

ChemComm

Chemical Communications

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: Y. Zhang, H. Chao, H. Liu, X. Wang, W. Xing, H. Hu and M. Wu, *Chem. Commun.*, 2020, DOI: 10.1039/D0CC04106H.



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 [Terms & Conditions](#) and the [Ethical guidelines](#) 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.

COMMUNICATION

Regulation of the cathode for amphi-charge storage in a redox electrolyte for high-energy lithium-ion capacitors

Yunlong Zhang,^a Huixia Chao,^a Haiyan Liu,^b Xiaoshan Wang,^a Wei Xing,^a Han Hu*^a and Mingbo Wu*^aReceived 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Operating the cathode of lithium-ion capacitors in an extended potential window for amphi-charge storage is proposed to combine with a redox electrolyte-enabled capacity for balancing the capacity gap between the anode and cathode. As a result, the as-obtained lithium-ion capacitors offer a 3-fold increase in energy density.

Our increasingly electrified society raises unprecedented demand for energy storage devices with high energy and large power.¹⁻⁴ In this regard, tremendous research efforts have been devoted to boosting the practical performance of the dominated energy storage devices, such as lithium-ion batteries (LIBs) and supercapacitors. LIBs are operated using bulk-involved faradic reactions, which contribute to high energy density but very limited power capability. While supercapacitors generally handle high power because of the fast ions adsorption/desorption at the interface between the electrode and electrolyte, they only exhibit very small energy density. As a result, neither LIBs nor supercapacitors can simultaneously offer high energy and large power and such an energy storage device remains to be explored. Since the pioneering work of G. Amatucci, the hybridization of LIBs and supercapacitors has been demonstrated as a promising strategy to combine high energy density and large power capacity into one device, namely lithium-ion capacitors (LICs).⁵⁻⁷

In general, LICs consist of one battery-type anode as the energy reservoir and one capacitive cathode as the power source.^{8, 9} Despite the breakthrough in design rationales, the imbalance between these two different types of electrodes in terms of kinetics and capacity remains to be a hurdle that needs to be overcome for the real application of LICs. Previous studies have revealed that the imbalanced kinetics can be resolved through construction of nanostructured anode materials with remarkable progress achieved in the past few years.¹⁰⁻¹² While for the imbalanced capacity, an excessive amount of cathode

materials, for example activated carbon (AC), compared to the anode materials needs to be employed to compensate the smaller specific capacity of the capacitive materials and this asymmetric mass loading design has been widely used in assembling LICs.^{13, 14} However, the extra amount of electrode materials can deteriorate the energy density.¹⁵ It is well known that the capacity contribution of capacitive materials can proportionally increase with extending the operating potential window (OPW).^{16, 17} In this regard, the loading mass of the capacitive materials can be reduced if they can work in a larger OPW.^{15, 18} Through properly modulating the potential of the zero voltage (E_{0V}), the capacitive electrodes can be allowed to operate in an extended OPW in an amphi-charge storable manner where the anions and cations contribute to capacitive energy storage at the potentials larger and smaller than 3.0 V vs Li/Li⁺, respectively.¹⁹ As a result, the loading mass of the cathode materials could be significantly reduced. This technology is highly effective for LICs with anodes working in the reductive decomposition potential range of the electrolyte.²⁰ As for LICs employing power-capable nanostructured lithium titanate (Li₄Ti₅O₁₂) as anode materials, the effect is limited due to the high plateau of LTO materials which promotes further exploring more effective technologies.

Herein, we combine the redox electrolyte with amphi-charge storage, to balance the large capacity gap between the AC cathode and the nanostructured Li₄Ti₅O₁₂ anode. In this regard, such an LIC operates at equal mass loading on both electrodes yet fully explores the capacity of the anode. The optimal LIC delivers an energy density of almost 100 Wh kg⁻¹, which is 4-fold higher than that of the traditional ones. Because of deliberately choosing low-cost electrode materials and employing a facile strategy, this kind of LICs may hold great promising to find their way in practical applications.

The traditional pairing strategy at an equal mass loading on both electrodes results in a large unexplored capacity in the Li₄Ti₅O₁₂ anode as the capacity of the anode is 4 to 5-time higher

^a State Key Laboratory of Heavy Oil Processing, Institute of New Energy, College of Chemical Engineering, China University of Petroleum (East China), Qingdao 266580, China. E-mail: hhu@upc.edu.cn, wumb@upc.edu.cn

^b YanKuang Group Co., Ltd. New Energy Division, Zoucheng, 273500, China.

Electronic Supplementary Information (ESI) available: [More details about material synthesis process and characterization]. See DOI: 10.1039/x0xx00000x

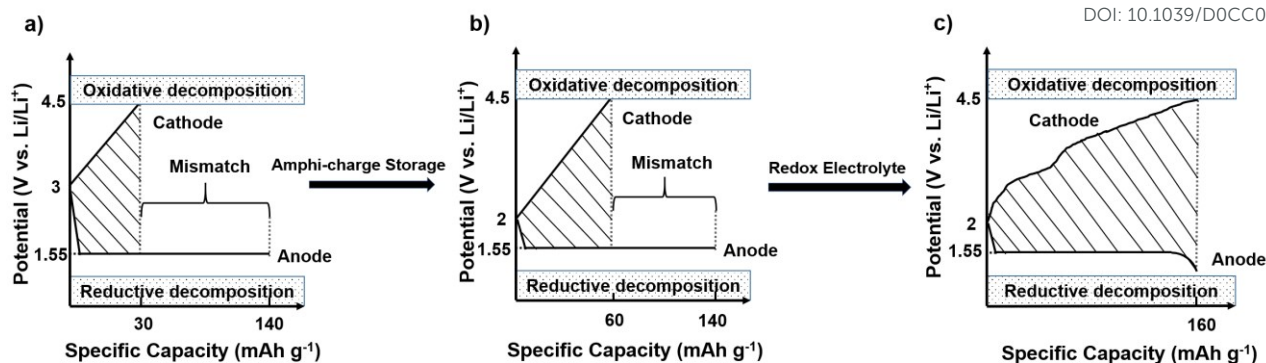
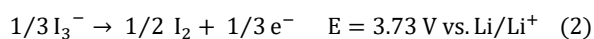


Fig. 1 Illustration of balancing the capacity gap between the AC cathode and LTO anode. a) The LICs with equal mass loading on both electrodes. b) The LICs with AC cathode operated in an amphi-charge storable manner. c) The LICs with an amphi-charge storable cathode in a redox electrolyte.

than that of the AC cathode (Fig. 1a).^{21–23} When mildly reducing the E_{OV} of both electrodes to a lower value, for example 2 V vs Li/Li⁺, a significantly increased utilization ratio of the capacity from the anode is expected (Fig. 1b). However, the relatively high voltage plateau of the Li₄Ti₅O₁₂ anode limits the possibility of fully exploring the potential of this method, which still results in a waste of quite some capacity of the anode.²⁴ Due to the potential of boosting the capacity at the desired electrode without extra mass loading, the involvement of redox electrolytes in energy storage systems, for example, supercapacitors, has been considered as an alternative means to improve the performance of these devices.^{25–30} In this scenario, a redox additive in the OPW of the cathode has been introduced, allowing the fully exploring the capacity of the anode (Fig. 1c).

The mechanism of gradually increased performance is investigated through systematical electrochemical characterization of the cathode operated using different strategies (Fig. 2). The typical AC with a large specific surface area (Fig. S1 and S2, ESI[†]) is used as the cathode material. When operated through the traditional manner, namely running in an OPW larger than 3 V vs Li/Li⁺, a rectangle-shape cyclic voltammetry (CV) curve and symmetric galvanostatic charge-discharge (GCD) profile are observed (Fig. 2), demonstrating the typical capacitive contribution from adsorption/desorption of anions in the electrolyte with a specific capacity of 30 mAh g⁻¹. By extending the lower limit of the OPW down to 2.0 V vs Li/Li⁺, the CV curve and GCD profile still reveal a capacitive contribution where the capacity from the upper portion of OPW (larger than 3.0 V vs Li/Li⁺) is derived from adsorption/desorption of anions on cathode materials while the reversible adsorption/desorption of Li⁺ is responsible for the capacity in the lower portion of OPW (smaller than 3.0 V vs Li/Li⁺) (Fig. S3, ESI[†]).^{19, 31} Through this simple modulation, the capacity is almost doubled. To further enhance the capacity, a redox additive with suitable redox potential and low cost, for example LiI, has been introduced in the electrolyte to provide extra capacity via the redox reactions as follow:³²



Two pairs of redox peaks can be clearly observed in the CV curve associated with the aforementioned redox reactions (Fig. 2a). As a result, an enlarged area is produced in the CV curves. Since these reactions occur on the surface of electrode materials, the amount of LiI should be properly optimized. Through a thorough investigation (Fig. S4 and Fig. S5, ESI[†]), the electrolyte with 50 mM LiI gives the optimized performance. Another interesting finding is that these Faradic reactions proceed very fast, as the GCD curve gives negligible distortion from the isosceles triangle-shaped profile of electrochemical double-layer capacitance. As the charging and discharging processes proceed, two-stage redox reactions, namely I⁻/I₃⁻ and I₃⁻/I₂ provide a large capacity for the cathode and the high reversibility secures a long-term stability (Fig. S6, ESI[†]). Through the synergistic combination of the amphi-charge storage and redox electrolyte-enabled capacity, the specific capacity of AC cathode increases from 30 to 150 mAh g⁻¹ (Fig. S6, ESI[†]), compared favorably to that of the Li₄Ti₅O₁₂ anode.

To verify the feasibility of this idea in real devices, three different kinds of LICs are constructed, namely Li₄Ti₅O₁₂//AC, Li₄Ti₅O₁₂//AC with modulated E_{OV} , Li₄Ti₅O₁₂//AC with modulated E_{OV} and a redox electrolyte, which are denoted as Li₄Ti₅O₁₂//AC-a, Li₄Ti₅O₁₂//AC-b, Li₄Ti₅O₁₂//AC-c, respectively. The Li₄Ti₅O₁₂ particles were prepared via the method reported previously.³³ These particles of around 1 μm are interconnected to form a highly porous framework (Fig. S7, ESI[†]) with high purity (Fig. S8a, ESI[†]). The electrochemical performances of the Li₄Ti₅O₁₂ particles were evaluated where the redox peaks in the

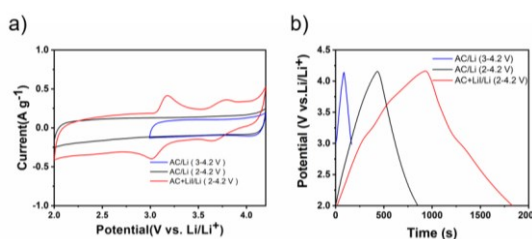


Fig. 2 a) CV curves and b) GCD profiles of AC/Li half cells with different working voltage range as well as using LiI as the redox additive recorded at a scan rate of 2 mV s⁻¹ and a current density of 0.5 A g⁻¹.

CV curves and the flat plateaus from the GCD curves further demonstrate the pure phase of the as-synthesized materials (Fig. S8b-d, ESI[†]). The potential variation of both electrodes during the device performance evaluation was also recorded to give an in-depth understanding of the practical operation manner of different LICs. Fig. 3 shows the GCD curves of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC-a}$. The potential of the AC cathode gradually increases from 3.0 to 4.2 V vs Li/Li^+ , which is very close to the upper limit of the electrolyte, while the plateau of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ quickly appears at around 1.55 V vs Li/Li^+ . The device voltage gradually increases from 0 to around 2.7 V. As for the $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC-b}$, the intentionally reduced E_{OV} permits a longer time for the AC cathode to reach the upper limit potential. As a result, more capacity from the plateau of the anode can be explored, giving rise to a longer charging and discharging time at the same current

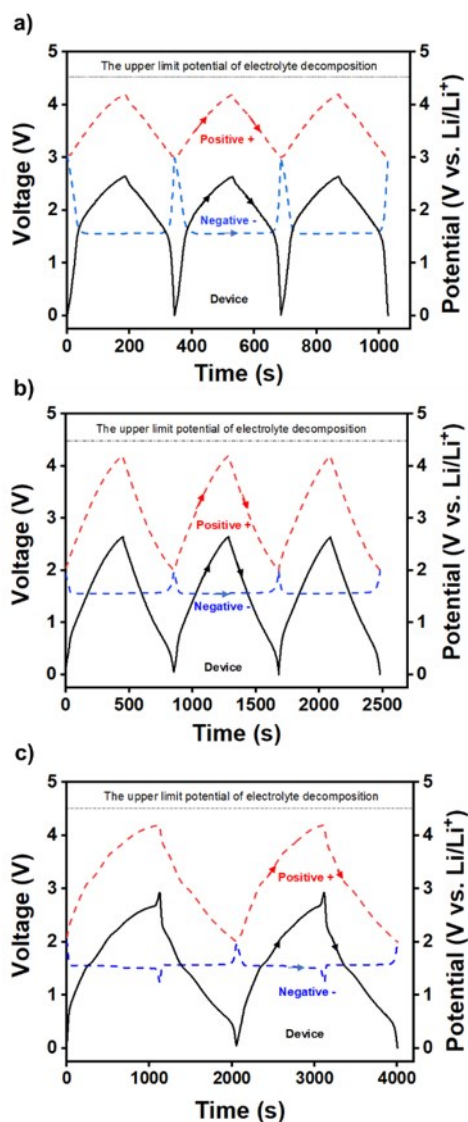


Fig. 3 GCD curves of a) $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC-a}$, b) $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC-b}$, and c) $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC-c}$ recorded at a current density of 0.5 A g^{-1} using a three-electrode split cell with a lithium wire as the reference electrode to monitor the potential variation of the cathode and anode.

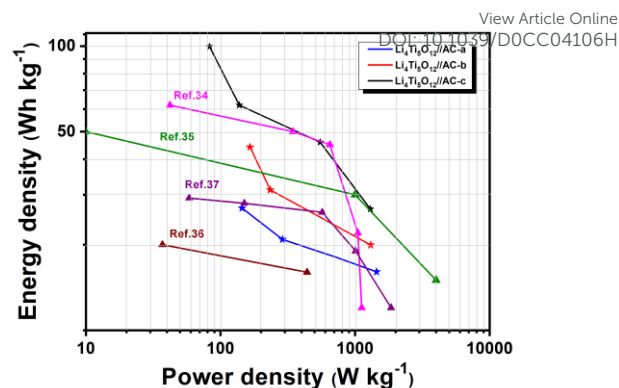


Fig. 4 Ragone plots of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC-a}$, $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC-b}$, $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC-c}$, and other previously reported $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC}$ devices.

density. Because of the further incorporation of the redox additive in the electrolyte of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC-c}$, the Li^+ ions-involved redox reactions allow a much longer time for the AC cathode to be fully charged, which are accompanied by the full exploration of the capacity of the anode. Thus, the charging and discharging time for this device is significantly extended compared to that of its counterparts (Fig. 3 and Fig. S9, ESI[†]).

Ragone plot is widely used to compare the practical performance of energy storage devices with the value of specific energy density plotting the specific power density. In order to have a practical view of the modulation strategy suggested in this work, the three different devices were plotted for a clear comparison (Fig. 4). The maximum energy density of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC-c}$ is almost 100 Wh kg^{-1} , while the $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC-a}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC-b}$ only give a specific energy density of 25 and 45 Wh kg^{-1} , respectively. Moreover, the practical performance of LICs constructed based on our idea is superior to many of the previously reported results (Fig. 4 and Table S1, ESI[†]),³⁴⁻³⁷ demonstrating the effectiveness of the synergistic combination of the amphi-charge storable cathode and the redox electrolyte.

In summary, we propose an alternative strategy to boost the energy density of LICs through operating the capacitive electrode in an amphi-charge storable manner in a redox electrolyte, other than the widely suggested methods of modulating the structure of electrode materials. The combined effect allows the gradual increase in the specific capacity of the cathode, which finally compares favorably to that of the anode. Moreover, the feasibility of this idea has been further demonstrated in the $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC}$ -based LICs where a 3-fold increase in the specific energy density is realized. The new finding in this work may pave an alternative avenue for further improving the performance of LICs.

This work is financially supported by the National Natural Science Foundation of China (21975287), the startup support grant from China University of Petroleum (East China), YanKuang Group Co., Ltd. New Energy Division, and Shandong Provincial Natural Science Foundation (ZR2018ZC1458).

Conflicts of interest

There are no conflicts to declare.

Notes and references

- 1 J. Fan, T. Wang, C. Yu, B. Tu, Z. Jiang, D. Zhao, *Adv. Mater.*, 2004, **16**, 1432-1436.
- 2 S. Han, B. Jiang, T. Kim, S. M. Oh, T. Hyeon, *Adv. Funct. Mater.*, 2005, **15**, 1845-1850.
- 3 M. Yu, D. Lin, H. Feng, Y. Zeng, Y. Tong, X. Lu, *Angew. Chem. Int. Ed.*, 2017, **129**, 5546-5551.
- 4 Y. Wang, Q. Qu, S. Gao, G. Tang, K. Liu, S. He, C. Huang, *Carbon*, 2019, **115**, 706-726.
- 5 G. G. Amatucci, F. Badway, A. U. Pasquier, T. Zheng, *J. Electrochem. Soc.*, 2001, **148**, A930-A939.
- 6 Y. Shao, M. F. El-Kady, J. Sun, Y. Li, Q. Zhang, M. Zhu, H. Wang, B. Dunn, R. B. Kaner, *Chem. Rev.*, 2018, **118**, 9233-9280.
- 7 P. Jezowski, O. Crosnier, E. Deunf, P. Poizot, F. Béguin, T. Brousse, *Nat. Mater.*, 2018, **17**, 167-173.
- 8 Y. Wang, Y. Song, Y. Xia, *Chem. Soc. Rev.*, 2016, **45**, 5925-5950.
- 9 J. Lang, X. Zhang, B. Liu, R. Wang, J. Chen, X. Yan, *J. Energy Chem.*, 2018, **27**, 43-56.
- 10 C. Han, H. Li, R. Shi, L. Xu, J. Li, F. Kang, B. Li, *Energy Environ. Mater.*, 2008, **1**, 75-87.
- 11 N. Arun, A. Jain, V. Aravindan, S. Jayaraman, W. C. Ling, M. P. Srinivasan, S. Madhavi, *Nano Energy*, 2015, **12**, 69-75.
- 12 S. He, C. Zhang, C. Du, C. Cheng, W. Chen, *J. Power Sources*, 2019, **434**, 226701.
- 13 X. Jiao, Q. Hao, X. Xia, Z. Wu, W. Lei, *Chem. Commun.*, 2019, **55**, 2692-2695.
- 14 X. Zhao, H. Wang, J. Chao, W. Cai, J. Sui, *Chem. Commun.*, 2017, **53**, 10723-10726.
- 15 Z. Weng, F. Li, D. Wang, L. Wen, H. Cheng, *Angew. Chem. Int. Ed.*, 2013, **52**, 3722-3725.
- 16 S. Zheng, Z. Wu, S. Wang, H. Xiao, F. Zhou, C. Sun, X. Bao, H. Cheng, *Energy Storage Mater.*, 2017, **6**, 70-97.
- 17 Y. Huang, Y. Zeng, M. Yu, P. Liu, Y. Tong, F. Cheng, X. Lu, *Small Methods*, 2018, **2**, 1700230.
- 18 K. L. Van Aken, M. Beidaghi, Y. Gogosi, *Angew. Chem. Int. Ed.*, 2015, **54**, 4806-4809.
- 19 N. R. Kim, S. M. Lee, M. W. Kim, H. J. Yoon, W. G. Hong, H. J. Kim, H. J. Choi, H. J. Jin, Y. S. Yun, *Adv. Energy Mater.*, 2017, **7**, 1700629.
- 20 V. Khomenko, E. Raymundo-Pinero, F. Béguin, *J. Power Sources*, 2008, **177**, 643-651.
- 21 R. Xue, J. Yan, L. Jiang, B. Li, *Mater. Chem. Phys.*, 2015, **160**, 375-382.
- 22 K. Leng, F. Zhang, L. Zhang, T. Zhang, Y. Wu, Y. Lu, Y. Huang, Y. Chen, *Nano Res.*, 2013, **6**, 581-592.
- 23 X. Sun, P. V. Radovanovic, B. Cui, *New J. Chem.*, 2015, **39**, 38-63.
- 24 B. Zhao, R. Ran, M. Liu, Z. Shao, *Mat. Sci. Eng. R.*, 2015, **98**, 1-71.
- 25 D. Vonlanthen, P. Lazarev, K. A. See, F. Wudl, A. J. Heeger, *Adv. Mater.*, 2014, **26**, 5095-5100.
- 26 Q. Wang, Y. Nie, X. Chen, Z. Xiao, Z. Zhang, *J. Power Sources*, 2016, **323**, 8-16.
- 27 D. Xu, W. Hu, X. Sun, P. Cui, X. Chen, *J. Power Sources*, 2017, **341**, 448-456.
- 28 X. Wang, R. S. Chandrabose, S. Chun, T. Zhang, B. Evanko, Z. Jian, S. W. Boettcher, G. D. Stucky, X. Ji, *ACS Appl. Mater. Interfaces*, 2015, **7**, 19978-19985.
- 29 L. Hu, C. Shi, K. Guo, T. Zhai, H. Li, Y. Wang, *Angew. Chem. Int. Ed.*, 2018, **57**, 8214-8218.
- 30 Y. Zhang, H. Hu, Z. Wang, B. Luo, W. Xing, L. Li, Z. Yan, L. Wang, *Nano Energy*, 2020, **68**, 104226.
- 31 K. V. Kravchuk, M. V. Kovalenko, *Adv. Energy Mater.*, 2019, **9**, 1901479.
- 32 W. Kwak, H. Kim, H. Jung, D. Aurbach, Y. Sun, *J. Electrochem. Soc.*, 2018, **165**, A2274-A2293.
- 33 H. Jung, S. Myung, C. Yoon, S. Son, K. Oh, K. Amine, B. Scrosati, Y. Sun, *Energy Environ. Sci.*, 2011, **4**, 1345-1351.
- 34 S. Dsoke, B. Fuchs, E. Gucciardi, M. W. Mehrens, J. Power Sources, 2015, **282**, 385-393.
- 35 N. Xu, X. Sun, X. Zhang, K. Wang, Y. Ma, *RCS Adv.*, 2015, **5**, 94361-94368.
- 36 J. Ni, L. Yang, H. Wang, L. Gao, *J. Solid State Electrochem.*, 2012, **16**, 2791-2796.
- 37 T. Yuan, W. Li, W. Zhang, Y. He, C. Zhang, X. Liao, Z. Ma, *Ind. Eng. Chem. Res.*, 2014, **53**, 10849-10857.