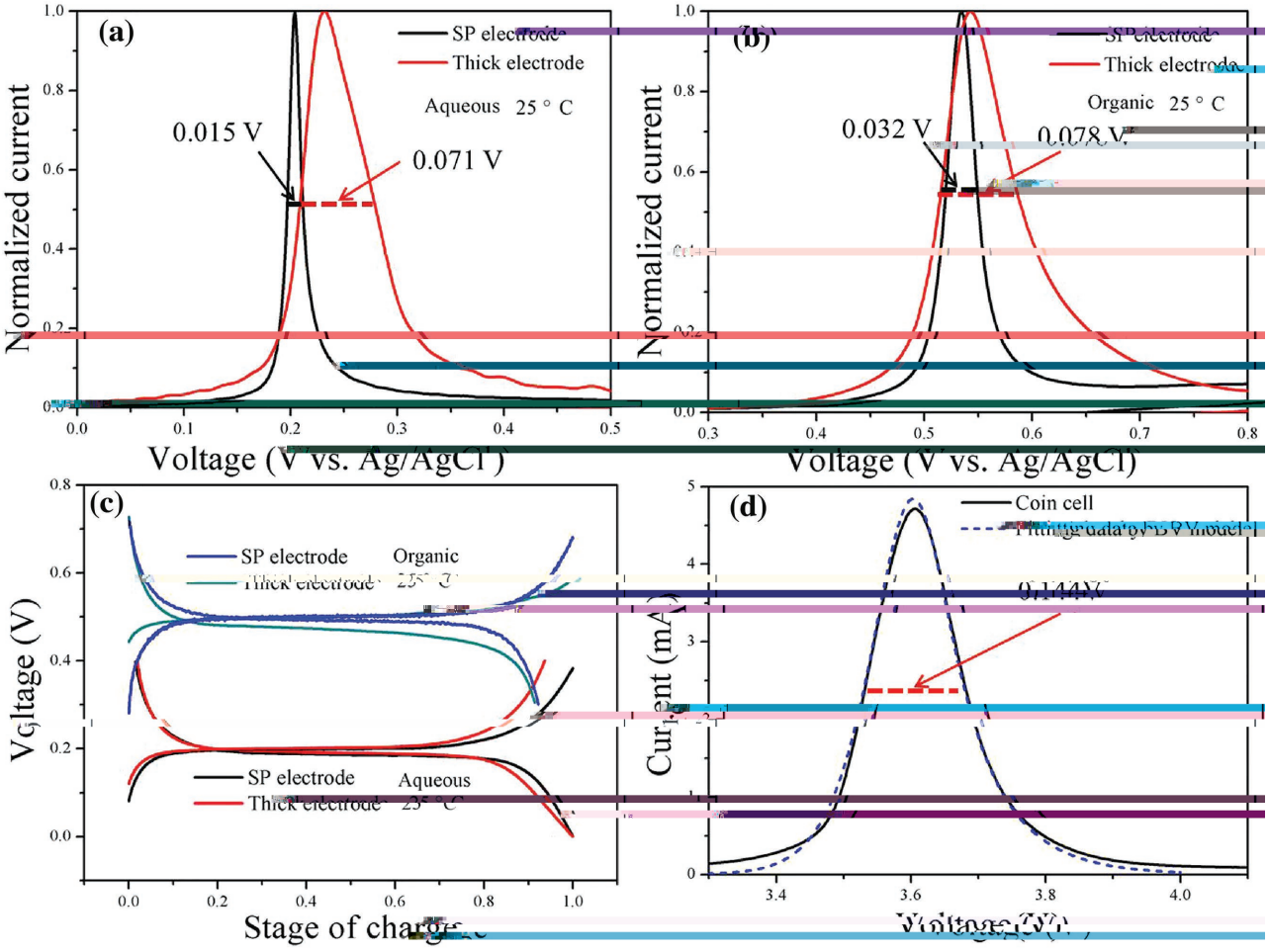


F 2. The CV data of SP electrode and thick electrode measured in a) aqueous and b) organic electrolyte at room temperature (25 °C) at 1 mV s^{-1}. c) The charge/discharge curves of SP electrode and thick electrode in aqueous and organic electrolyte at 0.2 C. d) The CV data of coin cell ($LiFePO_4$:C:PVDF = 7:2:1) at 1 mV s^{-1} and the fitting data by BV model.

%he heigh% f CV ea e e a i%%e diffe e %I de %c a e %he cha gi g %e d f CV c e c di , e a i ed %he b di ided %he a i a e f each CV ea , a h i **Figure 2**a,b. Ob i , c a ed i% %he %ic e ec% de a d a c i ce , i%ca be b e ed %a%%he a dic ea f SP e ec% de a e e ha , %he ha f- id% f SP e ec% de i ch a e , a d %he g adie % f f e' i i g edge i a highe . N % %a%ca% de ea f SP e ec% de h %he a e i d f e f a ce a h i Fig e S12 a d S13 f %he S % g I f a% . I % e % g , e % cha ge/di cha ge % %a-ca aci% % % f %he % e ec% de i a e a d ga ic e ec-% % a%0.2 C (1 C = 170 A g^{-1}), e ec%e , a d f d %ha% %he di cha ge c e f SP e ec% de a d %ic e ec% de e e a %c i cide %i b %a e ec% % (Fig e 2c). S a e % i a ed: h d %he cha ge/di cha ge % %a-ca aci% c e f SP a d %ic e ec% de ee i% %he a e i% %he i ia cha ge/di cha ge a% (ab %80% ca aci%e a%a % a e %ge), b %%he CV da% h ch a big diffe e ce be% ee SP a d %ic e ec% de , ch a %he f id% a%ha f a i f CV f SP e ec% de a d %ic e ec% de 0.015 a d 0.071 V i a e , a d 0.032 a d 0.078 V i ga ic e ec% % , e ec%e ?

2.3. Im

Ge e a , %he e a e % i d f CV i a% de : BV de a d MHC de (ee %he E i e % Sec%). The CV c e f c i ce i ga ic e ec% % ca be %%d e b e ica i a% ba ed BV de (Fig e 2d), i di-ca% g %he BV e a% ca be a ied % %ic e ec% de f $LiFePO_4$. The e ad %d %he ad %a fe c ef cie %a d diff i c ef cie % f BV de a d eac% c % % f MHC, hich de% i e %he ha e f CV, % %%he CV c e f SP e ec% de i %he % e ec% % . S i i g , e e he e ad %d %he e fac% % %he i i%, i%i % i - ib e % %%he e e i e % c e e (Fig e S14, S - % g I f a%). Ob i , %he BV a d MHC diff i de i i%b e % de c ibe %he SP e ec% de f $LiFePO_4$ a c % .

F %he i i ed e ec% che ica eac% , e a c ide ed %he a %a fe ce a d i % face cha ge %a fe ce . I e i CV a a i , %he %c - e c % ed a %a fe ce a eadi g i ha f i i% a e hi e %he i % face cha ge %a fe ce

i f% de c ibed b %he % da d B %e V e e a% .[18,19] H e e, $LiFePO_4$ d e % ee%%he e % c di% , a $LiFePO_4$ i diffe e %f %he ca%h de a% ia , ch a Li(Ni, C , A , M)O_2, hich e hibi%%he e e e %% e id- % S | % e i %he cha ac% i %c f % %a -ca aci% c e i a ge a ge a% %he -% e a% e.[20] M e e, i %he ca%h de a% ia , %he cha ge f i%i c ce %a% i e e di %ib %d i %he ce f cha gi g a d di cha gi g,[21] hi e %he i%i c ce %a% cha ge i %he ce f cha gi g a d di cha gi g i e e i $LiFePO_4$, a d %he e i a ig i ca % a% i %he % %a -ca aci% c e . N % %a%%he ca aci% ca be i dica%d b SOC. A a e %%he e a% hi be% ee %he % %a a d SOC %a%de ic%d b Ne %e a% a ied % B %e V e % i % i%b e f $LiFePO_4$. Be ide , $LiFePO_4$ SP e ec% de i a i% he ica diff i de %a% i i c i % % i% %he c di% f ha f i i% a e ead. H e e, i %he %ic $LiFePO_4$ e ec% de, a a a %c e i% a b ad di %ib % f a %c e i e a e b e % c %c% i% each %he . The i ic %a %d be% ee ad ace %c %- i% a d %he c i g f %e i% i% i che ica % %a d i g %he i%ia% de i%ia% ce d ead % %he c ce %a% a i a% , e ec% che ica a i a% , a d %he i % a i % fe e ce i%i %he e ec% de. Th %he e e i % c ce %a% diff i i %he h e e ec% de, a d %he BV e a% i a ia% % de c ibe %ic e ec% de f $LiFePO_4$.

Ba ed %he ab e a a i , e c % c%a e SP- de i %i hich i c ed f diff i ce a d i %- face cha ge %a fe ce . D i g %he ida% ce f CV ca i g, %he i % a Li-i i%i $LiFePO_4$ (LFP) a- %c e begi % ead % %he diff i ce a% e %he Fic ' diff i a (E a% (1), %he ig i ca% a d i% a e de ic%d i Tab e 2)

$$\frac{\partial C(x,t)}{\partial t} = \frac{D_{Li}}{x^2}\frac{\partial}{\partial x}\left(x^2\frac{\partial C(x,t)}{\partial x}\right) \quad (1)$$

A f %he i % face e ec% e cha ge ce de c ibed i %he B %e V e e a% (E a% (2)), %he %% eac- % a% i e a % %he ida% a% c % %(k_O) % ied b %he ed c% %% c ce %a% ($C(R,t)$) a d %he i %he ed c% a% c % %(k_{Re}) % ied b %he ida% %% c ce %a% ($C'(R,t)$)), hich a i% % SP- de

$$i = FA\left(k_O\, C(R,t) - k_{Re} C'(R,\%)\right) \quad (2)$$

H e e, i% h d be %d %ha%%he ed c% a d i- da% eac% a% f $LiFePO_4$ SP e ec% de ca % %%d b Ne %e a% (E a% (3) a d (4)). A % %ha% Ne %e a% ca be ed i %ic e ec% de f $LiFePO_4$ i%i c ce %a% a i a% , hich c d be a%%ib %d % %he i%i c ce %a% cha ge i %he ce f cha gi g a d di cha gi g d e % i % a %c e ' i % cha ge/di cha ge f $LiFePO_4$ i %he %ic e e% de [5] a d d e f i i a % id- % ca%h de a% ia (Fig e S15 (ed i e), S - % g I f a%)

$$k_{Re} = k^0 e^{\left\{-\alpha^{\circ}\frac{F}{RT}\left[E-E^0\right]\right\}} \quad (3)$$

$$k_O = k^0 e^{\left\{(1-\alpha)^{\circ}\frac{F}{RT}\left[E-E^0\right]\right\}} \quad (4)$$

The e % f SP de i %he eci e e a% hi be% ee eac% a% a d %ge (E a% (5)) hich i g % b i g %he ea % %a -ca aci% (a i ed a %ge-SOC) c e f $LiFePO_4$ (Fig e S15 b ac i e, S % g I f a- %) % e ace %he Ne %e a% , beca e %he Ne %e a- % ca % de c ibe % %a -SOC c e f %he $LiFePO_4$ a c % SP e ec% de

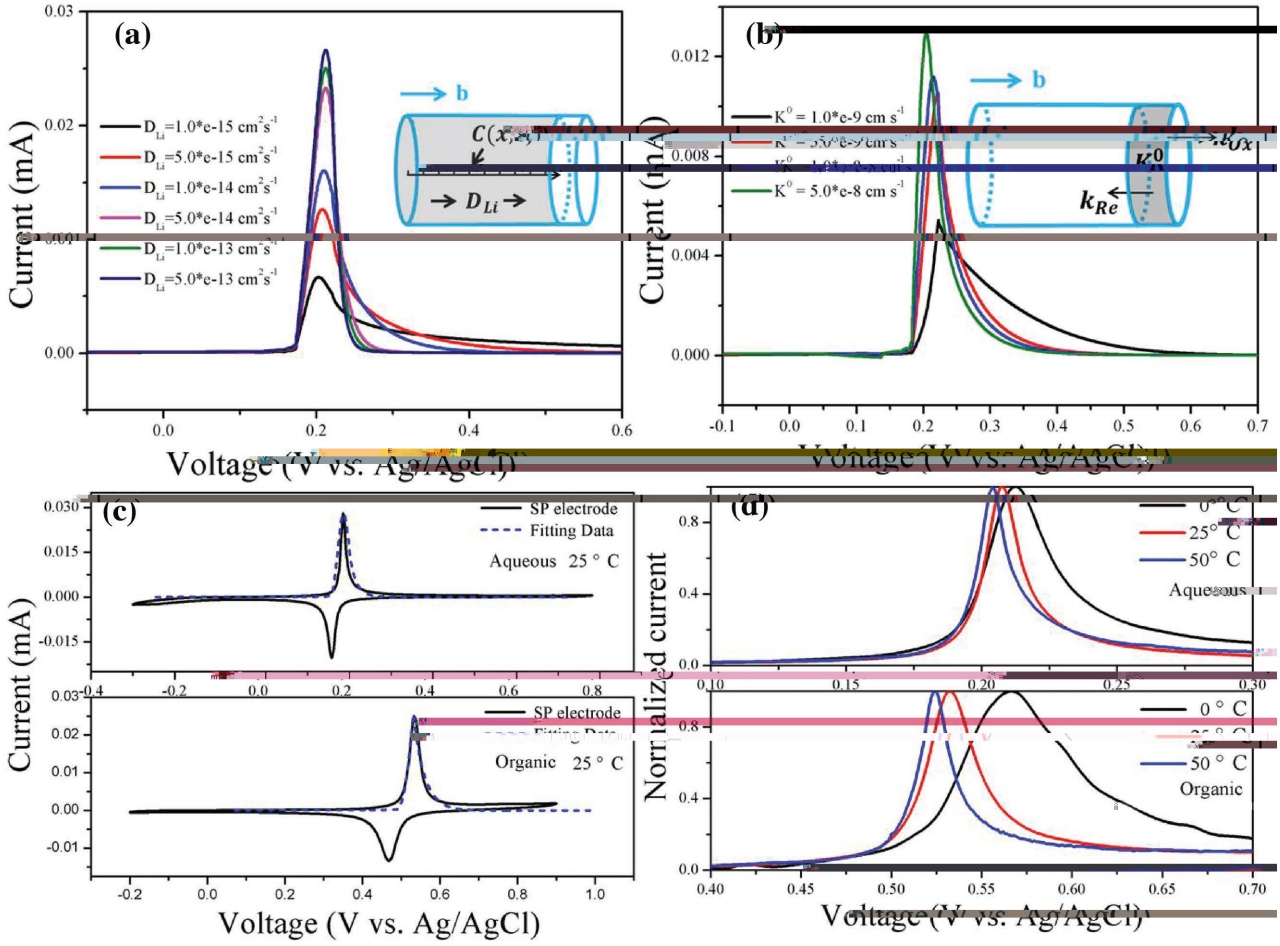
$$k_{Re} \propto -f(E(soc)),\ {}^{\infty}k_{Ox} \propto {}^{\circ}f(E(soc)) \quad (5)$$

$$K_{eq} = \frac{k_{Ox}}{k_{Re}} = \frac{(1-SOC)}{SOC} \quad (6)$$

B i g %he %he %ha% eac% a% a d %he c ce %a% (SOC) f %he ac% a%d c e a e %he i%e e a% hi (E a- % (6)) a d addi g E a% (5) a d (6) i % E a% (2), e ca ge%%he e a% hi be% ee %he %ge a d c e %%he % i - a% %he CV da% f SP e ec% de. (The de%ai ed i f a% ab % SP- de a de c ibed i %he E e i e % Sec% .) **Figure 3**a h h D_{Li} affec% %he ha e f a CV c e, ch a %he i - a%d CV c e i%i ed a a e% ($K^0 = 1\times10^{-8}$ c $^{-1}$, $\alpha = 0.5$) a d % i g D_{Li} (f 1×10^{-15} % 5×10^{-14} c ^{2} $^{-1}$). We ca ee %ha% he D_{Li} i c ea e , %he adia f fa i g edge f %he CV c e i a i c ea ed a d %he %ai i g i a i hed, b %%he ha f- id%i a % e % c % %Si i a , %he %e d f %he cha ge f CV ha e i%i K^0 (f 1×10^{-9} % 5×10^{-8} c $^{-1}$) a h i Fig e 3b he %he a a e% e e ed ($D_{Li} = 1\times10^{-14}$ c ^{2} $^{-1}$, $\alpha = 0.5$), i hich %he g adie % f i i g edge i i c ea ed b i- he ea ha f- id%i di i i hed i %he a e f i c ea i g

1. The simulation data of SP electrode at different temperatures in different electrolytes.

Parameters		Aqueous [°C]			Organic [°C]		
		0	25	50	0	25	50
D_{Li} (cm^2 s^{-1})	Charge	$>1.8\times10^{-14}$	$>2.8\times10^{-14}$	$>1.4\times10^{-14}$	$>1.5\times10^{-14}$	$>3.0\times10^{-14}$	$>3.0\times10^{-14}$
	Discharge	$>1.0\times10^{-14}$	$>2.0\times10^{-14}$	$>2.8\times10^{-14}$	$>1.5\times10^{-14}$	$>3.0\times10^{-14}$	$>3.1\times10^{-14}$
K^0 (cm s^{-1})	Charge	4.3×10^{-9}	2.0×10^{-8}	7.0×10^{-8}	8.0×10^{-10}	3.0×10^{-9}	9.0×10^{-9}
	Discharge	4.0×10^{-9}	1.8×10^{-8}	6.0×10^{-8}	7.0×10^{-10}	3.0×10^{-9}	9.0×10^{-9}



F 3. a) The variation tendency of CV curves with the increase of diffusion coefficient by SP-model. b) The variation tendency of CV curves with the increase of interfacial rate constant by SP-model. c) The CV curves of SP electrode and thick electrode in aqueous and organic electrolyte at 25 °C with the current density of 1 mV s^{-1}, the dotted lines are the simulation curves by the SP-model. d) The CV curves of SP electrode at different temperature in aqueous and organic electrolyte with the current density of 1 mV s^{-1}.

K^0. M e i %% %, %h gh SP- de (he e de) (Fig e S16, S %g I f a%%) b ad %g %he e a%d a a e%% , %he i a%d CV c e ca be %%d e fec% e i%h %he e e i e %% c c ic % g a f %he e a ed $LiFePO_4$ SP e ec% de (Fig e 3c) f %he %% e, a d %he b%i ed a a e%% e e de ic%d i **Table 1**. (The e cha ge c - e %de i% a e e ed i Tab e S2, S %g I f a%% .) I de % e if e e i e %% e%% d ad SP de, e ha e d e a c e a%% e e i e % i g CNT a %he c d c- %e e% , %he e e i e %%da%% a d a e %% a e h i Fig e S17 a d Tab e S3 f %he S %g I f a%% , a d %he i a%% e % e %a %%%e a e i%% %h e i g ca b b ac a %he c d c%e e% . M e e, e ha e a b i%a a%% de. The i%%i i %a %di ec% i b f $LiFePO_4$, a d e ca c a%%d %he e g%% ab %%%he (010) face b Sche e e a- % (27.3). C bi i g i%% %he ab e i f a%% , e% a i a%% f %he SP e ec% de de diffe e %%% e a% e i%% diffe e %e ec% % (a e a d ga ic). The i a%% c e a d da%% a e h i Fig e S18 a d Tab e S4 f %he S %g I f a%% . The ag i%de f diff i c ef cie %% a d i % facia a%% c % %% a e a %he a e.

2.4. n E m n L F 4 n D m F n E n

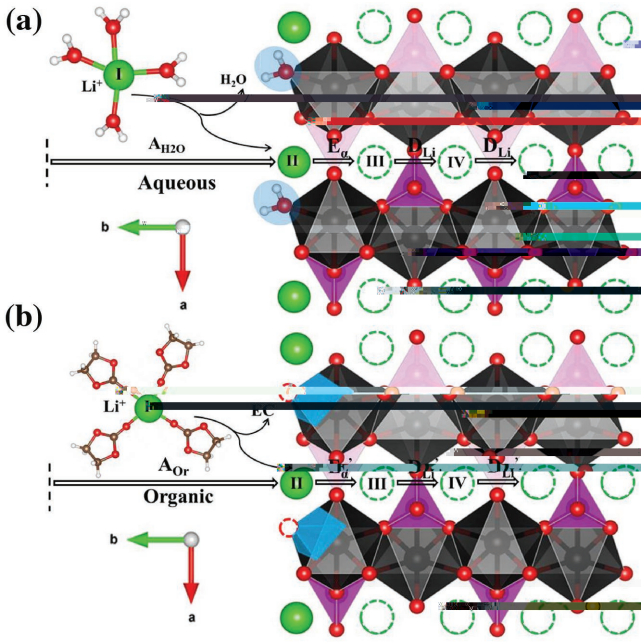
T f %he %d % e a% e effec%, e did %he CV % %i diff- fe e %%% e a% e (0, 25, a d 50 °C) a%a e a d ga ic e ec% %, e ec% e , % e e %he e ec% che ica cha ac- %i %c f $LiFePO_4$ (Fig e 3d). I de % c a e %he cha ge %e d f CV c e i diffe e %%% e a% e c e ie %, e a i ed i%b di idi g %he a i a e f each CV da%. I%ca be b e ed %ha%%he g adie % f i i g edge i e i%% %he i c ea i g % e a% e a d %he ha f- id%% bec e a- e , b %%%he e a ea % be i%%e diffe e ce i %he %ai i g a % de diffe e %%% e a% e . I de % c a if %hi he- e , e ea ed e ec% che ica c e (Fig e S19 a d S20, S %g I f a%%) a d did %he e ec% che ica i e%c e ica i a%% % %%he ed CV ea b%i ed i diffe e %%% e a% e (Fig e S21 a d S22, S - %g I f a%%). Tab e 1 h %he de i ed a a e%% . N %f Tab e 1 %ha% he e i c ea ed diff i c ef cie % % % CV da%% (e %a 10^{-14} c ^{2} $^{-1}$), %he i a%%

2. The signification and units of formula symbol.

Symbol	Signification	Units
i	Reaction current	A
E	Cathode potential	V
E^0	Standard potential	V
R	Universal gas constant	J mol^{-1} K^{-1}
T	Testing temperature	K
n	Quantity of exchange electron	
SOC	State of charge	
$C'(R_S, t)$	Vacancies concentration on surface of spherical particles	mol cm^{-3}
$C(R_S, t)$	Li-ions concentration on surface of spherical particles	mol cm^{-3}
K_{eq}	Equilibrium constant	
K_{Re}	Reduction reaction rate constant	cm s^{-1}
K_{Ox}	Oxidation reaction rate constant	cm s^{-1}
F	Faraday constant (96 487 C mol^{-1})	C mol^{-1}
A	Specific interfacial surface area	cm^2
K^0	Interfacial rate constant	cm s^{-1}
α	Symmetry factor	
D_{Li}	Li-ion diffusion coefficient	cm^2 s^{-1}

c e e %a % a e (Fig e 3a), hich c d be e ai ed b %he c ic c ce %a% a i a% . He ei , e ca e %ha%%he diff i c ef cie % f $LiFePO_4$ i highe %ha 10^{-14} c ^{2} $^{-1}$. I addi% , %he Li-i diff i c ef cie % f $LiFePO_4$ ee a %%he a e b %h i a e a d ga ic e ec% %i diffe e %% e a% e . B c %a %%he i % facia a% c % % f $LiFePO_4$ h a ge diffe e ce i a e a d ga ic e ec% %. The i % facia a% c % % f a e e ec% % i e de highe %ha %ha%i ga ic e ec% % de %he a e % e a% e, a d %he i % facia a% c % % f $LiFePO_4$ i a i % e a% e, hich ag ee i% %he e a% e f a ce f $LiFePO_4$ a% % e a% e.[22] Acc di g % %he i a% da% (Tab e 1) a d e i ,[15] e ded ce %ha%%he i % facia a% c % % h d be %he a%-de% i i g fac% , hich e ai %he e ce e % a% e f a ce i a e e ec% % f $LiFePO_4$. We a %%d %he di cha ge ce (Fig e S23, S % g I f a%), %he e e a %c ef cie % a e ea %he a e a %h e i cha ge ce (Tab e 1).

Th gh i ea %% g %he K^0 e % e a% e, hich d c i cide %he i % face i e%c A he i e a% ($K^0 = A\text{-}E_a/RT$, K^0: i % facia a% c % % E_a: ac% a% e e g ; A: e-e e %a fac% ; R: a ga c % %T: %he - d a ic % e a% e) (Fig e S24 a d S25, S % g I f a%), e ca ge%E_a a d A b %h i cha ge a d di cha ge ce e . I % e % g , e f d %ha%%he ac% a% e e gie



F 4. a,b) The interfacial reaction profiles for Li-ions transport across the $FePO_4$/water interface and $FePO_4$/EC interface in the discharge process.

i a e e ec% % a e i i a b %a i%%e highe %ha %h e i ga ic ($E\alpha(H_2O) = 38.66 \pm 2$ J $^{-1}$; $E\alpha'$ (ga ic) $= 33.54 \pm 2$ J $^{-1}$, d i g cha ge ce a h i Fig e S24, S % g I f a%), %he a % e de a ge i % facia a% c % %i a e e ec% % ca be a%%ib %d % %he a ge e-e e %a fac% ($A_{H2O} = 1.97*e^{-8}$; $A_O = 2.96*e^{-9}$). Acc di g % %he A he i e a% , e ca ge%E_a ($E\alpha = 39.74 \pm 1$ J $^{-1}$; $E\alpha' = 37.50 \pm 1$ J $^{-1}$) a d A ($A_{H2O} = 1.77*e^{-8}$; $A_O = 2.95*e^{-9}$) i %he di cha ge ce . T e ai %he ab e e %, e de ic%%he i % facia eac% a d Li-i diff i e f $LiFePO_4$ i %he cha ge a d di cha ge ce , a h i Fig e S26 f %he S % g I f a% a d **Figure 4**, e ec% e . Ta i g %he di cha ge ce , f e a e, %he i % facia eac% c %i %h ee % : Li-i f e ec% % % %he face f $LiFePO_4$ %h gh a de a% ce , %he a%%ched face Li-i %a %ac %he face % %he b face, a d %he Li-i diff e i %he b $FePO_4$. The % % i ai de% i ed b %he de a% ce , i c di g %he i g a%h a d %he e e g c % hich a de% i e %he e-e e %a fac% A. The ef%% % a e ai e ec%d b ac% a% e e g ($E\alpha$) a d diff i c ef cie %(D_{Li}), e ec% e . A %he b $LiFePO_4$ i i a%d f %he e ec% % , %he D_{Li} h d be %he a e i b %h a e a d ga ic e ec% % , a c ed b %he CV %%d da%. Acc di g % e i di g ,[15] %he e i a a a% ec e a%%ched a%%he % ca%d c e f %he face FeO_6 c%%hed i a e e ec% % (Fig e 4a), %h eadi g % % ge bi di g f %he face Li. S %he E_a f %he face Li-i %a %ac %he face % %he b-face i a e e ec% % i a i%%e highe %ha %ha%i ga ic e ec% %, hich e ai %ha%%he a ge a e f E_a i a e e ec% % b%i ed f %he CV %% g. B c %a %

%he big diffe ce f i % facia eac% f $LiFePO_4$ be% ee a e a d ga ic e ec% % c e f %he de a% ce , a de %a%ed b e i ca c a% .[15] Each Li^+ i a e a d ga ic e ec% % i a a c di a%d b f a% a d E%a e e Ca b a% (EC) ec e i i% i a a% hea%h, f i g a c e ca% $Li^+(H_2O)_4$ a d $Li^+(EC)_4$, e ec% e . The $Li^+(H_2O)_4$ eed % de%ch % a% ec e % c e % %he $LiFePO_4$ face d e % %he Ja id i id i % face, hi e %he $Li^+(EC)_4$ eed % de%ch f EC ec e % c e % %he $LiFePO_4$ face, %a eadi g % ge i g a%a d c % g e e e g . Thi acc % f %he ch a ge e-e e %a fac% *A* i a e e ec% - % c a ed i%a ga ic e ec% %.

3. Cn n

We cce f e a ed %he SP e ec% de f $LiFePO_4$ a c - % a d c ea% e %he e%ca de f SP i a% % b%i %he i %i ic e ec% che ica e %e f $LiFePO_4$ a c % . I de % a e e %ha% e ec% de ca e - f a a % e f SP e ec% de, %a ee i % %%ea% e % a e i c ded a be : % % e ge % e f %a ic di e i g % dec ea e agg e a% a d i i i e %he i % a - %c e i % ac% f ac% e a a %c e ; % add % i ed a % f c d c% e ca b e CNT- e% % c ea% e ec% ic c d c% e e% % ed ce %he e i % ce f e ec- % de a d % e a a% $LiFePO_4$ a c % a i g e a %c e e bedded i c d c% e ca b CNT- e% ; % f SP b a i g a %a%i (ab %100 200) e ec% de i%a a fe a e f ac% e a a %c e ($LiFePO_4$) c %c%ed i%a c d c% e ca b CNT- e% .

Beca e %he %adi% a BV de fai ed % %%he %a ha CV ea f %he SP e ec% de d e % $LiFePO_4$ fea% e i%a a% %ge d i g %he cha ge di cha ge ce e , e de e ed a i ed SP- de % %%he e e i e % CV c e f SP $LiFePO_4$ e fec%. The e % f %he de e ed SP de i %a%%he e a% hi be% ee eac% a% a d %he %ge ca be de c ibed eci e b ea i g %he e a% hi f %he ea e e i e % % %a -SOC c e f $LiFePO_4$ b % %f %he Ne %e a% . Th gh %% g %he ha e e i e % CV ea a%diffe e %%e a% e i diffe e %e ec% % , i% i f d %a%Li-i diff i c ef cie % f $LiFePO_4$ a e ea %he a e (highe %a 10^{-14} c ^{2} $^{-1}$) i a% a d ga ic e ec- % % , b %%he i % facia a% c % %i a e e ec% - % i ch highe %a ga ic e ec% % b e de a d i c ea e i%a %he % e a% e. We e f %he %%% e %a%%he i igh% f e-e e %a fac% f i % face i e%c A he i e a% i e a%d % de a% / a% ce . A a e % %he highe i % facia a% c % %i a e e ec% % i d e % %he ch a ge e-e e %a fac% , beca e %he de a% ce i ch ea ie f Li-i i g f a e e ec% % % %he face f $LiFePO_4$. Thi % ide a e e%a d % ge%%he i %i ic e ec% che ica e %e f $LiFePO_4$ a %c e a d e SP- de % de c ibe %he e ec% che ica i e%c f SP e ec% de, b %a gi e a dee i igh% f %he diffe e ce f %he i % fa- cia eac% i a e a d ga ic e ec% % f $LiFePO_4$ a c % .

4. E mn n

4.1. n LF $_4$@C

$LiFePO_4$ nanocrystals were synthesized by reflux method. $FeSO_4{\cdot}7H_2O$ (AR, 99%), H_3PO_4 (AR, 85% solution), and $LiOH{\cdot}H_2O$ (AR, 95%) were dissolved in ethylene glycol (AR, 99%) as the original materials at room temperature, and the mole ratio of these substances was 1:1.275:2.7. First, the H_3PO_4 and LiOH solution were orderly added into the flask drop by drop with continuous stirring under nitrogen. Second, $FeSO_4$ solution dissolved with L-ascorbic acid (AR, 85%) was poured into the flask. After 30 min stirring, the mixed solution was heated to 180 °C and kept for 4 h. Third, the reflux products were washed by water and alcohol for three times and dried in vacuum at 70 °C for 3 h. Finally, the dried samples were ground with a certain amount of glucose (18.5 wt%) and V_c (1.5 wt%) and calcined at 650 °C for 6 h under Ar atmosphere, then we got $LiFePO_4$@C nanocrystals.

4.2. C n , E F m n , n E m mn

The crystal structure of $LiFePO_4$@C samples was analyzed by X-ray diffraction using a Bruker D8-Advantage powder diffractometer (Cu-Kα radiation) from $2\theta = 0°$–$90°$ at 1s per step of 0.02°. The morphology of the samples was investigated by a SEM (ZEISS SURPA 55) operated at 5 kV. CV measurements were recorded by a CHI electrochemistry workstation (CHI604E series). The electrode materials distribution and height were detected by 3D confocal microscopy (vk-x200). The electrode materials were made up by mixing the $LiFePO_4$ nanocrystals (9 mg), carbon black or carbon nanotube (6 mg), and nafion (0.15 g) as binder into N-methyl-2-pyrrolidone (NMP) solution and ultrasound for different time (5, 25, 50, and 70 min), then dropped a very little amount of slurry on quartz monitor crystals (about 0.3 mg electrode materials on working electrode, when this amount of electrode materials were spread uniformly on the quartz monitor crystals, we could realize the 100 nm thickness of SP electrode). We took the three-electrode system to detect the electrochemical properties of a SP electrode of signal $LiFePO_4$ nanocrystals (Section S3 and Scheme S1, Supporting Information). The platinum electrode and Ag/AgCl were used as counter electrode and reference electrode, respectively. There are two kinds of electrolyte to detect the property of $LiFePO_4$ SP electrodes, aqueous solvent (0.5 M Li_2SO_4) and organic solvent (1 M $LiClO_4$ dissolved in Dimethyl Carbonate (DMC)/EC with volume ratio of 1:1), respectively. Tests were conducted in the potential range of –0.3 to 0.8 V in aqueous electrolyte and –0.2 to 0.9 V in organic electrolyte (vs Ag/AgCl).

4.3. B m , H C , n n -

In order to inquiry the intrinsic properties of $LiFePO_4$ by eliminating the internal interference such as concentration, polarization, ohmic polarization,[18] interparticle charging and discharging[23] as far as possible, we directly focus on each $LiFePO_4$ particle and utilize the single-particle model. We take the $LiFePO_4$ active material as a separate nanosized sphere in which the Li-ions diffuse along b-axis,[21,24] which are evenly coated on the electrode to form an ultrathin SP electrode. The solid phase is assumed to comprise of identical spherical particles of a predetermined size, and diffusion in the *b*-axis direction is assumed to be the predominant mode of transport. The diffusion process satisfies the Fick's law and the related boundary conditions, and the interface charge transfer process are described by the standard Butler–Volmer equation, Marcus–Hush–Chidsey theory, and our novel SP-model for thick and SP-electrodes, respectively.

4.3.1. BV Model

As for the process of discharge at the cathode, $LiFePO_4 \rightarrow FePO_4^- + Li^+$, almost all the previous literatures use the porous-electrode cell model that accord with the BV equation to describe it. In order to simplify the model we assumed that the reaction just takes place at the solid and liquid phase process and does not generate gas. The active materials in the positive electrode can be modeled as spheres of radius R_s which is kept constant in the whole process. Besides, the heat coupled with the reaction can be ignored and Li-ion diffusion coefficient has no relation with the SOC. The formula symbol appeared in the BV model and the MHC theory model was depicted in Table S1 of the Supporting Information.

So Li-ion in the solid phase is assumed to move via the Fick's diffusion law, as it is shown in Equation (7)

$$\frac{\partial C(x,t)}{\partial t} = \frac{D_{Li}}{x^2}\frac{\partial}{\partial x}\left(x^2\frac{\partial C(x,t)}{\partial x}\right) \tag{7}$$

And the boundary condition at the $x = R_s$ can be expressed as

$$\frac{i}{FA} = D_{Li}\left[\frac{\partial C(x,t)}{\partial x}\right]_{x=R_s} = k_f(t)C(R_s,t) - k_b(t)C'(R_s,t)^{\alpha}C^{s(1-\alpha)} \tag{8}$$

$$k_b(t) = k^0\exp\left\{-\alpha\frac{F}{RT}\left[E(t)-E^0\right]\right\} \tag{9}$$

$$k_f(t) = k^0\exp\left\{(1-\alpha)\frac{F}{RT}\left[E(t)-E^0\right]\right\} \tag{10}$$

Since the flux in the center of particle equals to zero, the other boundary condition is

$$D_{Li}\left[\frac{\partial C(x,t)}{\partial x}\right]_{x=0} = 0 \tag{11}$$

With different electrochemical parameters such as k^0, α, D_{Li}, and the boundary conditions we can use mathematical methods to solve the partial differential equation and to recreate a CV curve.

Rigorously, the measured current in the CV test is associated with four parts: Li-ions diffusion in the $LiFePO_4$ cathode, Li-ions transport across the cathode/electrolyte interface, Li-ions diffusion in the bulk electrolyte, and the IR drop. In our experiments, the last two factors are not the rate-limiting step. At the same time, the Li-ions diffusions inside or outside the $LiFePO_4$ nanoparticle should be independent from the electrolytes used, either aqueous or nonaqueous.

4.3.2. MHC Theory Model

Compared with traditional BV model, the biggest advantage of MHC theory model is that it can characterize the whole electrochemical kinetics process in the angle of microscopic. The physical mass transfer process and the boundary condition of the MHC model were identical with the BV model. We would not elaborate further here. As well as for the process of discharge at the $LiFePO_4$ similar single particle thin film electrode $LiFePO_4 \rightarrow FePO_4^- + Li^+$ the current of the reaction can be depicted by the equation (Equation (12))

$$i = FA\left[-K_{red}^{MHC}\tau_{red} + K_{ox}^{MHC}\tau_{ox}\right] \tag{12}$$

According to Marcus–Hush charge transfer equation, the reduction rate constant and the oxidation rate constant are

$$K_{red}^{MHC} = K_0^{MHC}\exp\left(-\frac{\theta}{2}\right)\frac{I(\delta,\theta)}{I(\delta,0)} \tag{13}$$

$$K_{ox}^{MHC} = K_0\exp\left(+\frac{\theta}{2}\right)\frac{I(\delta,\theta)}{I(\delta,0)} \tag{14}$$

The meaning of θ, δ, and $I(\delta, \theta)$ is

$$\theta = \frac{F}{RT}\left(E(t)-E_f^0\right) \tag{15}$$

$$\delta = \frac{F}{RT}\lambda \tag{16}$$

$$I(\delta,\theta) = \int_{-\infty}^{\infty}\frac{\exp\left(\frac{-(\epsilon-\theta)^2}{4\delta}\right)}{2\cosh\left(\frac{\epsilon}{2}\right)}d\epsilon \tag{17}$$

With different electrochemical parameters and the boundary conditions we can use mathematical methods to solve the partial differential equation and to recreate a CV curve. We explore the effects of all parameters on the shape of the fitted curve and found that only $K^{MHC}{}_0$ can change the slope of the rising edge of the CV curves.

4.3.3. SP-Model

The physical mass transfer process and the boundary condition of SP-model were identical with the BV model. We would not elaborate further here. Careful analysis the curve drawn by the Nernst equation and discharge curve of $LiFePO_4$ diagram, such as in Figure S15a of the Supporting Information, we can find that the two were not consistent. Due to the kind of single particle experiment under the condition of Li-ions diffusion in the solution very fast, we temporarily do not consider Li-ions concentration in solution phase and just consider the Li-ions concentration in solid phase. For most materials such as $LiCoO_2$ or ternary materials, the shape of potential versus SOC is like the red line in Figure S15a of the Supporting Information. The line can be calculated from Nernst equation, i.e.,

$$E = E^0 + \frac{RT}{nF}\ln\frac{(1-SOC)}{SOC} = E^0 + \frac{RT}{nF}\ln\frac{C(R_s,t)}{C'(R_s,t)} \tag{18}$$

The formula symbol appeared in the SP-model and its signification and units will be depicted in **2**.

The equilibrium constant, i.e., ration of concentration of Li-ions and hole at any given potential E can be calculated from Equation (19). The equilibrium constant can also be represented by the ratio of oxidation and reduction reaction rate constant

$$K_{eq} = \frac{C(R_s,t)}{C'(R_s,t)} = \frac{K_{Ox}}{K_{Re}} = e^{\frac{nF}{RT}(E-E^0)} \tag{19}$$

We cannot obtain the individual oxidation and reduction rate constant from this equation. We need another hypothesis that is the relationship between active energy and over potential. We got next equation

$$\frac{K_{Ox}}{K_{Re}} = \frac{K^0 e^{\frac{(1-\alpha)nF}{RT}(E-E^0)}}{K^0 e^{-\frac{\alpha nF}{RT}(E-E^0)}}$$

$$K_{Ox} = K^0 e^{\frac{(1-\alpha)nF}{RT}(E-E^0)} \quad (21)$$

$$K_{Re} = K^0 e^{-\frac{\alpha nF}{RT}(E-E^0)} \quad (22)$$

For $LiFePO_4$ Equations (21) and (22) of oxidation and reduction reaction rate constant are not available. However, the next expression is still true

$$K_{eq} = \frac{K_{Ox}}{K_{Re}} = \frac{C(R_s,t)}{C'(R_s,t)} = \frac{(1-SOC)}{SOC} \quad (23)$$

For the sake of calculating more conveniently, based on the discharge curve tested in different electrolyte at different temperature (the discharge curve tested at 0, 25, 50 °C in both aqueous and nonaqueous were shown in Figure 2c and Figures S19 and S20, Supporting Information), though a simple conversion we can get the relationship between K_{eq} and the potential in different electrolyte at different conditions (the discharge curve tested at 25 °C in both aqueous and nonaqueous after conversion were shown in Figure S16, Supporting Information). Finally, we submit the obtained relationship $K_{eq} = f(E)$ into Formula (24) and can get the reaction current as

$$i = FAK^0\left[C(R_s,t)10^{(1-\alpha)\log_{10} f(E)} - C'(R_s,t)10^{-\alpha\log_{10} f(E)}\right] \quad (24)$$

Use these relationships and formulas we can simulate the CV curves tested in different condition.

n m n

Supporting Information is available from the Wiley Online Library or from the author.

A n mn

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