

OPEN ACCESS

## Sustainable Potassium-Ion Battery Anodes Derived from Waste-Tire Rubber

To cite this article: Yunchao Li *et al* 2017 *J. Electrochem. Soc.* **164** A1234

View the [article online](#) for updates and enhancements.

### You may also like

- [Laboratory Investigation on the Effects of Natural Fine Aggregates and Recycled Waste Tire Rubber in Pervious Concrete to Develop More Sustainable Pavement Materials](#)  
Alessandra Bonicelli, Luis G Fuentes and Ibrahim Khalil Dawd Bermejo
- [A new class of magnetorheological elastomers based on waste tire rubber and the characterization of their properties](#)  
Ubaidillah, Fitriani Imaduddin, Yancheng Li et al.
- [Study on End-of-Life Tires \(ELTs\) Recycling Strategy and Applications](#)  
Habiba Afrin, Nazmul Huda and Rouzbeh Abbasi



### Your Lab in a Box!

The PAT-Tester-i-16: All you need for Battery Material Testing.

- ✓ All-in-One Solution with integrated Temperature Chamber!
- ✓ Cableless Connection for Battery Test Cells!
- ✓ Fully featured Multichannel Potentiostat / Galvanostat / EIS!

[www.el-cell.com](http://www.el-cell.com) +49 40 79012-734 [sales@el-cell.com](mailto:sales@el-cell.com)

**EL-CELL**<sup>®</sup>  
electrochemical test equipment





# Sustainable Potassium-Ion Battery Anodes Derived from Waste-Tire Rubber

Yunchao Li,<sup>a,b</sup> Ryan A. Adams,<sup>c,\*</sup> Anjela Arora,<sup>c</sup> Vilas G. Pol,<sup>c,z</sup> Alan M. Levine,<sup>d</sup> Richard J. Lee,<sup>d</sup> Kokouvi Akato,<sup>b,e</sup> Amit K. Naskar,<sup>b,e</sup> and Mariappan Parans Paranthaman<sup>a,b,\*,z</sup>

<sup>a</sup>Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

<sup>b</sup>The Bredesen Center for Interdisciplinary Research and Graduate Education, The University of Tennessee, Knoxville, Tennessee 37996, USA

<sup>c</sup>Davidson School of Chemical Engineering, Purdue University, West Lafayette, Indiana 47907, USA

<sup>d</sup>RJ Lee Group, Monroeville, Pennsylvania 15146, USA

<sup>e</sup>Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

The recycling of waste-tire rubber is of critical importance since the discarded tires pose serious environmental and health hazards to our society. Here, we report a new application for hard-carbon materials derived from waste-tires as anodes in potassium-ion batteries. The sustainable tire-derived carbons show good reversible potassium insertion at relatively high rates. Long-term stability tests exhibit capacities of 155 and 141 mAh g<sup>-1</sup> for carbon pyrolyzed at 1100°C and 1600°C, respectively, after 200 cycles at current rate of C/2. This study provides an alternative solution for inexpensive and environmental benign potassium-ion battery anode materials.

© The Author(s) 2017. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, <http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.1391706jes] All rights reserved.



Manuscript submitted January 30, 2017; revised manuscript received April 3, 2017. Published April 13, 2017.

With the fast application of renewable energy technologies, the demand for large-scale energy storage system has increased significantly and became a growing global concern.<sup>1-3</sup> The intermittent energy generated from solar, wind and wave requires energy storage systems to leverage the electrical grid loading. In the meantime, with the awareness of the societal costs for the extraction of fossil fuels and the gaseous emissions from combustion, the development of storage systems that can power electric vehicles attracts great attention. During the past two and half decades, great efforts have been devoted to Lithium-ion batteries (LIBs).<sup>4-10</sup> However, the limited global availability of lithium resources, safety and high cost of extraction hinder the application of LIBs in several energy storage systems. This demands alternative energy storage devices that are based on earth-abundant elements. Recently, sodium-ion batteries (NIBs) and potassium-ion batteries (KIBs) have gradually received more attention to realize affordable rechargeable batteries for large scale systems.<sup>11-13</sup> Rapid progress has been made to advance NIB technologies. Many of the layered metal oxides and polyanionic compounds exhibited good capacity and cyclability as cathode materials in NIBs.<sup>13</sup> On one side, developing anodes for NIBs is still a great challenge as only very limited amounts of Na can be intercalated into graphite due to the larger ionic radius of sodium (1.0 Å for Na<sup>+</sup> vs. 0.76 Å for Li<sup>+</sup>).<sup>14</sup> On the other hand, despite its even larger ionic size (1.40 Å), potassium ion based graphite intercalation compounds (GICs) have been demonstrated.<sup>15</sup> The high abundance and lower cost of potassium raw materials (1000 USD t<sup>-1</sup> for K<sub>2</sub>CO<sub>3</sub> vs. 6500 USD t<sup>-1</sup> for Li<sub>2</sub>CO<sub>3</sub>), mean that K-ion based electrochemical energy storage technologies can exhibit their potentials in many applications.<sup>16</sup> Also, similar to sodium, potassium does not alloy with aluminum at lower potentials, enabling the use of aluminum as the anode current collector instead of high cost copper. Moreover, the redox potential of K/K<sup>+</sup> (-2.94 V vs. standard hydrogen electrode, SHE) is lower than that of Na/Na<sup>+</sup> (-2.71 V vs. SHE), indicating a higher working potential for K-ion batteries. In addition, K<sup>+</sup> ions show higher transport numbers and mobility in non-aqueous electrolytes due to weaker Lewis acidity and smaller Stoke's radius of solvated ions.<sup>17</sup> A few potassium intercalation cathode materials such as Prussian blue and its analogues,<sup>11,18,19</sup> FeSO<sub>4</sub>F,<sup>20</sup> amorphous FePO<sub>4</sub><sup>21</sup> and layered K<sub>0.3</sub>MnO<sub>2</sub><sup>16</sup> have been reported. As for the anode, the use of K metal is not applicable due

to its severe safety concerns. Hence, identifying the potential anode materials for KIBs is of great importance. Recently, carbon based materials (graphite, graphene and hard carbons) and tin-based composites have been studied as anodes for KIBs.<sup>15,22-26</sup> Among these materials, hard carbons showed the most promise because graphite and tin-based composites suffered pronounced capacity fade and lower rate capability while the high cost of graphene prevents its application in the price sensitive large-energy storage field.<sup>22,25</sup>

The widespread use of vehicles results in large quantities of end-of-life tires and it was estimated on a yearly basis that approximately 1.5 billion tires are disposed globally.<sup>27</sup> The discarded tires pose serious environmental and health threats to our society since they are non-biodegradable, flammable and could produce harmful gases. The pyrolysis of sulfonated waste-tire rubber into high value-added hard carbon provides many promising applications of waste tires in electrochemical energy storage systems.<sup>28-31</sup> Here, we investigated the low-cost, tire-derived carbon as a potential anode material for potassium-ion batteries, presenting another important application for the waste-tire recycling products.

## Experimental

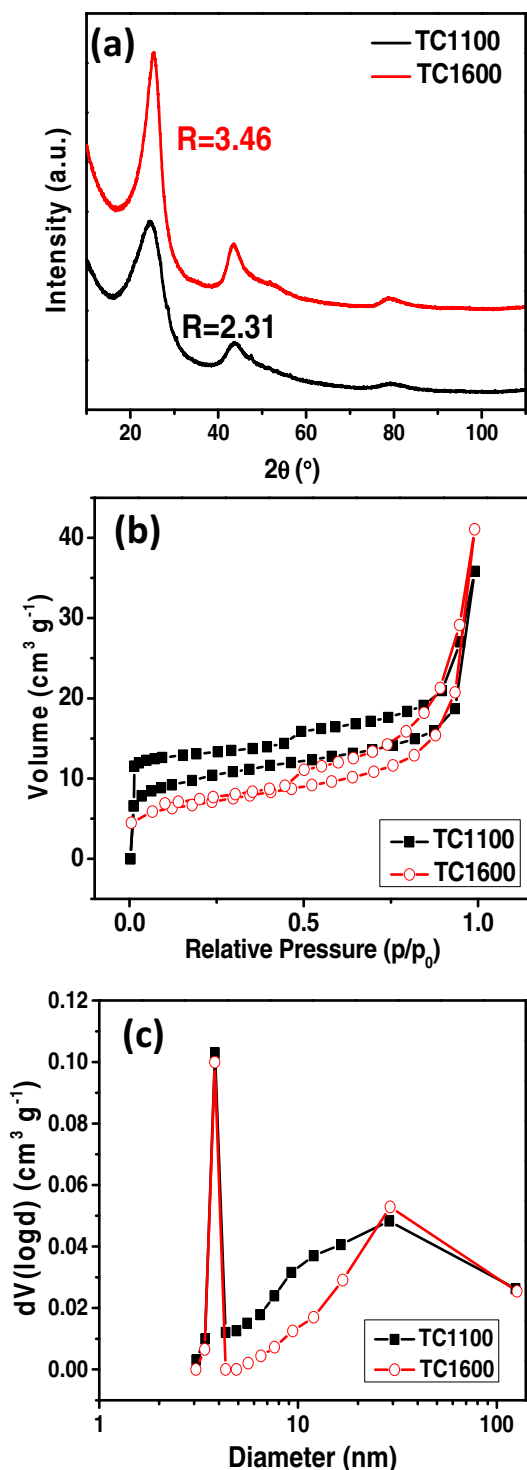
Tire crumb rubber (~1.5" × 1.5" in size) was soaked in concentrated sulfuric acid bath at 120°C overnight to yield sulfonated tire rubber. The obtained carbon product was then washed and filtered with deionized water. After drying, the sulfonated tire rubber was pyrolyzed in a tube furnace under flowing nitrogen gas from room temperature to 400°C at a ramp rate of 1°C/min, followed by increasing the temperature to 1100°C and 1600°C, respectively at a ramp rate of 2°C/min. The carbon products are hereafter designated as TC1100 and TC1600 corresponding to the peak pyrolysis temperature.

The X-ray diffraction (XRD) data were collected with a PANalytical Empyrean diffractometer equipped with Cu Kα radiation (λ = 1.5406 Å). Nitrogen adsorption desorption isotherms were obtained with a Quantachrome NovaWin1000 surface area & porosity analyzer at 77.4 K. The specific surface area was determined by the Brunauer-Emmett-Teller (BET) method. The pore size distribution was obtained by the Barret-Joyner-Halenda (BJH) method. A Hitachi S4700 scanning electron microscope operated at 1.5 kV was used to characterize the surface morphologies of the samples.

Electrochemical properties were characterized with half cells against a potassium-metal electrode. The working electrode was prepared by spreading the slurry consisting of 80% active

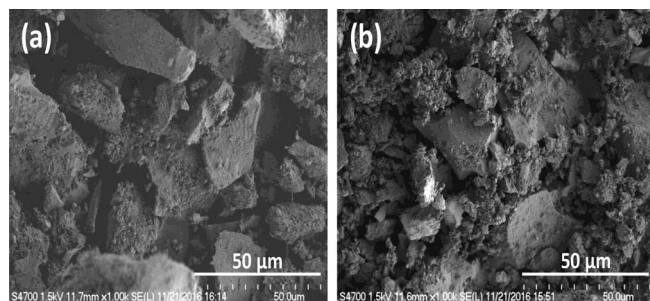
\*Electrochemical Society Member.

<sup>z</sup>E-mail: [paranthamanm@ornl.gov](mailto:paranthamanm@ornl.gov); [vpol@purdue.edu](mailto:vpol@purdue.edu)



**Figure 1.** (a) X-ray powder diffraction patterns, (b)  $N_2$  adsorption-desorption plots and (c) pore volume distribution of TC1100 and TC1600.

TC1100/TC1600 material, 10% conducting carbon (Timcal Super C65) and 10% PVDF binder in N-methyl-2-pyrrolidone (NMP) solvent. The resulting slurry was mixed for 20 min using a Thinky mixer and subsequently coated onto a copper foil. After drying for 12 h in a vacuum oven at  $80^\circ\text{C}$ , 12 mm diameter electrodes were punched out with an active material density of  $\sim 2 \text{ mg cm}^{-2}$ . The conductivity of TC1100 film coated on the glass slide shows a conductivity of  $1.2 \text{ S/cm}$  with a four probe conductivity measurement compared to the  $6.1 \text{ S/cm}$  measured for the graphite film tested at the same condition. Coin cells (CR2032 type) were assembled in a high purity Argon



**Figure 2.** SEM images of (a) TC1100 and (b) TC1600 carbon.

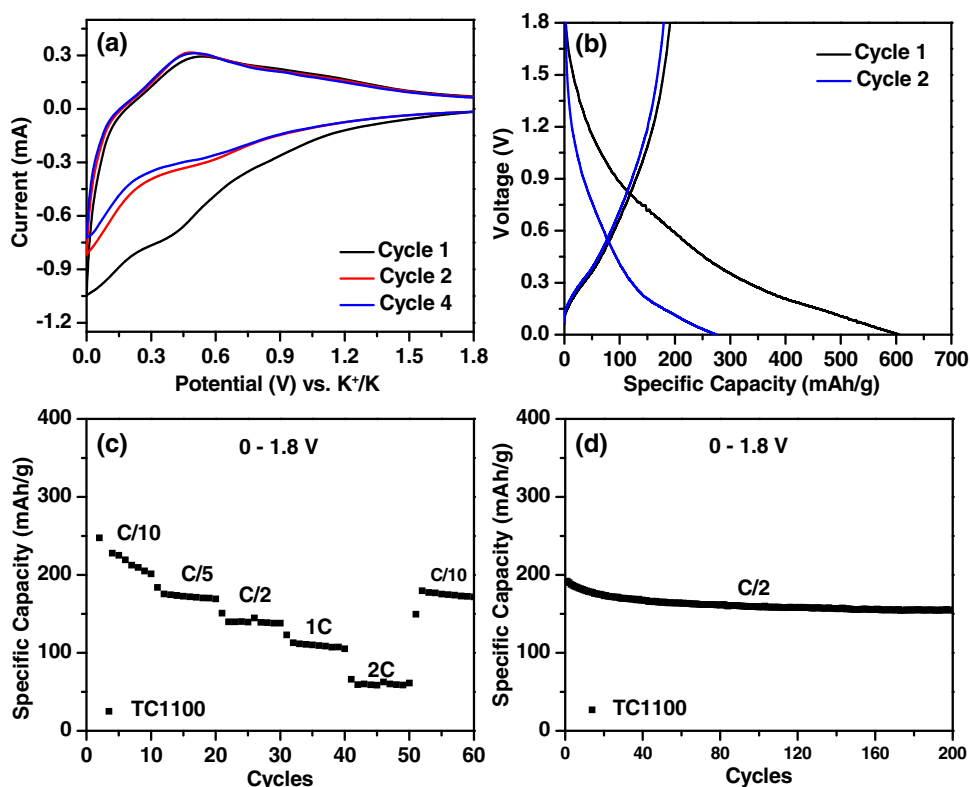
(99.998%) glove box, with potassium metal foil utilized as the counter electrode. The electrolyte utilized consisted of 0.8 M  $\text{KPF}_6$  dissolved in a 1:1 volume mixture of ethylene carbonate (EC)/diethyl carbonate (DEC). Whatman glass fiber was utilized as the separator. Cyclic voltammetry was performed utilizing a Gamry Reference 600+ instrument, at a scanning rate of  $0.2 \text{ mV s}^{-1}$ . Potentiostatic electrochemical impedance spectroscopy (EIS) was recorded from  $0.01 \text{ Hz}$  -  $10^6 \text{ Hz}$  with a  $10 \text{ mV}$  ac perturbation signal, for cells at OCV ( $2.5 \text{ V}$ ) and at  $0.3 \text{ V}$  after the first discharge. Galvanostatic cycling was performed using an Arbin cycler, with  $1\text{C} = 279 \text{ mA g}^{-1}$  utilized to calculate current densities for all C-rates described in this manuscript. The voltage range of  $0.005$  to  $3.0 \text{ V}$  was used for all cycling tests. Since the TC1100 and TC1600 will only work as anodes in K-ion batteries, only the capacities below  $1.8 \text{ V}$  will count as effective capacity. Hence, all the discharge capacities discussed below are calculated based on the potassium storage capability between  $0$  to  $1.8 \text{ V}$ . All potentials listed in this manuscript are versus  $\text{K/K}^+$  unless otherwise stated.

## Results and Discussion

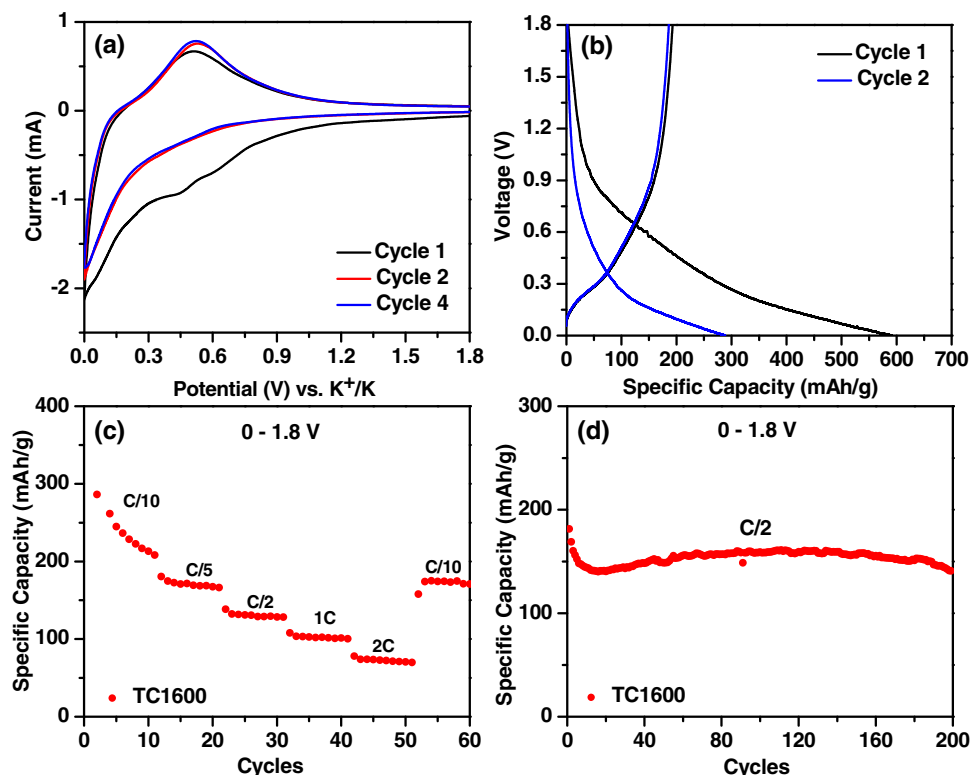
Fig. 1a shows the comparison of the X-ray Diffraction (XRD) patterns of tire-derived carbon heat-treated at  $1100^\circ\text{C}$  and  $1600^\circ\text{C}$ . R value is often used to quantify the proportion of graphene layers with parallel neighbors in the carbon materials. This value is defined as the peak height divided by the background at the position of the peak.<sup>32</sup> The R value of TC1600 is determined to be 3.46, which is much higher than that of TC1100 with an R value of 2.31. These values indicate that the higher temperature treated carbon has a large fraction of parallel graphene layers. Nitrogen adsorption-desorption plots for the tire-derived carbons are shown in Fig. 1b and the pore volume distribution is shown in Fig. 1c. The BET surface areas of TC1100 and TC1600 are  $34.5$  and  $23.2 \text{ m}^2 \text{g}^{-1}$ , respectively. The pore size distributions of TC1100 and TC1600 indicate mesoporosity of the materials with a large portion of  $3\text{--}4 \text{ nm}$  and  $29 \text{ nm}$  pore widths. The small surface area could minimize solid electrolyte interface (SEI) formation during cycling and the unique mesoporosity could increase the cation mobility during charging and discharging.

The scanning electron microscope (SEM) images in Figs. 2a and 2b exhibit the surface morphologies of TC1100 and TC1600, respectively. Both of the samples present a wide particle size distribution ranging from several microns to around  $50 \mu\text{m}$ . There is no major difference between these two SEM images, which indicates that increasing heat-treatment temperatures from  $1100^\circ\text{C}$  to  $1600^\circ\text{C}$  will not significantly change the surface morphology of the carbon.

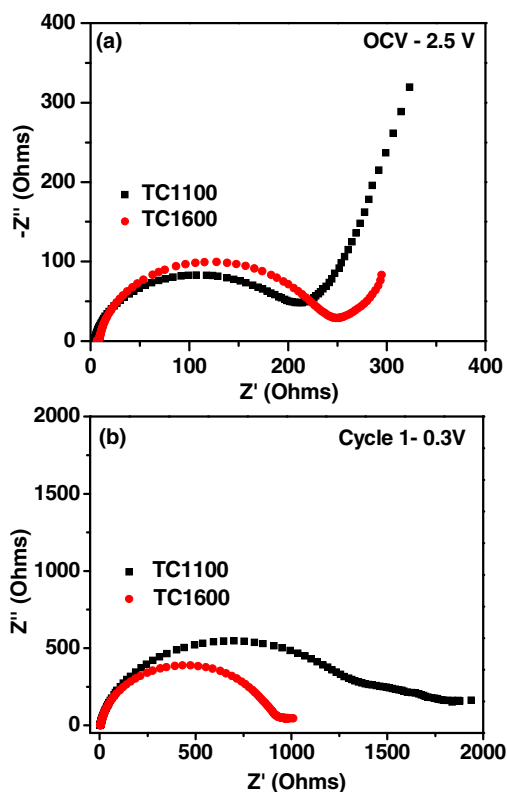
The electrochemical test data of TC1100 vs. potassium metal in a half cell configuration is shown in Fig. 3. The cyclic voltammetry (CV) plot obtained at a scan rate of  $0.2 \text{ mV s}^{-1}$  is shown in Fig. 3a. The reduction process (potassiation) at the first cycle results in a small peak at about  $0.91 \text{ V}$  and a larger reduction current, which is normally attributed to the electrolyte decomposition and SEI formation. In the depotassiation process, an oxidation peak is observed at around  $0.54 \text{ V}$ . Galvanostatic discharge-charge experiments were carried out to evaluate the potassium storage performance of the samples. As shown in Fig. 3b, the voltage profiles of charge-discharge at C/10



**Figure 3.** Electrochemical performance of TC1100 as K-ion anode. (a) Cyclic voltammetry plots at  $0.2 \text{ mV s}^{-1}$  rate, (b) First two charge-discharge cycles at a current density of  $\text{C}/10$  ( $27.9 \text{ mA g}^{-1}$ ), (c) Rate capability test, and (d) Discharge capacity retention at long-cycle stability test.



**Figure 4.** Electrochemical performance of TC1600 as K-ion anode. (a) Cyclic voltammetry plots at  $0.2 \text{ mV s}^{-1}$  rate, (b) First two cycles at a current density of  $\text{C}/10$  ( $27.9 \text{ mA g}^{-1}$ ), (c) Rate capability test, and (d) Discharge capacity retention at long-cycle stability test.



**Figure 5.** Nyquist diagrams of electrochemical impedance spectroscopy for TC1100 and TC1600 K-ion anodes. (a) At OCV of 2.5 V before galvanostatic cycling. (b) After full first discharge at 0.3 V.

(27.9 mA g<sup>-1</sup>) show a very large irreversible capacity at first cycle, which results in only 37.1% efficiency. This value is quickly improved to 76.4% at the following charge-discharge cycles. Further cycling test at C/2 is shown in Fig. 3d and it reveals a good cyclability of TC1100 carbon. The initial discharge capacity below 1.8 V is 192 mAh g<sup>-1</sup> and it remains at a capacity of 155 mAh g<sup>-1</sup> after 200 cycles, which corresponds to 80.7% capacity retention. The rate study of TC1100 at current densities of C/10, C/5, C/2, 1C and 2C was conducted and shows a discharge capacity of 220, 173, 139, 110, and 60 mAh g<sup>-1</sup>, respectively in Fig. 3c. As shown in Fig. 3c, the discharge capacity was almost recovered once the current was changed from 2C to C/10, which suggests that the structure of the material can sustain high current densities.

Sample TC1600 was also tested against potassium metal to evaluate the influence of the heat-treatment conditions. The CV plots of TC1600 are shown in Fig. 4a, where a reduction peak appears at around 0.72 V. During charging, an oxidation peak emerges at ~0.52 V which is close to that of TC1100. It is also noticeable that the low voltage reduction peak is much narrower and shaper (more capacity below 0.3 V) compared to the CV of TC1100. Similar to the TC1100 charge-

discharge voltage profiles, TC1600 in Fig. 4b also shows a sloping discharge curve. This property is different than that of the TC1600 as a sodium battery anode.<sup>29</sup> When sodiated, TC1600 has a sloping discharge profile with a small portion of the capacity at a voltage above 0.2 V while most of its capacity is delivered close to 0 V and the discharge curve shows a plateau. Such potential profile for potassium batteries reduces the risks associated with metal plating. As shown in Fig. 4d, the long-term charge and discharge cycling at C/2 shows a discharge capacity between 0 to 1.8 V decreases from 181 to 141 mAh g<sup>-1</sup> after 200 cycles, which represents 22% loss of its initial capacity. There is a slightly increase in capacity during the middle of cycling for TC1600, which is not seen for the TC1100 sample. Such property could be related to the activation process of TC1600.<sup>33</sup> The rate capability test (Fig. 4c) exhibits discharge capacities of ~220, 171, 131, 103 and 72 mAh g<sup>-1</sup> at current densities of C/10, C/5, C/2, 1C and 2C, respectively. Both TC1100 and TC1600 show good stability as anodes for potassium-ion batteries. It is also very interesting to mention that although K<sup>+</sup>-ion has a 40% larger ionic radius compared to Na<sup>+</sup>-ion, both TC1100 and TC1600 samples have better electrochemical cycling performances at high rates in potassium-ion batteries than those in sodium-ion batteries compared to our previously published work on sodium-ion batteries.<sup>26</sup> Such phenomenon has also been reported in the literature for other types of hard carbons.<sup>22,23</sup> For example, Ji et al. shows higher diffusion coefficients of K<sup>+</sup> in hard carbons than that of Na<sup>+</sup> in hard carbons and such observation was attributed to lower K-ion activation energy caused by different binding energies between K/C and Na/C as well as a lower charge density of larger K-ions.<sup>23</sup>

EIS analysis of TC1100 and TC1600 are shown for fresh cells at an OCV of 2.5 V in Figure 5. Charge transfer resistance, indicated by the semicircle in the high-medium frequency range, is decreased for TC1100 compared to TC1600, possibly due to the presence of heteroatoms from lower pyrolysis process temperature improving material conductivity. Additional EIS spectra after the first discharge at 0.3 V (Figure 5b), illustrates additional resistance generation due to the SEI formation. TC1600 has decreased resistance compared to TC1100, likely due to decreased first cycle loss and surface area, resulting in a less thick SEI layer formation comparatively.

A comparison table of the recently reported anode materials for potassium-ion batteries along with our results on tire-derived carbon is shown in Table I. As can be seen, TC1100 and TC1600 have good potassium storage performance at relatively large current densities. In addition, the cost of producing large quantities of tire-derived carbon is estimated to be much lower compared to the cost of reduced graphene oxide, N-doped graphene or even the commercial graphite. Also, the well-developed tire recycling industry and the easily scalable carbon recovery process provides an excellent pathway for tire-derived carbon over other potential anode candidates.

## Conclusions

In summary, we demonstrated a pathway for the recovery of high value-added carbon from waste-tire rubber as a potential potassium-ion battery anode material. Tire-derived carbon anodes exhibit much

**Table I.** Comparison of the potassium storage performance for state-of-the-art KIB anodes.

| Materials as KIBs Anode      | Performance                                                                  | Rate                       | Reference |
|------------------------------|------------------------------------------------------------------------------|----------------------------|-----------|
| Graphite                     | 197 mAh g <sup>-1</sup> at 1st cycle, 100 mAh g <sup>-1</sup> after 50 cycle | C/2                        | 22        |
| Soft carbon                  | ~160 mAh g <sup>-1</sup> after 50 cycles                                     | 2C                         |           |
| Hard carbon microspheres     | 216 mAh g <sup>-1</sup>                                                      | C/10                       | 23        |
| Tin-based Composite          | 110 mAh g <sup>-1</sup> after 30 cycles                                      | 25 mA g <sup>-1</sup>      | 25        |
| Reduced graphene oxide (RGO) | 90 mAh g <sup>-1</sup>                                                       | 50 mA g <sup>-1</sup>      | 15        |
|                              | ~50 mAh g <sup>-1</sup>                                                      | 100mA g <sup>-1</sup>      |           |
| N-doped Graphene             | ~220 mAh g <sup>-1</sup> after 100 cycles                                    | 50 mA g <sup>-1</sup>      | 24        |
| Tire-derived Carbon          | TC1100: 155 mAh g <sup>-1</sup> after 200 cycles                             | C/2 140 mA g <sup>-1</sup> | This work |
|                              | TC1600: 141 mAh g <sup>-1</sup> after 200 cycles                             |                            |           |

better rate capability in potassium-ion batteries compared to those in sodium-ion batteries. Moreover, they show very good capacity retention after 200 cycles. This research demonstrates the potential of using tire-derived carbon as anodes for KIBs and also provides a high value-added and sustainable way of recycling waste tires.

### Acknowledgments

The evaluation of the new materials as novel battery electrodes was sponsored by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division. The research on the conversion of recycled tires to carbon powders was funded by Oak Ridge National Laboratory's Technology Innovation Program. PU authors thanks to the Purdue University and School of Chemical Engineering for their generous startup funding.

**Notice:** This manuscript has been authored by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U. S. Department of Energy. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes. The Department of Energy will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (<http://energy.gov/downloads/doe-public-access-plan>).

### References

1. V. Etacheri, R. Marom, R. Elazari, G. Salitra, and D. Aurbach, *Energy Environ. Sci.*, **4**, 3243 (2011).
2. J. B. Goodenough and Y. Kim, *Chem. Mater.*, **22**, 587 (2010).
3. J. B. Goodenough and K. S. Park, *J. Am. Chem. Soc.*, **135**, 1167 (2013).
4. Y. Li, G. Y. Fu, M. Watson, S. Harrison, and M. P. Paranthaman, *Chemnanomat*, **2**, 642 (2016).
5. Y. C. Li, M. P. Paranthaman, L. W. Gill, E. W. Hagaman, Y. Y. Wang, A. P. Sokolov, S. Dai, C. Ma, M. F. Chi, G. M. Veith, A. Manthiram, and J. B. Goodenough, *J Mater Sci*, **51**, 854 (2016).
6. J. Pan, Q. Zhang, X. Xiao, Y. T. Cheng, and Y. Qi, *ACS Appl. Mater. Interfaces*, **8**, 5687 (2016).
7. Q. Zhang, J. Pan, P. Lu, Z. Liu, M. W. Verbrugge, B. W. Sheldon, Y. T. Cheng, Y. Qi, and X. Xiao, *Nano Lett.*, **16**, 2011 (2016).
8. Y. F. Yue, Y. C. Li, Z. H. Bi, G. M. Veith, C. A. Bridges, B. K. Guo, J. H. Chen, D. R. Mullins, S. P. Surwade, S. M. Mahurin, H. J. Liu, M. P. Paranthaman, and S. Dai, *J Mater Chem A*, **3**, 22989 (2015).
9. Y. Li, S. Wan, G. M. Veith, R. R. Unocic, M. P. Paranthaman, S. Dai, and X. -G. Sun, *Advanced Energy Materials*, **7**, 1601397 (2017).
10. J. Pan, Q. Zhang, J. Li, M. J. Beck, X. Xiao, and Y. -T. Cheng, *Nano Energy*, **13**, 192 (2015).
11. P. Padigi, J. Thiebes, M. Swan, G. Goncher, D. Evans, and R. Solanki, *Electrochim. Acta*, **166**, 32 (2015).
12. B. L. Ellis and L. F. Nazar, *Curr. Opin. Solid State Mater. Sci.*, **16**, 168 (2012).
13. H. Pan, Y. -S. Hu, and L. Chen, *Energy Environ. Sci.*, **6**, 2338 (2013).
14. Y. Wen, K. He, Y. Zhu, F. Han, Y. Xu, I. Matsuda, Y. Ishii, J. Cumings, and C. Wang, *Nature communications*, **5**, 4033 (2014).
15. 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.*, **15**, 7671 (2015).
16. C. Vaalma, G. A. Giffin, D. Buchholz, and S. Passerini, *J. Electrochem. Soc.*, **163**, A1295 (2016).
17. S. Komaba, T. Hasegawa, M. Dahbi, and K. Kubota, *Electrochem. Commun.*, **60**, 172 (2015).
18. C. D. Wessells, S. V. Peddada, R. A. Huggins, and Y. Cui, *Nano Lett.*, **11**, 5421 (2011).
19. A. Eftekhari, *J. Power Sources*, **126**, 221 (2004).
20. N. Recham, G. Rousse, M. T. Sougrati, J. -N. Chotard, C. Frayret, S. Mariyappan, B. C. Melot, J. -C. Jumas, and J. -M. Tarascon, *Chem. Mater.*, **24**, 4363 (2012).
21. V. Mathew, S. Kim, J. Kang, J. Gim, J. Song, J. P. Baboo, W. Park, D. Ahn, J. Han, L. Gu, Y. Wang, Y. -S. Hu, Y. -K. Sun, and J. Kim, *NPG Asia Mater.*, **6**, e138 (2014).
22. Z. Jian, W. Luo, and X. Ji, *J Am Chem Soc*, **137**, 11566 (2015).
23. Z. Jian, Z. Xing, C. Bommier, Z. Li, and X. Ji, *Advanced Energy Materials*, **6**, 1501874 (2016).
24. K. Share, A. P. Cohn, R. Carter, B. Rogers, and C. L. Pint, *ACS Nano*, **10**, 9738 (2016).
25. I. Sultana, T. Ramireddy, M. M. Rahman, Y. Chen, and A. M. Glushenkov, *Chem Commun (Camb)*, **52**, 9279 (2016).
26. Y. Liu, F. Fan, J. Wang, Y. Liu, H. Chen, K. L. Jungjohann, Y. Xu, Y. Zhu, D. Bigio, T. Zhu, and C. Wang, *Nano Lett.*, **14**, 3445 (2014).
27. B. Danon, P. van der Gryp, C. E. Schwarz, and J. F. Görgens, *J. Anal. Appl. Pyrolysis*, **112**, 1 (2015).
28. M. Boota, M. P. Paranthaman, A. K. Naskar, Y. Li, K. Akato, and Y. Gogotsi, *Chem-suschem*, **8**, 3576 (2015).
29. Y. C. Li, M. P. Paranthaman, K. Akato, A. K. Naskar, A. M. Levine, R. J. Lee, S. O. Kim, J. S. Zhang, S. Dai, and A. Manthiram, *J. Power Sources*, **316**, 232 (2016).
30. A. K. Naskar, Z. H. Bi, Y. C. Li, S. K. Akato, D. Saha, M. F. Chi, C. A. Bridges, and M. P. Paranthaman, *Rsc Adv*, **4**, 38213 (2014).
31. K. Park, B. -C. Yu, and J. B. Goodenough, *Advanced Energy Materials*, **6**, 1502534 (2016).
32. J. R. Dahn, W. Xing, and Y. Gao, *Carbon*, **35**, 825 (1997).
33. J. Zheng, J. Tian, D. Wu, M. Gu, W. Xu, C. Wang, F. Gao, M. H. Engelhard, J. G. Zhang, J. Liu, and J. Xiao, *Nano Lett.*, **14**, 2345 (2014).