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锂离子电池中苯衍生物氧化还原穿梭分子的一种稳定性模型:同时考虑成键/断键反应和还原反应

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摘要:提出了锂离子电池中苯衍生物氧化还原穿梭分子的一种稳定性模型。此模型同时考虑了电池中氧化还原穿梭分子的成键/断键反应和还原反应,在100%穿梭分子保护充电次数的实验值(用对数表示)和组合反应指数(E_b(ER)+0.3E_b(Li))之间得到了很好的线性关系,其中E_b(ER)和E_b(Li)分别是氧化还原穿梭分子阳离子在模型反应中与乙基(ER)、Li原子团中单个Li原子的结合能。

关键词:锂离子电池; 苯衍生物; 氧化还原穿梭分子; 稳定性模型
中图分类号:O561.4;O646.2 **文献标志码**:A

A Stability Model for Benzene Derivative Redox Shuttles in Lithium-Ion Batteries: Including both Bond Forming/Breaking Reactions and Reduction Reactions

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Abstract: A stability model is presented for the benzene derivative redox shuttles in lithium-ion batteries. This model takes both bond forming/breaking reactions and reduction reactions of redox shuttles in batteries into account and obtains a very good linear correlation between the experimental numbers of 100% shuttle-protected overcharge cycles in logarithm scale and the combined reactivity indexes, E_b(ER)+0.3E_b(Li), where the values of E_b(ER) and E_b(Li) are the binding energy of the redox shuttle cation in the model reactions with an ethyl radical (ER) and a Li atom in bulk, respectively.

Key words: lithium-ion battery; benzene derivative; redox shuttle; stability model

、 [4]。
。 (Redox shuttle additives)
, [5-17]。 ( )
。 , : ,
。 S E_{ox}(
[1-2], [1,3], 0.3~0.4 V) , S
[1-3], S^+, S^+ ,

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S, 。 ,
S^+
,
, ,
。

、 。 [18] 58
, 2,5- - -1,4-
(DTDMB) ,100%
(N_{cycle}) 300 , 5 N_{cycle} 12～33
, 52 N_{cycle} 9 [18]。Chen
Amine [11,19-20] DTDMB、1,4-
(DMB)
、 。
, /
。

1

(Dalhousie) Dahn
[6-10,12-16]。 :Li
$LiFePO_4/Li_{4/3}Ti_{5/3}O_4$, 0.7 mol/L
(LiBOB) , (
(PC)、 (DMC)、
(EC)、 (DEC) 1∶2∶1∶2
), 0.1 mol/L
(0.1 mol/L,
)。$LiFePO_4$ Phostech Lithium
(Montreal, PQ, Canada), $Li_{4/3}Ti_{5/3}O_4$ NEI
Corp. (Piscataway, NJ, USA), LiBOB
Chemetall。 w = 10% Super S
(MMM Carbon, Belgium) w=10%
(PVDF) 2 。$LiFePO_4$
$Li_{4/3}Ti_{5/3}O_4$ 。
20% ,
($LiFePO_4$), Li/Li^+
。 10 h
100% , 200%
(100%)
(Li/Li^+ 4.9 V)[8-9,15-16]。
Gaussian03 ,
B3LYP [21], Becke
Lee-Yang-Parr [22]。

2

S S^+, S^+
S, S
, 。 S^+
,
,
。 S^+ ,
, S
。
, S^+
,
, 。
S^+ ,
[23-24], (1) S^+ C_2H_5—
(ER) ,
E_b(ER) S^+ , E_b(ER)
(2)。 ER S^+ ,
E_{el}(ER_S^+) , (2) 。
ER S^+ ,
ER_S^+ ,
E_b(ER) 。E_b(ER) S^+
, S^+ / ,
E_b(ER) , S^+ 。

$$ER + S^+ \rightarrow ER\_S^+ \quad (1)$$

$$E_b(ER) = -\{\min[E_{el}(ER\_S^+)] - [E_{el}(ER) + E_{el}(S^+)]\} \quad (2)$$

1 (2) 20
E_b(ER) , (E_{ox})
100% (N_{cycle})。N_{cycle}
,
N_{cycle} , 。E_b(ER)
1.43～2.16 eV , N_{cycle} 50 5 ,
15 , 2～49 。N_{cycle}
E_b(ER) 1 , E_b(ER) , N_{cycle}
, S^+ ,
。
,

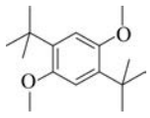
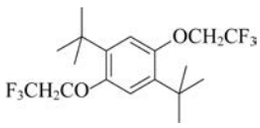
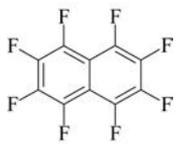
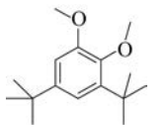
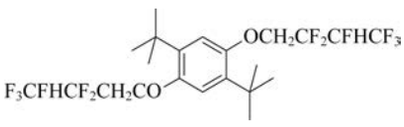
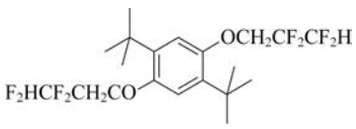
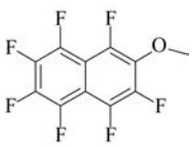
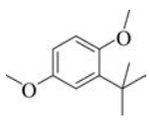
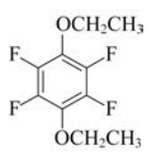
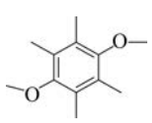
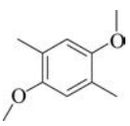
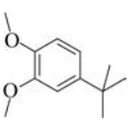
$$d = |\ln N_{cycle,fit} - \ln N_{cycle}| = \left|\ln \frac{N_{cycle,fit}}{N_{cycle}}\right|,$$

$D_f = \exp(d)$, d 0, D_f 1,
。 $N_{cycle,fit}$ 。 1

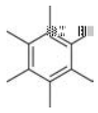
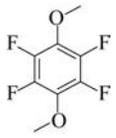
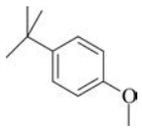
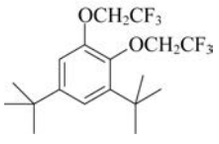
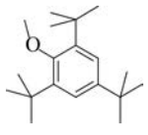
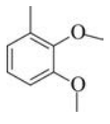
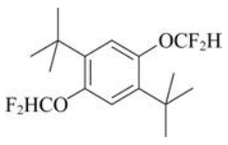
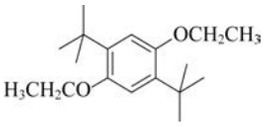
$$\ln N_{cycle,fit} = -5.453\ E_b(ER) + 12.63 \quad (3)$$

表 1 20

Table 1 Activity parameters of twenty benzene derivatives

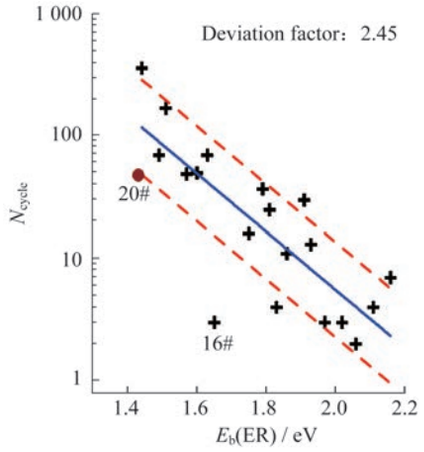
No.	Benzene derivatives	Redox shuttle molecule	E_{ox}(exp)/V	N_{cycle}	E_b(ER)/eV	E_b(Li)/eV
1	2,5-Di-*t*-butyl-1,4-dimethoxybenzene (DTDMB)		3.96	363	1.44	1.77
2	2, 5-Di-*t*-butyl-1, 4-bis (2, 2, 2-trifluoroethoxy)benzene		4.25	170	1.51	2.47
3	Octafluoronaphthalene		4.85	70	1.49	2.66
4	3,5-Di-*t*-butyl-1,2-dimethoxybenzene (DBDB)		4.05	70	1.63	2.36
5	2,5-Di-*t*-butyl-1,4-bis(2,2,3,6,6,6-hexafluorobutoxy)benzene		4.30	50	1.60	2.78
6	2, 5-Di-*t*-butyl-1, 4-bis (2, 2, 3, 3-tetrafluoropropoxy)benzene		4.31	49	1.57	2.59
7	2-Methoxy-heptafluoronapthalene		4.50	37	1.79	2.45
8	2-*t*-Butyl-1,4-dimethoxybenzene		3.87	30	1.91	1.87
9	1,2,4,5-Tetrafluoro-3, 6-diethoxybenzene		4.47	25	1.81	2.56
10	2,3,5,6-Tetramethyl-1, 4-dimethoxybenzene		4.10	16	1.75	2.15
11	2,5-Dimethyl-1,4-dimethoxybenzene		3.80	13	1.93	1.72
12	4-*t*-Butyl-1,2-dimethoxybenzene		4.07	11	1.86	2.65

(1)

No.	Benzene derivatives	Redox shuttle molecule	E_{ox}(exp)/V	N_{cycle}	E_b(ER)/eV	E_b(Li)/eV
13	Hexamethylbenzene		4.20	7	2.16	2.56
14	1,2,4,5-Tetrafluoro-3, 6-dimethoxybenzene		4.49	4	1.83	2.60
15	4-*t*-Butyl-1-methoxybenzene		4.15	4	2.11	2.35
16	3,5-Di-*t*-butyl-1,2-bis (2,2,2-trifluoroethoxy)benzene		4.50	3	1.65	3.17
17	1,3,5-*t*-Butyl-2-methoxybenzene		4.40	3	2.02	2.54
18	2,3-Dimethoxytoluene		4.05	3	1.97	2.71
19	2,5-di-*t*-Butyl-1,4-bis (difluoromethoxy) benzene		4.90	2	2.06	2.62
20	2,5-di-*t*-Butyl-1,4-diethoxybenzene (DTDBE)		3.80	48	1.43	1.65

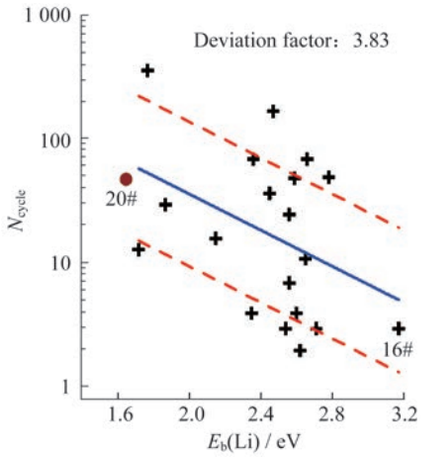
1 , ,
0.896, D_f 2.45, $N_{cycle,fit}$/2.45 。
$2.45N_{cycle,fit}$ E_b(ER) , 1 S^+ ,
2 , 79% 2 / , ,
。 , E_b(ER) S^+ 。
1.60 eV, (7) $N_{cycle,fit}=50$。 , , (4) , Li
, ,
79% 20～123 。 20#(DTBEB) E_b(Li) S^+ ,
E_b(ER) 1.43 eV (7) (5) 1。 ,Li S
125, 2.45, 51～ , Eb(Li) , 。
307 79%。 48, $Li + S^+ \rightarrow Li\_S^+$ (4)
51 。 E_b(ER) $E_b(Li) = -\{\min[E_{el}(Li\_S^+)] - [E_{el}(Li(bulk)) + E_{el}(S^+)]\}$ (5)
DBDB

2 1#～19# E_b(Li) N_{cycle} ,N_{cycle} E_b(Li) ,ln $N_{cycle,fit}$ E_b(Li) , 3.83, $N_{cycle,fit}$/3.83 3.83$N_{cycle,fit}$, $N_{cycle,fit}$ 68%, 1 。



1 N_{cycle} E_b(ER)

Fig. 1 Relationship between N_{cycle} and E_b(ER) of the benzene derivatives



2 N_{cycle} E_b(Li)

Fig. 2 Relationship between N_{cycle} and E_b(Li) of the benzene derivatives

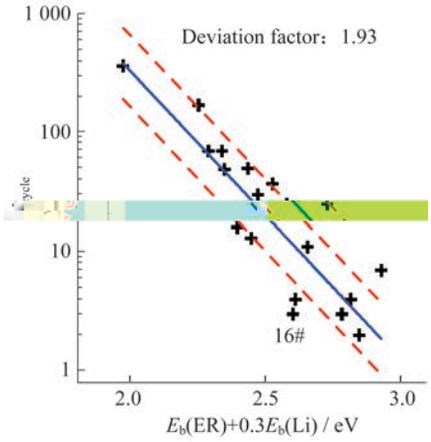
/ , ln N_{cycle} E_b(ER) E_b(Li) :

$$\ln N_{cycle} \approx -a[E_b(\mathrm{ER}) + bE_b(\mathrm{Li})] + c \quad (6)$$

a,b,c 。 (6) b。 1 1#～19# , D_f b 。 b 0.2,0.3 0.4 , 2.00,1.93 1.96; b=0.3 , 1#～19# 3 , 17#, 18# , 3 ln N_{cycle} E_b(ER)+0.3E_b(Li) , d 0.66, D_f 1.93,

$$\ln N_{cycle,fit} = -5.566[E_b(\mathrm{ER}) + 0.3E_b(\mathrm{Li})] + 16.92 \quad (7)$$

3 1.93, $N_{cycle,fit}$/1.93 1.93$N_{cycle,fit}$。 68% $N_{cycle,fit}$/1.93 1.93$N_{cycle,fit}$ 。 , (7) E_b(ER)+0.3 E_b(Li) 100% , 68% $N_{cycle,fit}$/1.93～1.93$N_{cycle,fit}$ 。 , 。 3 N_{cycle}>10 1#～12# 。 12 , (7) 1.69。



3 19 N_{cycle} E_b(ER)+0.3E_b(Li)

Fig. 3 Relationship between N_{cycle} and E_b(ER)+0.3E_b(Li) for 19 benzene derivatives

1 16# (3,5- -1,2- (2,2,2-) , 。16# E_b(ER) , 1.65 eV。 E_b(ER) (3) $N_{cycle,fit}$=38, N_{cycle} 3, D_f=12.7, d=2.54, (0.896) 2.8 。 16# E_b(Li) (3.17 eV) E_b(ER)=1.65 eV (7) , $N_{cycle,fit}$=11.5, 3 , 3.8, 1.34, (0.66) 2.0 ,

E_b(ER) 。

，

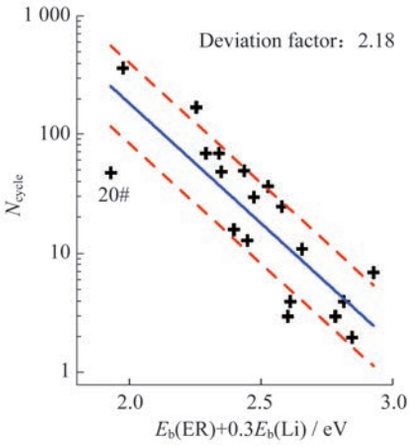
、 ，

。 1 1#～19# ，1#
(DTDMB) ， E_b(ER) (1.44 eV)
E_b(Li) (1.77 eV) ， /
、 。4#
(DBDB) ， DTDMB (1#)
， 。 DTDMB (1#)，
DBDB(4#) 1-
， ，E_b(ER) 1.63
eV， 1,2-
， ，E_b(Li)
0.59 V， 2.36 eV。
，2# 1#(DTDMB) 、
， 1# 1,4-
(—O—CH_3)
(—OCH_2CF_3)， ，E_b(Li)
2.47 eV， 1#(1.77 eV) 0.7 V。
16# DBDB，
—CH_2CF_3， 2 ，
E_b(ER)(1.65 eV) DBDB(2#) (1.63 eV)
， E_b(Li) 3.06 eV(1.77+0.59+
0.70)， 3.17 eV 。

20# (DTDEB)， :20#(DTDEB)
1#(DTDMB) ， 1,4-
。20#DTDEB
E_b(ER) E_b(Li) 1.43 eV 1.65 eV，
1#DTDMB 1.44 eV 1.77 eV
。 ， ，
，20# DTDEB 1#DTDMB
。 ，20# 100%
48， 1# 363 ， (7)
495 。 20#DTDEB
，20 ln N_{cycle}
E_b(ER)+0.3E_b(Li) 4 ，
:

$$\ln N_{cycle,fit} = -4.608[E_b(ER)+0.3E_b(Li)]+14.41 \quad (8)$$

2.18。 20#
DTDEB $N_{cycle,fit}$=255， (48)
5.3 。 4 ， 19
， DTDEB ，
2.4 。
DTDEB 48 ，
。
， ，Amine [17]
2,5- -1,4- (2-)
(DBBB)，
($C/2$ ，N_{cycle}=180)。 ，
20#DTDEB —OCH_2CH_3
—$OCH_2CH_2OCH_3$，
DBBB。 ，
， 。
， 20#DTDEB 100%
48 。



4 20 N_{cycle} E_b(ER)+0.3E_b(Li)

Fig. 4 Relationship between N_{cycle} and E_b(ER)+0.3E_b(Li) for 20 benzene derivatives

3

。 E_b(ER) ，
:
(1)
E_b(ER) E_b(Li) ， /
。 ，

5 eV
。
(2) 19 ，
E_b(ER)， 100%
(E_b(ER)+0.3E_b(Li))
。 1.93，
2.45。

(3) 3 100% 16# 3,5- -1,2- (2,2,2-), E_b(ER) 1.65 eV, , E_b(Li) 3.17 eV, 。 E_b(ER) 16# 38 , , , 11.5, 。

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