View Article Online

ChemComm

Chemical Communications

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: Q. Deng, C. Tian, Z. Luo, Y. Zhou, B. Gou, H. Liu, Y. Ding and R. Yang, *Chem. Commun.*, 2020, DOI: 10.1039/D0CC05248E.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/chemcomm

Published on 31 August 2020. Downloaded by Cornell University Library on 8/31/2020 12:08:28 PM.

COMMUNICATION

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Qijiu Deng*^a, Congcong Tian,^a Zongbin Luo^a, Yangyang Zhou^a, Bo Gou^a, Haixuan Liu^a, Yingchun Ding *^{ab} and Rong Yang^c

Endowing Ultrahigh Initial Coulombic Efficiency for Potassium-ion

Organic 2,5-dihydroxy-1,4-benzoquinone Potassium Salt

Here we propose a newly organic 2,5-dihydroxy-1,4-benzoquinone potassium salt ($K_2C_6H_2O_4$) endowing ultrahigh initial Coulombic efficiency of 96% as an advanced anode in potassium-ion batteries. Theoretical calculation and experimental results suggest that K⁺ can reversibly insert into this organic compound due to the flexible and stable structure of $K_2C_6H_2O_4$ molecule as well as fast K⁺ kinetics in the selected dimethyl ether-based electrolyte.

With the increasingly growing environmental and ecological issues from conventional fossil energy, the development and storage of efficient and clean new energy systems are of great significance.^{1,2} As an important electrochemical energy storage device, lithium-ion (Li-ion) batteries are widely applied in aerospace devices, electric vehicles and daily life notebook, mobile phones, et.al.³ Nevertheless, the shortage of lithium resource and its imbalance of distribution are gradually serious problem. Advantageously, potassium-ion (K-ion) batteries are expected to be a strong competitor for the growing large-scale energy system.⁴⁻⁶ For one thing, the potassium resources were much larger than that of lithium from the economic and cost aspect. For another, the low standard potential of K⁺/K (-2.88 V) suggest a high energy density can be dramatically obtained. Moreover, the weaker Lewis acidity of K will result in a fast K⁺ transport capability, consequently determining the high rate performance.⁷

Inspiring by the successfully commercialized "rocking chair" Li-ion batteries, constructing high safety "rocking chair" K-ion batteries were extremely in need. Accordingly, the suitable anode host were widely studied in the very recent years. For example, the most concerned carbon-based

materials, including hard carbon, soft carbon, graphite and their derivatives could deliver noticeable electrochemical performance but their low K-insert potential (below 0.2 V) resulting in the formation of unavoidable K dendritic crystal at low voltage.⁸⁻¹⁰ Other reported inorganic transition metals and their compounds suffer from much large volume change effect as compared to that of Li-ion or Na-ion batteries.¹¹⁻¹³ Consequently, the formed unstable solid electrolyte interface (SEI) will result in the irreversible capacity loss in the repeated cycles and the formed K dendritic crystal at low voltage may lead to internal short with safety concern. Compared with traditional anode materials, organic compounds show many advantages with high theoretical specific capacity, low cost, recycling, easy design and processing and safe operation of the system.14,15 Unfortunately, due to the high activity of the K substance in the organic electrolyte, a thick SEI layer is consequently formed and other surface side reactions might occur. As a result, a low first cycle Coulombic efficiency (CE) is thus obtained leading to the inefficiency in the commercialized full batteries.^{16,17} Afterwards, many organic carbonyl compounds and others were introduced as anode host in K-ion batteries, with encouraging enhanced specific capacity or rate performance.¹⁸⁻²² Nevertheless, to the best of our knowledge, their initial coulombic efficiency is still low (below 70%) and it is an urge to develop organic anode materials with a storage voltage higher than 0.8 V to avoid the formation of a SEI layer.

In this communication, a newly organic carbonyl compound, namely, 2,5 benzoquinone-1,4 di-potassium salt $(K_2C_6H_2O_4)$ was initial introduced as the high-performance anode host in K-ion batteries. The reversible K-insertion and de-insertion were located at 1.2 and 1.48 V, which can prevent the formation of solid electrolyte interface, resulting in a super high initial CE of 96%. The as-modified $K_2C_6H_2O_4$ /graphene composite can exhibit a reversible capacity of 158 mAh g⁻¹ at a current density of 100 mA g⁻¹. The advanced K-storage mainly attributed to the flexible structure of $K_2C_6H_2O_4$ molecule, the enhanced electronic conductivity from two-dimensional layered graphene as well as fast K⁺ kinetics.

^{a.} Department International Research Center for Composite and Intelligent Manufacturing Technology, School of material science and engineering, Institute of Chemical Power Sources, Xi'an University of Technology Xi'an 710048, China.E-mail: dengqijiu@xaut.edu.cn

^{b.} College of Optoelectronics Technology, Chengdu University of Information Technology. Chengdu 610225, China Xi'an 710048, China. E-mail: dvccazx@cuit.edu.cn

^{c.} School of science,Xi'an University of Technology,Xi'an 710048, China

⁺ Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

Journal Name

Published on 31 August 2020. Downloaded by Cornell University Library on 8/31/2020 12:08:28 PM.



Fig. 1. (a)the FT-IR and (b) XRD of $K_2C_6H_2O_4$ and its precursor $C_6H_4O_4$ and (c)the ¹H NMR spectrum and (d) the TGA-DSC curve of $K_2C_6H_2O_4$.

Fig. 1a shows the FT-IR spectrum of the K₂C₆H₂O₄ materials compared with its precursor 2,5 dihydroxy-1,4 benzoquinone ($C_6H_4O_4$). The vibration peak at 1680 -1380 cm⁻¹ are ascribed to $v_{c=o}$ vibration peak on the benzene ring for $C_6H_4O_4$, which disappears in the corresponding wavenumber of the generated K₂C₆H₂O₄. Instead, new peaks were emerged at 1583,1400,1280 cm⁻¹ after the reaction, and the $v_{c=o}$ characteristic peaks on the benzene ring shifted to right, which was related to the increasing molecular weight of the introduced alkali metal cations. The corresponding XRD patterns is shown in Fig. 1b, where the organic compounds deliver a certain crystallization behavior before and after the reaction, indicating that there is a strong interaction between these molecules. Resolving the single crystal structure of $K_2C_6H_2O_4$ is still ongoing in a forthcoming paper. Subsequently, the ¹H NMR determination of as-prepared $K_2C_6H_2O_4$ (Fig. 1c) and $C_6H_4O_4$ (Fig. S2) were thus performed, where an obvious H signal peak located at 4.66 ppm for the as-synthesized salt, which was ascribed to the chemical shift H in the D_2O . From the TGA-DSC curve in Fig. 1d, $K_2C_6H_2O_4$ could exhibits no weight loss from room temperature to 480 °C, and the fast weight loss after 480 °C indicates the collapse and decomposition of $K_2C_6H_2O_4$. The above discussion suggests the successfully synthesis of K₂C₆H₂O₄ with high purity. The microstructure of $K_2C_6H_2O_4$ was then characterized as shown in Fig. S1. The SEM image shows that the surface of the material was a combination of some gravel-like structures with the particle sizes ranging from 300 nm to 1 μ m.

The K-storage behavior of as-prepared $K_2C_6H_2O_4$ was initially investigated as shown in Fig. 2. The initial discharge and charge specific capacity of as-synthesized $K_2C_6H_2O_4$ were 214 mA g⁻¹ and 207 mA g⁻¹, respectively, at a current density of 10 mA g⁻¹ corresponding to an initial coulombic efficiency(CE) of 96% which is much superior than the reported organic and inorganic anode materials (Fig. 2c).²³⁻²⁵ Besides, a couple of explanate platform can be exhibited in the first and following

cycles, suggesting a fast two-electron transport interaction in the previous reported.¹⁶ Herein, the exceller of instant control of the K₂C₆H₂O₄ electrode material could be attributed to the redox peaks of the material appear at 1.48 V /1.2 V during the charge/discharge processes, which efficiently reduces the formation of the SEI film during the electrochemical reaction. Subsequently, the cyclic voltammetric (CV) test was performed with the voltage ranging from 1-2 V (insert in Fig. 2a). A reduction peak appeared near 1.13 V in the first cycle and it was stabilized at 1.2 V in the following cycles. And its oxidation peak is stably located at 1.48 V . It can be concluded from the CV that $K_2C_6H_2O_4$ electrode material exhibits excellent reversibility which agreed well with its charge/discharge curves.





To further comprehend the reversible mechanism of asprepared $K_2C_6H_2O_4$ based materials, ex-situ FT-IR measurements of $K_2C_6H_2O_4$ at different charge/discharge states in the first cycle (A,B,C,D,E points are represent: pristine state, discharge to 1.2 V, discharge to 1 V, recharge to 1.4 V and recharge to 2 V, respectively) were performed to observe the molecule vibrations during the electrochemical reaction, as illustrated in Fig. 3a-c. The represent v_s (C=O) vibration at 1642 cm⁻¹ can be gradually vanished and recovered from point A to C, and then to point E. These results suggest opening and recovering the C=O double bond in the organic ligand during Published on 31 August 2020. Downloaded by Cornell University Library on 8/31/2020 12:08:28 PM.

Journal Name

the discharge and charge processes. Additionally, the highest occupied molecular orbital (HOMO) plot of $C_6H_2O_4^{2-}$ with two negative charge (Fig. 3d) shows that the charge mainly locates on the K atoms and the molecular structure is maintained after accepting two negative charge, indicating that $K_2C_6H_2O_4$ is chemically stable with two K⁺ insertion/extraction. As shown in the optimized structure of $K_4C_6H_2O_4$, the inserted K⁺ is coordinated with two O atoms, further suggesting the structure stability of $K_4C_6H_2O_4$ (Fig. 3e). As a result, $K_2C_6H_2O_4$ can reversibly store K⁺ reversibly and the K-storage mechanism (as illustrated in Fig. 3f) of the material is the open and recovery of conjugated hydroxyl groups, which is consistent with the assumption of its energy storage mechanism at the beginning of $K_2C_6H_2O_4$ material design.



Fig. 3. (a) the selected charge-discharge states of $K_2C_6H_2O_4$;(b) ex-situ FT-IR spectrum of $K_2C_6H_2O_4$ at different states; (c) the partial enlarged drawing of the corresponding FT-IR; (d) the HOMO plot of $C_6H_2O_4^{2-}$;(e) the optimized structure of $C_6H_2O_4^{4-}$ after accepted to electrons and (f) the proposed reaction mechanism of $K_2C_6H_2O_4$ in K-ion batteries.

To improve the rate property and depress its dissolution in the organic electrolyte according to "like dissolves like" principle as we previously discussed^[7], a simple in-situ synthesis methodology was then utilized to contrast a $K_2C_6H_2O_4$ /graphene composite (see detail in the experiment part). Obviously, the addition of graphene is consistent with the peak position of the $K_2C_6H_2O_4$ material from the XRD pattern (Fig. S3), which indicates that the addition of graphene does not change the original crystal structure of the K₂C₆H₂O₄ material. Meanwhile, the graphene peaks did not appear in the XRD test, which might be weak intensity of graphene were beyond the detector. The morphology structure of the as- $K_2C_6H_2O_4$ /graphene composite prepared was further characterized by FE-SEM and TEM as shown in Fig. S4. It can be observed directly that the $K_2C_6H_2O_4$ particles are relatively randomly distributed on the surface and interlayer of the transparent, thin as cicada's wing graphene sheets. Subsequently, the rate performance of the $K_2C_6H_2O_4$ and $K_2C_6H_2O_4$ /graphene composite were comparatively investigated in Fig. 4a. The reversible discharge specific capacity of $K_2C_6H_2O_4$ is 183,172,153,118,40 mAh g⁻¹ at the current density of 20,50,100,200,400 mA g⁻¹, respectively which is still noticeable compared to reported reference.18,27

COMMUNICATION

And the reversible specific capacity is restored to 168 mA g-1 when the current density reset to 20 mA gH1 Interesting 152718 K-storage electrochemical behavior of K₂C₆H₂O₄/graphene K-storage composite could deliver much better electrochemical behavior than the bulk one. For instance, a reversible capacity of 243 mAh g⁻¹ were obtained at the current density of 20 mA g⁻¹ which is very closed to the theoretical capacity (the calculated specific capacity of K₂C₆H₂O₄ is 248 mAh g⁻¹). Advantageously, the specific capacity of $K_2C_6H_2O_4$ / graphene composite could maintain 245, 220, 170 and 110 mAh g⁻¹, respectively, at higher current densities 50,100, 200, and 400 mA g⁻¹. When the current density is reset to 20 mA g⁻¹, the reversible specific capacity can be restored to about 230 mAh g⁻¹, suggesting the structure $K_2C_6H_2O_4$ /graphene composite can be stably maintained in fast charge/discharge processes. The corresponding charge/discharge curves were further displayed in Fig. 4b. It can be observed directly that similar curves are displayed at different rates, all of which show a certain electrochemical platform, which indicates that K₂C₆H₂O₄/graphene composite has a stable electrode reaction process. However, a polarization phenomenon of the charge/discharge curves occurs for the bulk $K_2C_6H_2O_4$ at high current density, which could be attributed to the poor electronic conductivity (Fig. S5) as well as existing agglomeration issue resulting the instability of the electrode reaction. Herein, graphene exhibits negligible capacity ranging from 1 to 2 V in K-ion batteries (Fig. S6).



Fig. 4. (a) the rate performance of as-prepared $K_2C_6H_2O_4$ and $K_2C_6H_2O_4/graphene$ composite;(b) the charge-discharge curves of $K_2C_6H_2O_4/graphene$ composite at different current density; (c) the cyclic performance of $K_2C_6H_2O_4/graphene$ composite; and (d) the fitting relationship diagram of scan rates and peak currents for $K_2C_6H_2O_4$ and $K_2C_6H_2O_4/graphene$ composite.

From the cyclic performance of $K_2C_6H_2O_4$ /graphene composite in Fig. 4c, a reversible specific capacity of 130 mAh g⁻¹ could be achieved with a CE of 99% at the current density of 100 mA g⁻¹ over 50 cycles. The solubility test of bulk $K_2C_6H_2O_4$ and $K_2C_6H_2O_4$ /graphene is carried out, as shown in Fig. S7. Both the $K_2C_6H_2O_4$ powder and $K_2C_6H_2O_4$ /graphene composite were dissolved in the selected DME electrolyte solvent. The

COMMUNICATION

supernatant of $K_2C_6H_2O_4$ becomes turbid and some orange particles precipitate at the bottom of the bottle after vibration and standing for 2h, 24h and still a week. On the contrary, the K₂C₆H₂O₄/graphene composite material is relatively clear without obvious turbid phenomenon after staying the same time. The experimental results obviously illustrate the dissolution issues can be obvious depressed by constructing a $K_2C_6H_2O_4$ /graphene composite which is accordance well with performance electrochemical the enhanced of $K_2C_6H_2O_4$ /graphene composite compared with the raw $K_2C_6H_2O_4$ material. All in all, the introduction of $K_2C_6H_2O_4$ particles into the graphene lamellae not only makes the adjacent graphene sheets separate, but also reduces the agglomeration problem which makes the fully utilization rate of active materials obviously during charge/discharge. Accordingly, the as-synthesized composite can construct a good electronic conductive network for the rapid transport of K⁺, increases the infiltration range of the electrolyte, and shorten the ion diffusion path to accelerate the electrode reaction. To further understand the superior K-storage behavior of as-prepared K₂C₆H₂O₄/graphene composite, the relationship of scan rates and peak currents for K₂C₆H₂O₄ and $K_2C_6H_2O_4$ /graphene composite were thus performed (Fig. 4d). It can be concluded from the fitting relationship diagram that potassium diffusion ability of the the prepared $K_2C_6H_2O_4$ /graphene composite is much better than that of $K_2C_6H_2O_4$ raw material (Fig.S8). Herein, the addition of graphene can efficiently depress the dissolution issues and improve the electrolyte and shortens the ion diffusion pathway²⁶, which is consistent with the electrochemical test results.

Conclusions

In conclusion, a newly organic carbonyl salt, namely 2,5dihydroxy-1,4-benzoquinone potassium salt (K₂C₆H₂O₄) with an ultrahigh initial CE of 96% was initially introduced as a suitable anode host in K-ion batteries. The intercalated and deintercalated potassium potential of K₂C₆H₂O₄ is higher than 1 V, effectively preventing the formation of the SEI film high performance. The as-modified reuslting in $K_2C_6H_2O_4$ /graphene composite could exhibit a reversible capacity of 130 mAh g⁻¹ at a current density of 100 mA g⁻¹. The superior K-storage behavior is mainly ascribed to the flexible structure of $K_2C_6H_2O_4$ molecule, the enhanced electronic conductivity original from two-dimensional layered graphene as well as fast K⁺ kinetics in the selected dimethyl ether (DME)based electrolyte. The results provide important reference for the design and modification of the electrode material for K-ion batteries.

This work was supported by Natural Science Foundation of Shaanxi Province(2019JQ-730); Natural and Scientific Programs (20JS105) funded by Education Department of Shaanxi Provincial Government; China Postdoctoral Science Foundation Funded Project (2018M633544); Postdoctoral Science Foundation of Shanxi Province of China (2018BSHEDZZ120); Innovation Capability Support Programment Shaanxi (2018GHJD-17). DOI: 10.1039/D0CC05248E

Conflicts of interest

There are no conflicts to declare

Notes and references

- 1 M. Armand and J. M. Tarascon, *Nature*, 2008, **451**, 652-657.
- 2 J. M. Tarascon and M. Armand, *Nature*, 2001, **414**, 359.
- 3 D. Larcher and J. M. Tarascon, Nat Chem, 2015, 7, 19-29.
- 4 L. Fan, R. Ma, Q. Zhang, X. Jia and B. Lu, *Angew Chem Int Edit*, 2019, **131**.
- 5 X. Wang, X. Liu, G. Wang, Y. Xia and H. Wang, *J Mater Chem A*, 2016, 10.1039.C1036TA07452A.
- 6 J. Wang, B. Wang and B. Lu, *Adv Energy Mater*, 2020, **10**.
- 7 J. Ge, B. Wang, J. Wang, Q. Zhang and B. Lu, *Adv Energy Mater*, 2020, **10**.
- 8 W. Luo, J. Wan, B. Ozdemir, W. Bao, Y. Chen, J. Dai, H. Lin, Y. Xu, F. Gu, V. Barone and L. Hu, *Nano Lett*, 2015, **15**, 7671-7677.
- 9 Z. Jian, W. Luo and X. Ji, J Am Chem Soc, 2015, **137**, 11566-11569.
- 10 J. Zhao, X. Zou, Y. Zhu, Y. Xu and C. Wang, Adv Funct Mater, 2016, 26, 8103-8110.
- 11 11. B. Kishore, G. Venkatesh and N. Munichandraiah, J Electrochem Soc, 2016, **163**, A2551-A2554.
- 12 V. Lakshmi, Y. Chen, A. A. Mikhaylov, A. G. Medvedev, I. Sultana, M. M. Rahman, O. Lev, P. V. Prikhodchenko and A. M. Glushenkov, *Chem Commun*, 2017, **53**, 8272.
- 13 Z. Hu, C. Zhou, R. R. Prabhakar, S. X. Lim, Y. Wang, J. A. van Kan, H. Cheng, S. G. Mhaisalkar and C.-H. Sow, *Journal of Applied Physics*, 2013, **113**.
- 14 Y. Chen, W. Luo, M. Carter, L. Zhou, J. Dai, K. Fu, S. Lacey, T. Li, J. Wan, X. Han, Y. Bao and L. Hu, *Nano Energy*, 2015, **18**, 205-211.
- 15 Q. Deng, S. Feng, C. Tian, Y. Ding, R. Yang, Y. Yan and Y. Xu, J Electroanal Chem, 2018, **827**, 145-150.
- 16 Q. Deng, J. Pei, C. Fan, J. Ma, B. Cao, C. Li, Y. Jin, L. Wang and J. Li, *Nano Energy*, 2017, **33**, 350-355.
- 17 K. Lei, F. Li, C. Mu, J. Wang, Q. Zhao, C. Chen and J. Chen, Energ Environ Sci, 2017, **10**.
- 18 C. Fan, M. Zhao, C. Li, C. Wang, B. Cao, X. Chen, Y. Li and J. Li, Electrochimi Acta, 2017, 253.
- 19 C. Li, Q. Deng, H. Tan, C. Wang, C. Fan, J. Pei, B. Cao, Z. Wang and J. Li, ACS Appl Mater Inter, 2017, **9**.
- 20 Y. An, H. Fei, Z. Zhang, L. Ci, S. Xiong and J. Feng, ChemCommun, 2017.
- 21 C. Wang, W. Tang, Z. Yao, B. Cao and C. Fan, *ChemCommun*, 2019.
- 22 C. Wang, W. Tang, Z. Yao, Y. Chen, J. Pei and C. Fan, *Org Electron*, 2018, **62**, 536-541.
- 23 X. Ren, Q. Zhao, W. D. McCulloch and Y. Wu, Nano Res, 2017, 10, 1313-1321.
- 24 Q. Zhang, J. Mao, W. K. Pang, T. Zheng, V. Sencadas, Y. Chen, Y. Liu and Z. Guo, Adv Energy Mater, 2018, 8.
- 25 Q. Zhao, J. Wang, Y. Lu, Y. Li, G. Liang and J. Chen, *Angew Chem Int Edit*, 2016, **55**, 12528-12532.
- 26 Yuxing, Liao, Chao, Li, Xiaobing, Lou, Peng, Wang, Qi and Yang, J Colloid Interf Sci, 2017.
- 27 X. Wang, K. Chen, G. Wang, X. Liu and H. Wang, *Acs Nano*, 2017, acsnano.7b06625.

Journal Name

emcomm Accepted Manuscrii

ChemComm Accepted Manuscript

Table of Contents Entry



A newly organic 2,5-dihydroxy-1,4-benzoquinone potassium salt ($K_2C_6H_2O_4$) with ultrahigh initial Coulombic efficiency of 96% was initially proposed as an advanced anode in potassium-ion batteries.