2015

Electrochemical performance of Ti$_3$C$_2$ supercapacitors in KOH electrolyte

Yupeng GAO  
*School of Materials Science and Engineering, Henan Polytechnic University, Jiaozuo 454000, China*

Libo WANG  
*School of Materials Science and Engineering, Henan Polytechnic University, Jiaozuo 454000, China*

Zhengyang LI  
*School of Materials Science and Engineering, Henan Polytechnic University, Jiaozuo 454000, China*

Yafei ZHANG  
*School of Materials Science and Engineering, Henan Polytechnic University, Jiaozuo 454000, China*

Baolin XING  
*School of Materials Science and Engineering, Henan Polytechnic University, Jiaozuo 454000, China*

See next page for additional authors

Follow this and additional works at: [https://tsinghuauniversitypress.researchcommons.org/journal-of-advanced-ceramics](https://tsinghuauniversitypress.researchcommons.org/journal-of-advanced-ceramics)  

Part of the Ceramic Materials Commons, and the Nanoscience and Nanotechnology Commons

**Recommended Citation**
Yupeng GAO, Libo WANG, Zhengyang LI et al. Electrochemical performance of Ti3C2 supercapacitors in KOH electrolyte. *Journal of Advanced Ceramics* 2015, 4(2): 130-134.

This Research Article is brought to you for free and open access by Tsinghua University Press: Journals Publishing. It has been accepted for inclusion in Journal of Advanced Ceramics by an authorized editor of Tsinghua University Press: Journals Publishing.
Electrochemical performance of Ti$_3$C$_2$ supercapacitors in KOH electrolyte

Authors
Yupeng GAO, Libo WANG, Zhengyang LI, Yafei ZHANG, Baolin XING, Chuanxiang ZHANG, and Aiguo ZHOU

This research article is available in Journal of Advanced Ceramics:
https://tsinghuauniversitypress.researchcommons.org/journal-of-advanced-ceramics/vol4/iss2/7
Electrochemical performance of Ti$_3$C$_2$ supercapacitors in KOH electrolyte

Yupeng GAO, Libo WANG, Zhengyang LI, Yafei ZHANG, Baolin XING, Chuanxiang ZHANG, Aiguo ZHOU*

School of Materials Science and Engineering, Henan Polytechnic University, Jiaozuo 454000, China

Received: January 05, 2015; Accepted: January 24, 2015
© The Author(s) 2015. This article is published with open access at Springerlink.com

Abstract: Two-dimensional (2D) carbide Ti$_3$C$_2$ was synthesized by exfoliating Ti$_3$AlC$_2$ in HF solution and used for supercapacitive performance investigation in 3 M KOH electrolyte. The specific surface area (SSA) of as-synthesized Ti$_3$C$_2$ was 22.35 m$^2$/g. Ti$_3$C$_2$-based supercapacitor electrodes exhibited good energy storage ability and had a volumetric capacitance 119.8 F/cm$^3$ at the current density of 2.5 A/g. Moreover, the addition of carbon black into Ti$_3$C$_2$ powders greatly improved the performance of Ti$_3$C$_2$-based capacitors because carbon black restrained the preferred orientation of 2D Ti$_3$C$_2$, providing fast ion transport channels, and in turn, decreasing electrical resistance from 16.7 $\Omega$ to 3.5 $\Omega$.

Keywords: MXene; Ti$_3$AlC$_2$; two-dimensional (2D) carbide; supercapacitors

1 Introduction

Supercapacitors have fast charge/discharge rates, high power density, and good cyclability compared with batteries, and have attracted extensive research interest due to the increasing demand for portable and clean energy storage devices. In principle, supercapacitors store charges at the interface between electrode and electrolyte, thus large specific surface area (SSA) of electrode is favorable for high capacitance [1]. Therefore, many materials with large SSA were used as electrode, such as activated carbons [2,3], carbide-derived carbons [4,5], and carbon nanotubes [6,7]. Two-dimensional (2D) materials prepared by exfoliating precursors with layered structure [8,9] have high SSA, which are regarded as one of promising candidates for supercapacitor electrodes. The first and most investigated 2D material is graphene. Graphene or graphene-based electrodes for supercapacitors have been successfully prepared and their supercapacitor performance has been investigated extensively [10–13].

Recently, a new family of 2D materials was prepared by exfoliating ternary carbides or carbonitrides with the name of MAX phases [14,15]. The 2D materials were named as MXenes to emphasize their graphene-like structure and the removing of A-site atoms from MAX structure. MAX phases, the precursors of MXenes, have the general formula of M$_{n+1}$AX$_n$, where M is an early transition metal; A is an A-group element (mostly group IIIA or IVA); and X is either carbon or nitrogen [16,17].

MXenes have important application in many areas, such as hydrogen storage [18,19], lead adsorption [20], and catalysis [21]. Especially, as conductive and hydrophilic 2D materials [14], MXenes are promising electrode materials for electrochemical energy storage.
Ti$_3$C$_2$ is a typical MXene. Its performance as supercapacitor electrode was investigated. Additive-free paper-like Ti$_3$C$_2$ can yield the volumetric capacitance of 350 F/cm$^3$ in KOH electrolyte [26], and Ti$_3$C$_2$ with binder and carbon black can yield the capacitance of 415 F/cm$^3$ in H$_2$SO$_4$ electrolyte [27]. In this paper, Ti$_3$C$_2$ was fabricated and its supercapacitive performance with/without carbon black in KOH electrolyte was investigated.

2 Experimental methods

Ti$_3$AlC$_2$ powders (98 wt% pure, −200 mesh) were made from the mixture of TiH$_2$, Al, and TiC at 1450 °C for 2 h in Ar atmosphere [28]. 2D Ti$_3$C$_2$ was produced by immersing Ti$_3$AlC$_2$ in 49% HF (Aladdin Reagent, China) at 60 °C for 24 h followed by washing with deionized water for several times. Finally Ti$_3$C$_2$ powders were centrifugally separated from the obtained suspension and dried in vacuum at 80 °C.

X-ray diffraction (XRD) patterns of the as-fabricated powders were obtained with a diffractometer (Bruker AXS Co., Germany) using Cu K$_\alpha$ radiation. A field emission scanning electron microscope (FESEM; Hitachi, S4800, Japan) was used to characterize the microstructure of the as-prepared powders. Nitrogen sorption isotherm measurements were performed by an automatic gas adsorption analyzer (Autosorb-iQ-MP, Quantachrome, USA) at 77 K. The specific surface area (SSA) was calculated by Brunauer–Emett–Teller (BET) method.

Galvanostatic charge/discharge cycling and cyclic voltammetry (CV) tests were performed by a CSCT supercapacitor test system (Arbin, USA). Electrochemical impedance spectroscopy (EIS) was tested by a potentiostats-electrochemistry work station (Parstat 2273, Princeton Applied Research). Two types of working electrodes were prepared and labeled with Electrode-I and Electrode-II, respectively. Electrode-I was 95 wt% MXene and 5 wt% polytetrafluoroethylene (PTFE); Electrode-II was 85 wt% MXene, 10 wt% carbon black (CB, BP2000, Cabot Corporation, USA), and 5 wt% PTFE. The mixed slurries were pressed under a pressure of 10 MPa to completely adhere together as a disc with diameter of 13 mm and thickness of 0.15 mm. Finally, the electrodes were dried at 120 °C in vacuum for 4 h. Both Electrode-I and Electrode-II were assembled into symmetric supercapacitor devices and labeled as SC-1 and SC-2, respectively. The supercapacitive performance of SC-1 and SC-2 was characterized by three-electrode cells in 3 M KOH electrolyte.

3 Results and discussion

3.1 Characterization of Ti$_3$C$_2$

Figure 1(a) shows the XRD patterns of Ti$_3$AlC$_2$ and Ti$_3$C$_2$ MXene. During etching process, Ti$_3$AlC$_2$ was exfoliated and Ti$_3$C$_2$ MXene with low content of TiC

---

Fig. 1 (a) XRD patterns of Ti$_3$AlC$_2$ and Ti$_3$C$_2$ MXene; (b) SEM images of Ti$_3$C$_2$ MXene with 2D structure, and the inset is the SEM image of Ti$_3$AlC$_2$ before exfoliation; and (c) N$_2$ sorption isotherm of Ti$_3$C$_2$.

www.springer.com/journal/40145
impurity was obtained. Figure 1(b) shows the FESEM image of the as-synthesized 2D Ti$_3$C$_2$. The original Ti$_3$AlC$_2$ grains (shown in the inset of Fig. 1(b)) were fully exfoliated and 2D Ti$_3$C$_2$ was formed with thickness of ~40 nm [15,21]. The N$_2$ sorption isotherm of the as-synthesized Ti$_3$C$_2$ is shown in Fig. 1(c). The shape of hysteresis loop indicates slit-shaped mesopores. The SSA calculated from BET equation is 22.35 m$^2$/g.

### 3.2 Electrochemical properties

Figure 2 shows the galvanostatic charge/discharge curves of the supercapacitors at different current density. The charge/discharge curves of both SC-1 and SC-2 are almost isosceles triangle, which indicate a good reversibility of SC-1 and SC-2. The capacitance of SC-2 is 71.2 F/g at the current density of 2.5 A/g, corresponding to volumetric specific capacitance of 119.8 F/cm$^3$, which is higher than that of graphite oxide (110 F/cm$^3$) [29]. Figure 3 shows the capacitance decay with increasing discharge current density. The capacitance of SC-2 retains 60.4 F/g at the current density of 5 A/g. This indicates the electrodes of SC-2 possess the good conductivity and have good interfacial contact with electrolyte, which provide fast ion transport channels for KOH electrolyte. The capacitance of SC-2 is obviously larger than that of SC-1. Thus, it can be concluded that the addition of carbon black in Ti$_3$C$_2$ MXene can significantly improve the performance of supercapacitors. Normally, because of the 2D structure, Ti$_3$C$_2$ has obvious preferred orientation. Due to the pressure exerted during the electrode fabrication process, most Ti$_3$C$_2$ sheets are lying parallel to the current electrode surface, namely, perpendicular to the direction of ion diffusion, which is unfavorable for the diffusion of electrolyte ions. However, if some carbon black particles are added and located between Ti$_3$C$_2$ 2D sheets, the preferred orientation is resisted, and thus more ion diffusion channels are generated by the random orientation of 2D Ti$_3$C$_2$, especially for those Ti$_3$C$_2$ sheets parallel to the direction of ion diffusion. Therefore, the addition of carbon black can greatly increase ion conductivity. This explains the better performance of SC-2.

The cyclic voltammograms (CV) at scan rate of 1 mV/s are presented in Fig. 4. Both CV curves are similar to rectangles and have good symmetry. Thus the supercapacitors are typical electrochemical capacitors.

The impedance spectra are shown in Fig. 5. From the inset, equivalent resistance of SC-1 and SC-2 devices can be calculated to be 16.7 Ω and 3.5 Ω, respectively. It is clear that Ti$_3$C$_2$ with carbon black electrode yields smaller cell resistance and higher capacitance than pure Ti$_3$C$_2$ electrode.

A capacitance retention test was performed by...
galvanostatic cycling at 2.5 A/g and the results are showed in Fig. 6. There is almost no degradation in performance of SC-1 after 1000 cycles. Although the capacitance of SC-2 decays with increasing cycle numbers in the beginning cycles, the performance holds steady after 800 cycles, and remains 94.2% of the maximum capacitance. SC-2 still has a good cycling stability and can deliver the high volumetric capacity of 112.9 F/cm³ after 1000 cycles.

4 Conclusions

Ti₃C₂ with SSA of 22.35 m²/g was used to prepare supercapacitors. A volumetric capacitance of 119.8 F/cm³ has been achieved at the current density of 2.5 A/g. It has a good cycling stability and can deliver a volumetric capacity of 112.9 F/cm³ after 1000 cycles. Carbon black addition in Ti₃C₂ can avoid the preferred orientation of Ti₃C₂, increasing ion diffusion channel and reducing the diffusion resistance of ion. Equivalent resistance was decreased from 16.7 Ω to 3.5 Ω.

Acknowledgements

This work was supported by National Nature Science Foundation of China (51472075, 51205111), Plan for Scientific Innovation Talent of Henan Province (134100510008), Program for Innovative Research Team of Henan Polytechnic University (T2013-4), State Key Laboratory of New Ceramic and Fine Processing Tsinghua University (KF201313), and Opening Project of Henan Key Discipline Open Laboratory of Mining Engineering Materials (MEM12-11).

Open Access: This article is distributed under the terms of the Creative Commons Attribution License which permits any use, distribution, and reproduction in any medium, provided the original author(s) and the source are credited.

References

[1] Chmiola J, Yushin G, Gogotsi Y, et al. Anomalous increase
in carbon capacitance at pore sizes less than 1 nanometer. Science 2006, 313: 1760–1763.

[2] Jänes A, Kurig H, Lust E. Characterisation of activated nanoporous carbon for supercapacitor electrode materials. Carbon 2007, 45: 1226–1233.

[3] Xing W, Huang CC, Zhuo SP, et al. Hierarchical porous carbons with high performance for supercapacitor electrodes. Carbon 2009, 47: 1715–1722.

[4] Torop J, Palmre V, Arulepp M, et al. Flexible supercapacitor-like actuator with caride-derived carbon electrodes. Carbon 2011, 49: 3113–3119.

[5] Chmiola J, Largeot C, Taberna P-L, et al. Monolithic caride-derived carbon films for micro-supercapacitors. Science 2010, 328: 480–483.

[6] Hsieh T-F, Chuang C-C, Chen W-J, et al. Hydrous ruthenium dioxide/multi-walled carbon-nanotube/titaniun electrodes for supercapacitors. Carbon 2012, 50: 1740–1747.

[7] Wang Q, Yan J, Wang Y, et al. Template synthesis of hollow carbon spheres anchored on carbon nanotubes for high rate performance supercapacitors. Carbon 2013, 52: 209–218.

[8] Novoselov KS, Geim AK, Morozov SV, et al. Electric field effect in atomically thin carbon films. Science 2004, 306: 666–669.

[9] Novoselov KS, Jiang D, Schedin F, et al. Two-dimensional atomic crystals. P Natl Acad Sci USA 2005, 102: 10451–10453.

[10] Chang H-H, Chang C-K, Tsai Y-C, et al. Electrochemically synthesized graphene/polypyrrrole composites and their use in supercapacitor. Carbon 2012, 50: 2331–2336.

[11] Hu J, Kang Z, Li F, et al. Graphene with three-dimensional architecture for high performance supercapacitor. Carbon 2014, 67: 221–229.

[12] Novoselov KS, Fal’ko VI, Colombo L, et al. A roadmap for graphene. Nature 2012, 490: 192–200.

[13] Vivekhand SRC, Rout CS, Subrahmanya KS, et al. Graphene-based electrochemical supercapacitors. J Chem Sci 2008, 120: 9–13.

[14] Naguib M, Mashitlar O, Carle J, et al. Two-dimensional transition metal carbides. ACS Nano 2012, 6: 1322–1331.

[15] Naguib M, Kurtoglu M, Presser V, et al. Two-dimensional nanocrystals produced by exfoliation of Ti3AlC2. Adv Mater 2011, 23: 4248–4255.

[16] Barsoum MW. MAX Phases: Properties of Machinable Ternary Carbides and Nitrides. Weinheim, Germany: John Wiley & Sons, 2013.

[17] Sun ZM. Progress in research and development on MAX phases: A family of layered ternary compounds. Int Mater Rev 2011, 56: 143–166.

[18] Hu Q, Sun D, Wu Q, et al. MXene: A new family of promising hydrogen storage medium. J Phys Chem A 2013, 117: 14253–14260.

[19] Hu Q, Wang H, Wu Q, et al. Two-dimensional Sc2C: A reversible and high-capacity hydrogen storage material predicted by first-principles calculations. Int J Hydrogen Energ 2014, 39: 10606–10612.

[20] Peng Q, Guo J, Zhang Q, et al. Unique lead adsorption behavior of activated hydroxyl group in two-dimensional titanium carbide. J Am Chem Soc 2014, 136: 4113–4116.

[21] Gao Y, Wang L, Li Z, et al. Preparation of MXene–Cu2O nanocomposite and effect on thermal decomposition of ammonium perchlorate. Solid State Sci 2014, 35: 62–65.

[22] Naguib M, Come J, Dyatkin B, et al. MXene: A promising transition metal carbide anode for lithium-ion batteries. Electrochem Commun 2012, 16: 61–64.

[23] Tang Q, Zhou Z, Shen P. Are MXenes promising anode materials for Li ion batteries? Computational studies on electronic properties and Li storage capability of TiC2 and TiC2X2 (X= F, OH) monolayer. J Am Chem Soc 2012, 134: 6909–6916.

[24] Sun D, Wang M, Li Z, et al. Two-dimensional Ti3C2 as anode material for Li-ion batteries. Electrochem Commun 2014, 47: 80–83.

[25] Come J, Naguib M, Rozier P, et al. A non-aqueous asymmetric cell with a TiC2-based two-dimensional negative electrode. J Electrochem Soc 2012, 159: A1368–A1373.

[26] Lukatskaya MR, Mashitlar O, Ren CE, et al. Cation intercalation and high volumetric capacitance of two-dimensional titanium carbide. Science 2013, 341: 1502–1505.

[27] Dall’Agnese Y, Lukatskaya MR, Cook KM, et al. High capacitance of surface-modified 2D titanium carbide in acidic electrolyte. Electrochem Commun 2014, 48: 118–122.

[28] Li L, Zhou A, Xu L, et al. Synthesis of high pure Ti3AlC2 and Ti3AlC2 powders from TiH2 powders as Ti source by tube furnace. J Wishan Univ Technol 2013, 28: 882–887.

[29] Murali S, Quarles N, Zhang LL, et al. Volumetric capacitance of compressed activated microwave-expanded graphite oxide (a-MEGO) electrodes. Nano Energy 2013, 2: 764–768.