

Short Communication

A High Energy Density Li-ion Battery with Lithium Titanium Oxide Anode

S.Z.J. Zaidi^{1,*}, M.H.Nazir², M.Raza¹, S. Hassan³

¹ Institute of Chemical Engineering and Technology, University of the Punjab, 54000, Lahore, Punjab, Pakistan.

² School of Engineering, University of South Wales, Wales, United Kingdom.

³ Department of Mechanical Engineering, The University of Hong Kong, Pokfulam, Hong Kong.

*E-mail: zohaib.icet@pu.edu.pk

Received: 31 October 2021 / Accepted: 8 February 2022 / Published: 4 March 2022

To solve the problems of climate change and pave the way towards a more sustainable future, research is being carried out to develop new electrode materials for high-performance batteries. Great efforts are underway to find new materials that can fulfil the demanding requirements for new batteries. Transition metals are a class of materials that are being considered as new electrode materials for rechargeable Li-ion batteries. Such metal oxide structures are attractive due to their high energy density. Lithium titanium oxide is reported here as an electrode for Li-ion batteries having a high energy density and stable structure. Titanium has a low density and high strength which make it a perfect candidate to be used as an electrode for future high energy density. Furthermore, the felt design of the reported titanium also improves the reverse capability of Li-ion batteries. Lithium titanium oxide had a specific capacity of 253.6 mAh/g and retained an excellent 90% of its capacity over 100 cycles. The performance is compared with widely used LiMnO₂ chemistry, against which Lithium titanium oxide performed better in almost all the fields. By using lithium titanium oxide we can produce batteries having energy density well above 1000 Wh/l.

Keywords: Li-ion Battery, Lithium Titanium Oxide, anodic material

1. INTRODUCTION

We are facing unprecedented challenges of rising water levels and unbearable heat waves due to changing climate conditions. The electrification of everything is required from our cars to our devices of everyday uses. However, the batteries that are available now cannot meet the current challenges, and they heat up quickly, have low capacity and extremely low energy density as compared to fossil fuels, so new kinds of materials are being studied to meet these challenges [1-3]. We need to develop batteries

with comparable energy density so that they can replace fossil fuels [4-8]. Lithium-ion batteries are the most widely used batteries from, battery electric vehicles to portable electronics such as smartphones and they are a good candidate to meet the demand for high energy density batteries [9-11]. But, graphite is the prominent anode for Lithium-ion batteries and it has limited specific capacity [12]. Many other alternate anode electrodes have been suggested but they all face many challenges before they are widely adapted such as silicon (which swells up to 400% after only 2-4 cycles [13-15]). Transition metals are also reported in the literature for different kind of batteries such as sodium ion and metal-air batteries where the electrode material is made up of transition metal oxides, and these batteries show excellent results, performing much better than the traditionally produced lithium-ion batteries [16-19].

Titanium is one of the transition metals which is being looked at as an alternate electrode material for Li-ion batteries [20-22]. Properties of Titanium like low density, high strength, stable structure and high ionic conductivity [23-25]. The ion-storage mechanism of Titanium is also very important. Due to the vacancies and huge empty size observed in Titanium, the intercalation and de-intercalation of Li-ion becomes fast and easy [26]. This result in an excellent rate capability and high capacity of Li-ion batteries where Titanium is used as an anode; stability of the whole structure observed in the battery is also due to this reason [27]. Titanium is also being used in photocatalysts and nanotubes which further proves its effective track record as a medium for use in alternate energy [28-29].

In this paper, Lithium titanium oxide(LTO) has been evaluated as an electrode material for Lithium-ion batteries. The performance has been evaluated against the most widely used electrode material, LiMnO_2 , in commercial coin cell batteries which power small devices like watches. Electrochemical experiments were carried out of both materials and compared. LTO as an anode for Li-ion batteries was much better than LiMnO_2 in every aspect. It showed higher specific capacity, lower capacity fade, better structural stability and no degradation of electrolyte. The ionic conductivity of LiMnO_2 was more affected by temperature change as compared to LTO. Due to a phase change that occurs during a cycling test, Titanium specific capacity increased for a few cycles.

2. EXPERIMENTAL AND CHARACTERIZATION METHOD

2.1. Preparation of LTO

LTO electrodes were prepared using a 5 nm TiO_2 anatase powder obtained from US-nano. LTO Electrodes containing 50 wt% Li_2CO_3 (Fisher scientific 99%), 40 wt% TiO_2 , 6 wt% Nafion(Sigma Aldrich) and 4 wt% PTFE (Sigma Aldrich). Li_2CO_3 , TiO_2 , Nafion and propanol (3 g of liquid contents with 1 g dried powder) were thoroughly mixed using a high-speed shear mixer at 7000 rpm for 80 min. The formed slurry further mixed with PTFE and was sonicated for a further 70 min. The ink is carefully pasted under controlled inert environment onto Ti Felt (NV Bekaert SA, 99.9%) current collectors and allowed to settle under ambient conditions. LTO electrodes were further coated to achieve catalytic loadings as enhanced as 2.5 mg cm^{-2} coating a surface with an area of 5 cm^2 .

2.2. Electrolyte Preparation

Electrolyte solution is prepared by mixing 1 mol/L LiPF₆ (Capchem, LiPF₆ 99.9%) in a 1:1 solvent ratio, by mass, of ethylene carbonate (Capchem, E.C<20 ppm H₂O) and diethyl carbonate (Capchem, D.E.C<20 ppm H₂O). 1%, by mass, of the electrolyte additive LiPO₂F₂ (Capchem) was also added to the solutions before being used in the coin cell.

2.3. Assembling coin cell

The coin cell was assembled in a vacuum glove box (vti-glovebox, Super) at moisture level <1ppm. The cell is assembled in a CR2032 coin cell case (tob machine, stainless steel with Gasket). A disc cutter (MTI, MSK-T-10) is used to cut to size the LTO and separator 9mm x 2.5mm to fit into CR2032. The LTO is placed within the CR2032 and a than between two separators (Entek, Entek EP) of 20µm thickness. The electrolyte is added with the help of a Syringe (Saviour Pharma, Saviour Syringe). A lithium reference with a wire is placed to measure the cell potential with metal tweezers. Plastic tweezers are used to place a Lithium metal chip (China Energy Lithium Co., Ltd, Lithium chip) on top of it (as lithium will be highly reactive if it comes in contact with metal. Finally, a spacer (MTI, AG7) and wave spring (MTI, SS304) are placed and the cell assembly is completed by placing the negative case on top. The final dimensions of the assembled coin cell was 20mm x 6mm.

The most widely used chemistry, LiMnO₂, in a coin cell is purchased from an outside vendor (Maxwell, CR2032).

2.4. Electrochemical Measurement

The charge/discharge performance was measured by potentiostat/galvanostat (Ivium, Vertex) under temperature-controlled conditions. The initial formation was done at 0.1C charging cycle against a 0.2C discharging cycle. The cyclic voltammetry was performed at variable voltage 2.5V-5.5V and the current range was set between -0.02A-0.05A. The specific capacity is measured at variable temperature to observe how the coin cell performance is affected by temperature change. The cyclic measurements are taken at different C rates. The theoretical capacity is observed to be 290 mAh/g per Li-ion insertion.

3. RESULT AND DISCUSSION

3.1. Electrochemical evaluation of LTO

Insertion and exertion of li-ions is evaluated by a slow cyclic voltammogram as shown in figure 1(a). The oxidation and reduction points are marked as O₁, O₂ and R₁, R₂ respectively. This is due to the redox phenomena being intercepted as a two-stage insertion and exertion phenomena of Li-ion charge and discharge step [30]. At O₁, the Lithium-ions are inserted into the LTO at Potential of about 4V by the formation of Li⁺-ion. The similar phenomenon of oxidation is observed during the Peak at O₂ at 4.5V.

The reduction phase at R_1 and R_2 are observed to repeat the same phenomena during the charging phase, meaning when the Li^+ -ion is exorted from the negative electrode.

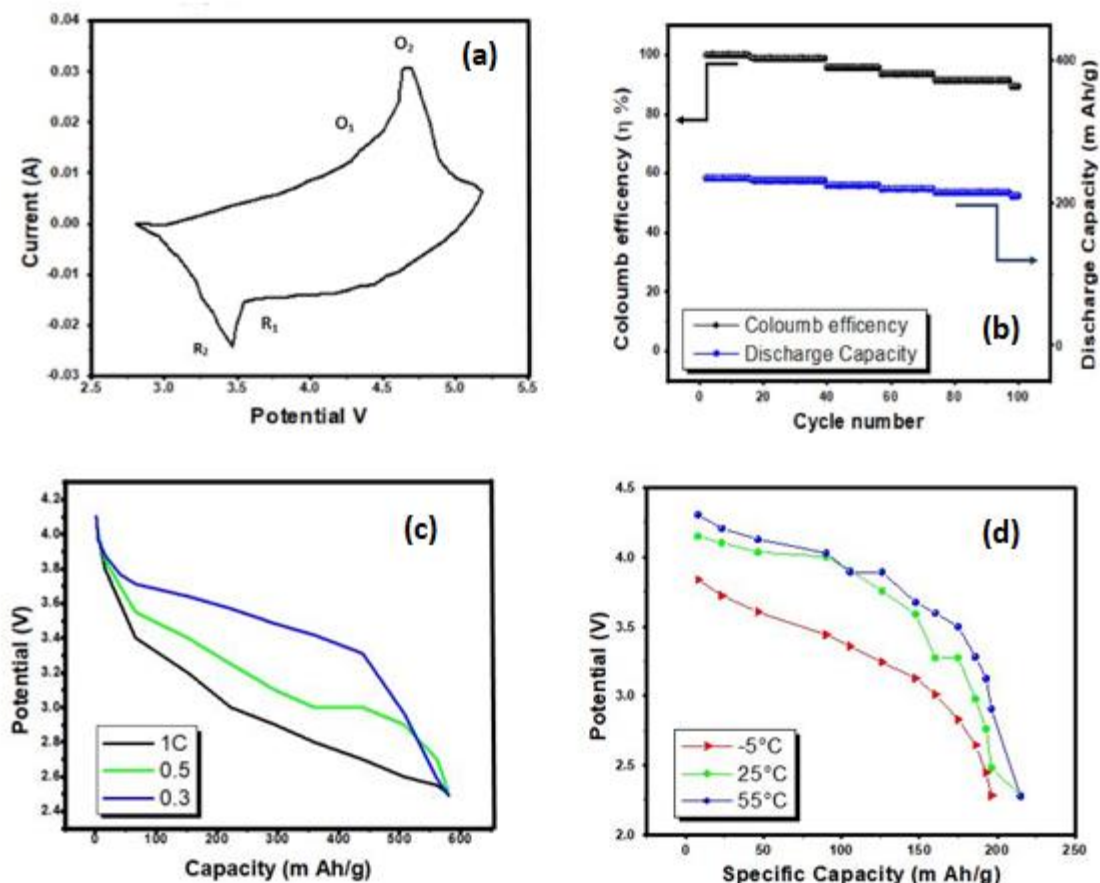


Figure 1. Electrochemical Properties of LTO. a, Cyclic Voltammety of LTO at a sweep rate of 100mV/s. b, Measurement of *coulomb* efficiency and discharge capacity over 100 discharge cycles. c, The charge/discharge curve at different C rates of 1C, 0.5C and 0.33C. d, Measuring temperature effect on capacity at the variable potential range.

The *coulomb* efficiency and discharge capacity are shown in figure 1(b). The *coulomb* efficiency remains about 90% even at the end of 100 cycles and the discharge capacity is just below 90% of the total capacity even after 100 cycles. In the first cycle, the capacity observed is 253.8 mAh/g which drops to about 228 mAh/g. This tells us that LTO forms a stable structure when Li^+ -ion is inserted in the felt. This is due to the structure of felt which is like a thread, as we can see from SEM images, resulting in Li^+ -ion not strongly held by the felt during discharge and the Li^+ -ion are easily exorted from the felt. The discharge of the coin cell is measured at Different C rates; where 1C represent the discharge in 1 hour. The discharge is measured at 1C, 0.5C and 0.3C. The results are in line which are usually observed, that are, at lower C rate the cell capacity that it retains is higher against the potential. In figure 1(d) the impact of temperature is observed on the performance of LTO. The mass load was $3.16\text{g}/\text{cm}^2$. Even at a low temperature of -5°C , the performance is remarkable. At the higher temperatures of 25°C and 55°C , the

performance is nearly identical. This means that higher temperatures do not significantly retard the performance of LTO. So, it can be reasonably inferred that LTO will be a good electrode even at higher temperatures.

3.2. Electrochemical evaluation of Li-MnO₂

Figure 2(a) shows the cyclic voltammogram of MnO₂. The two Plateaus observed at O₁ and O₂ are known to occur due to degradation of electrolyte at a voltage greater than 5.2 [31]. This means that the first plateau O₁ is where the insertion of Li⁺-ion is happening whereas the second plateau at O₂ represents the damage happening to the electrolyte. This is why the peak observed at R₁ is smaller than that of O₁. The exertion of Li⁺-ion from MnO₂ occurs at R₂ and also no damage is observed at R₁ to the electrolyte as this peak is observed at a voltage which is less than 5.2V. It also means that the best operating voltage for a LiMnO₂ is between 3.5V-5V.

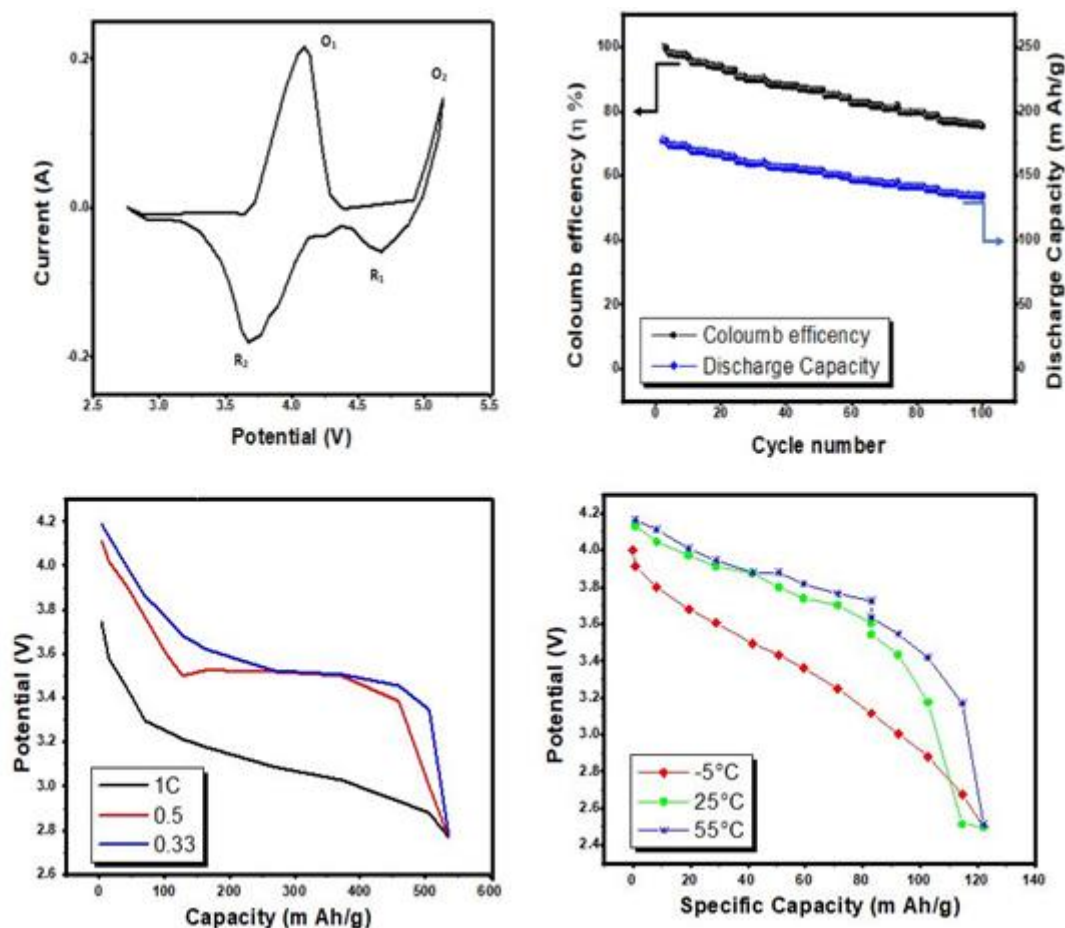


Figure 2. Electrochemical Properties of LiMnO₂ a, Cyclic Voltammetry of MnO₂ at sweep rate of 100mV/s. b, Measurement of *coulomb* efficiency and discharge capacity over 100 discharge cycles. c, The charge/discharge curve at different C rates of 1C, 0.5C and 0.33C. d, Measuring temperature effect on capacity at the variable potential range.

Figure 2(b) shows the *coulomb* efficiency and discharge capacity fade over 100 cycles. The capacity of LiMnO₂ decreases from 177.56 mAh/g to 136.56 mAh/g over 100 cycles. This capacity fade means that LiMnO₂ 77% of its original capacity after 100 cycles. This capacity fade is due to electrolyte degradation and loss of irreversible capacity [32]. The *coulomb* efficiency also declines as a result of this capacity loss.

Figure 2(c) shows discharge at different rates. The rates are 1C, 0.5C and 0.33C. The voltage is varied between 2.5V-4.3V and A significant difference is observed between discharge rate at 1C and 0.5C, 0.33C. The capacity fades quickly when the rate is set at 1C. There is no huge discharge rate difference between 0.5C and 0.33C. In figure 2(d) we can see how temperature affects the performance of LiMnO₂. The performance at -5°C is not good as compared to 25°C and 55°C. Even though the voltage is low, the specific capacity is still low. This means that temperature has a huge effect on the performance of LiMnO₂. The effect of temperature on performance at high temperatures is non-significant as we can observe from figure 2(d). At 25°C and 2.4V, MnO₂ specific capacity drops even below -5°C; this may be due to the phenomena observed from cyclic voltammetry where the oxidation occurs at O₁ at 4V. The high temperature may have compensated for the performance degradation at 55°C, which is not observed at 25°C.

3.3. Comparison of LTO and LiMnO₂

The comparison of cyclic voltammetry from figure 1(a) and 2(a), we can see that LTO is even stable at high voltages whereas LiMnO₂ is unable to remain stable at high voltages due to the degradation of electrolytes. The cyclic stability of LTO is also better than that of LiMnO₂ as evident from figure 1(b) and 2(b), which also results in a lower coulomb efficiency of LiMnO₂. The temperature does not affect the performance of LTO as much as it affects the performance of LTO. The specific capacity of LTO is also higher at 253.8 mAh/g than the specific capacity of LiMnO₂ at 177.56 mAh/g as we can observe from figure 3(a). An increase in specific capacity is observed between cycle number 20 and 25 of LTO. This is due to a phase change that occurs between these cycles. This phase change can be clearly seen from SEM images.

The Arrhenius plot of ionic conductivity is shown in figure 3(b). It can be clearly seen that temperature has a negligible effect on the ionic conductivity of LTO. This also reinforces the observation recorded in figure 1(d). The temperature has a much greater impact on ionic conductivity of LiMnO₂ as we can see from figure 3(b). This too reinforces the observation from figure 2(d). The ionic conductivity is almost identical at the start but it starts diverting as the temperature is increased. The ionic conductivity at much higher temperature is observed to be drastically reduced. It means that at very high temperatures the capacity of MnO₂ decreases. The fall in ionic conductivity of LTO is low as compared to that of LiMnO₂.

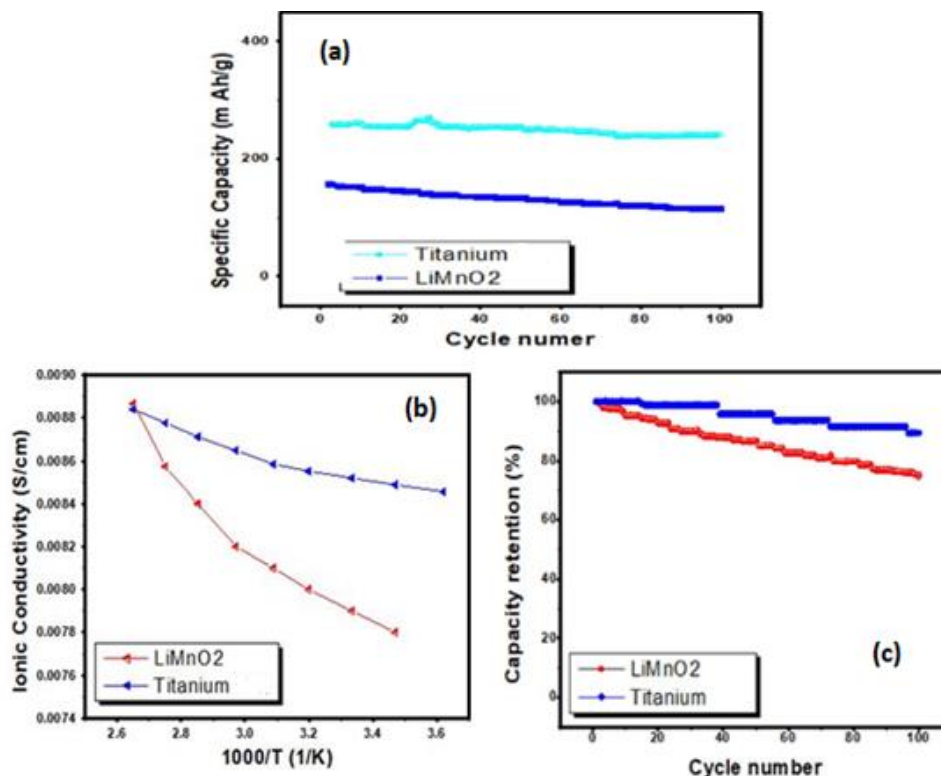


Figure 3. Comparison of electrochemical properties of LiMnO₂ and LTO a, Specific Capacity comparison of LTO and LiMnO₂ at 1C. b, Arrhenius Plot of LiMnO₂ and LTO ionic conductivities against temperature. c, Capacity retention comparison of LiMnO₂ and LTO after 100 Cycles

The capacity retention of LTO is almost 90%, whereas capacity retention of LiMnO₂ is 77% as we can see from figure 3(c). This is due to a multitude of factors which are reported in this paper such as degradation of electrolyte at higher voltages, temperature affect on ionic conductivity and specific capacity [33] measured at different C rates.

4. CONCLUSION

In this paper, a comparison has been carried out between LTO and LiMnO₂ as electrodes for Li-ion batteries. LTO outperformed LiMnO₂, from having a higher specific capacity and also retaining a higher percentage of that capacity over 100 cycles, in every comparison that was carried out in this paper. LTO is also very light and high strength material. Its structural stability and a thread-like structure design allows for easy intercalating and de-intercalating of Li-ions during charging and discharging. It retains its structure even after 100 cycles. This stability also results in no retardation in higher voltages circumstances. This will lead to a shorter charging time. In conclusion, LTO is an excellent candidate to be used as an electrode in high energy density Li-ion batteries.

References

1. J.W. Fergus, *Journal of Power Sources*, 195 (2010) 4554-4569.
2. K. Takada, *Acta Materialia*, 61 (2013) 759-770.
3. R. Yanbio, Z. Shichao, Z. Lincai and H. Xiowu, *Journal of Materials Research and Technology*, 9 (2019) 1549-1558.
4. W. Cao, J. Zhang and H. Li, *Energy Storage Materials*, 26 (2020) 46-55.
5. M.D. Leonard, E.E. Michaelides and D.N. Michaelides, *Renewable Energy*, 145 (2020) 951-962.
6. A. Fathy, H. Rezk and A.M. Naseef, *Renewable Energy*, 139 (2019) 147-160.
7. Y. Li, J. Yang and J. Song, *Renewable and Sustainable Energy Reviews*, 65 (2016) 685-697.
8. T. Kim, J. Lim, M. Oh and J. Kim, *Journal of Power Sources*, 361 (2017) 15-20.
9. S. Goriparti, E. Miele, F. De Angelis, E. Di Fabrizio, R. Proietti Zaccaria and C. Capiglia, *Journal of Power Sources*, 257 (2014), 421-443.
10. M. Armand and J.M. Tarascon, *Nature*, (2008), 652-657.
11. P. Poizot, S. Laruelle, S. Grugeon, L. Dupont and J.M. Tarascon *Nature*, 407 (2000), 496-499.
12. S. Denis, E. Baudrin, F. Orsini, G. Ouvrard, M. Touboul and J.M. Tarascon, *Journal of Power Sources*, 81-82 (1999), 79-84.
13. J. Ko and Y. S. Yoon, *Thin Solid Films*, 673 (2019), 119-125.
14. F. Wang, L. Ma and C. Yuan, *Procedia Manuf*, 33 (2019), 501-507.
15. T. Hasegawa, S.R. Mukai, Y. Shirato and H. Tarmon, *Carbon*, 42 (2004) 2573-2579.
16. Q. Wang, S. Chu and S. Guo, *Chin Chem Lett*, 30 (2019) 2167-2176.
17. R. Gao, Z. Zheng, P. Wang, C. Wang, H. Ye and F. Cao, *Energy Stor. Mater*, 30 (2020), 9-26.
18. H. Lin, R. Jin, A. Wang, S. Zhu and H. Li, *Ceram. Int*, 45 (2019), 17996-18002.
19. J. Do, I. Kim, H. Kim and Y. Jung, *Energy Stor. Mater*, 25 (2020), 62-69.
20. Y. Kee, N. Dimov, K. Minami and S. Okada, *Electrochim. Acta*, 174 (2015), 516-520.
21. Y. Pan, Y.Q. Li, Q.H. Zheng and Y. Xu, *J. Alloys Compd*, 786 (2019), 621-626.
22. J. Yang, J. Hou, Y. Niu, W. Li, F. Yi, S. Liu G. Liu and M. Xu, *J. Alloys Compd*, 722 (2017), 414-419.
23. S.S. Tang, G.R. Li, B.H. Liu and Z.P. Li, *Electrochim. Acta*, 125 (2014), 199-205.
24. J.K. Ha, G.S. Chauhan, J.-H. Ahn, H.-J. Ahn and K.K. Cho, *Electrochim. Acta*, 215 (2016), 674-681.
25. M.Q. Zhao, M. Torelli, C.E. Ren, M. Ghidui, Z. Ling, B. Ansori, M.W. Barsoum, Y. Gogotski, *Nano Energy*, 30 (2016), 603-613.
26. N. Sakai, Y. Ebina, K. Takada and T. Sasaki, *J. Am. Chem. Soc*, 126 (2004), 5851-5858.
27. D.-H. Lee, B.-H. Lee, A.K. Sinha, J.-H. Park, M.-S. Kim, J. Park, H. Shin, K.-S. Lee, Y.-E. Sung and T. Hyeon, *J. Am. Chem. Soc*, 140 (2018), 16676-16684.
28. G.B.O.D.L. Plata, O.M. Alfano and A.E. Cassano, *Chem. Eng. J*, 137 (2008), 396-410.
29. Y. Ghayeb and M.M Momeni, *Ceram. Int.*, 42 (2016), 11209-11216.
30. B. Ying, W. Chuan, W. Feng and W.G. -Qing, *Trans. Nonferrous Met. Soc. China*, 16 (2006), 402-408.
31. Y. Xia, Y. Zhou and M. Yoshi, *J. Electrochem. Soc*, 144 (1997), 2593-2600.
32. Z. Cao, X. Chen, L. Xing, Y. Liao, M. Xu, X. Li, X. Liu and W. Li, *Journal of Power Sources*, 379 (2018), 174-181.
33. N. Takami, H. Inagaki, Y. Tatebayashi, H. Saruwatari, K. Honda and S. Egusa, *Journal of Power Sources*, 244 (2012), 469-475.