



Short communication

Enhanced rate capability due to highly active Ta₂O₅ catalysts for lithium sulfur batteries



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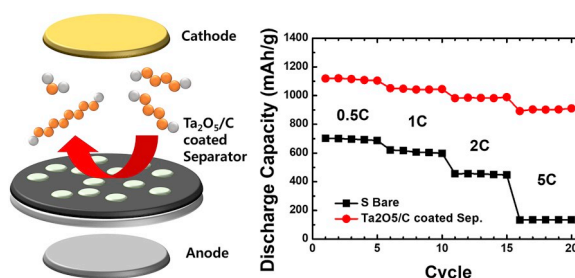
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HIGHLIGHTS

- Heterogeneous catalysts as reaction intermediates can enhance battery performance.
- Ta₂O₅ is one of the most promising heterogeneous catalysts for Li-S battery.
- Strong chemical bonding between S and Ta₂O₅ result in catalytic effect of Ta₂O₅.
- Ta₂O₅ can accelerate slow disproportionation reaction of LiPS.
- Modified separator can help achieving long cycle life and enhanced rate capability.

GRAPHICAL ABSTRACT



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ABSTRACT

The heterogeneous catalysis is widely recognized to promote polysulfide fragmentations can play a key role for the rate capability enhancement of lithium sulfur batteries (LSB). In this study, we report the most active catalysts (Ta₂O₅) for LSB which showed an enhanced rate capability (914 mAh g⁻¹ at 5 C) in comparison with the previously reported catalysts, TiN (865 mAh g⁻¹ at 5 C). The addition of Ta₂O₅ into the carbon-coated separator facilitates the chemical disproportionation of reaction intermediates, Li₂S₄ into Li₂S₈ and Li₂S effectively, which leads to the greatly lengthened second plateau in discharge profile. The heterogeneous catalysis of Ta₂O₅ is clearly verified with the UV-Vis spectra directly showing the change of Li₂S₄ concentration and the battery performance tests without any active elemental sulfur.

1. Introduction

Lithium sulfur batteries (LSB) is attracting many interests with much higher theoretical capacity (1675 mAh g⁻¹) and energy density

(2600 Wh kg⁻¹) than conventional lithium ion batteries (LIB) [1–6]. Also, sulfur has many advantages such as natural abundance, low cost, non-toxic and environmental friendliness [7–10]. However, the main drawbacks of LSB are seriously low cyclability due to the dissolution of

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polysulfide, and the slow kinetics leading to low redox activity of sulfur [10–18].

In order to control the dissolution of polysulfide and enhance the conductivity of sulfur, various approaches have been suggested, such as the sulfur impregnation in mesoporous carbon [6,16,19–23], carbon coating [24–28], carbon interlayer [15,29–33], polysulfide absorbents and sulfur catalysts [34–38]. Recently, many attempts for modified separators like using Nafion [39], porous graphene [40], Nano-TiO₂ [41], CoP nanosphere [42], Tin sulfide [43] and Conductive MOF [44] for LSB have been studied. The use of modified separators has exhibited good capacity and cycle retention, which could facilitate fast electron or ion transport and inhibit the polysulfide dissolved in the electrolyte [45]. Contrary to the various solutions of low cyclability, the slow kinetics issues have been much less covered in the literature, in which the most common approaches were simple employment of highly conducting carbon material hosts.

A number of literature have reported that using transition metal compounds like sulfides [46–48], oxides [49–51], nitrides [52,53] are effective to enhance cell performance associated with rate capability and cyclability. Most of literature have reported that such additives acted as the effective reservoirs for polysulfides based on their strong affinity to sulfur rather than the electrochemical catalysts to enhance the electrochemical redox reaction by promoting the reactions of polysulfides conversion, as shown in this work.

In our previous report, we suggested a unique solution to improve the slow kinetics and to enhance the rate capability; the heterogeneous catalysis in LSB. The simple addition of TiN facilitated the chemical disproportionation of reaction intermediates, Li₂S₄ into Li₂S₈ and Li₂S effectively, which led to the greatly lengthened second plateau in discharge profile [35]. The role of heterogeneous catalysis was verified using the combined computational and experimental approaches that an ultrastrong adsorption of elemental sulfur on TiN surfaces resulted in a spontaneous fragmentation into shorter chains of polysulfides.

In this study, we introduce a new type of heterogeneous catalyst, Ta₂O₅, which played a similar role as TiN, but it demonstrated an increased rate capability compared to TiN. In particular, the combination with Ta₂O₅ catalysts and carbon coated separator led to the maximized performance of LSB without any employment of noble carbon hosts which required complex synthetic routes.

2. Result and discussion

We begin with the examination of battery performance for LSB having Ta₂O₅ added cathode by galvanostatic cycling. First, we examined the electrochemical characteristics of Ta₂O₅, prepared by the thermal oxidation of polycrystalline Ta pellet with a tube induction heater in oxygen atmosphere. Fig. 1(a) shows cyclic voltammograms (CV) of Ta₂O₅ layer on polycrystalline Ta pellet and glassy carbon (GC) electrode in the sulfur dissolved electrolyte. The GC exhibited characteristic peaks at around 2.0 and 2.4 V (vs. Li/Li⁺) in the negative sweep corresponding to the electrochemical reduction from S₈ to Li₂S₈ and from Li₂S₈ to Li₂S_n (1 ≤ n < 8) respectively. On the contrary, the Ta₂O₅ demonstrated no characteristic peak like GC, but showed only a slight increase of reduction current, which was attributable to the formation of sulfur passivation layer [35]. The variation of CV with or without sulfur in the electrolyte can be found in the supporting information (Fig. S1). The discharge capacities were examined with Ta₂O₅ bare (Ta₂O₅ + carbon), S bare (sulfur + carbon) and Ta₂O₅ + S (sulfur + carbon + Ta₂O₅) cathode to understand the role of Ta₂O₅ additives. The areal loading of sulfur was 1 mg/cm², and its size was about 4–10 μm on electrode as in Fig. S2. At first, no discharge capacity was observed for the Ta₂O₅ bare as expected in the CV for polycrystalline Ta₂O₅ layer without sulfur (Fig. S3). This implies that Ta₂O₅ in itself has no activity for the electrochemical reduction of sulfur and also no capacity for lithium intercalation. Ta₂O₅ + S however showed a superior performance to S bare in general as in Fig. 1(b). It is interesting

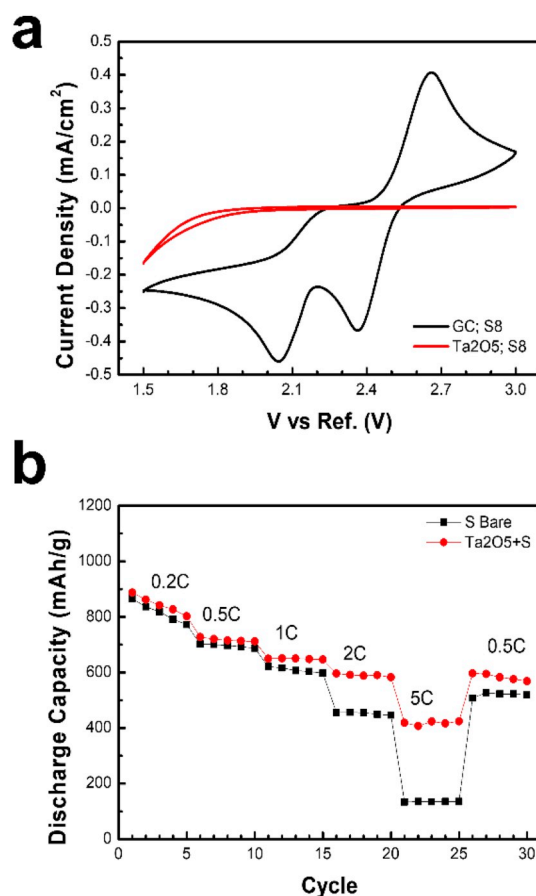


Fig. 1. (a) CV curves of Ta₂O₅ layer on polycrystalline Ta pellet and GC electrode. (b) Discharge capacity of S bare and Ta₂O₅ + S cathode in various C-rates.

to note that the difference of discharge capacity for two kinds of cathodes is marginal in low C-rate, while it becomes larger drastically in high C-rate region. In particular, the discharge capacity of Ta₂O₅ + S is about 3 times higher than S bare in 5 C, indicating that Ta₂O₅ additives are selectively effective on the enhancement of rate capability for high C-rate. This is attributable to the fact that Ta₂O₅ possesses no electrochemical activity to the sulfur reduction reaction but the heterogeneous catalytic activity to the chemical disproportionation reaction as we reported in the former literature [35]. In our previous work, TiN acted as a heterogeneous catalyst to promote the fragmentation of lithium polysulfide. This unique phenomenon was attributed to the ultrastrong chemical bonding between S and TiN surface. The S-passivated TiN surfaces provided the suitable sites for the stabilization of short-chain lithium polysulfides and the fragmentation of long-chain ones into shorter chains. Hence, it was hypothesized that the Ta₂O₅ also acted as heterogeneous catalysts similar to the case of TiN.

In order to verify this hypothesis, we carried out some experiments like XPS studies on Ta₂O₅ surfaces exposed to the elemental sulfur, and UV-Vis spectroscopy to observe the chemical disproportionation on Ta₂O₅ surfaces. In our previous work, we reported that the elemental sulfur is unstable on the TiN surface, allowing the Ti-S bond primarily [35]. In this context, we examined the interaction between sulfur and Ta₂O₅ by XPS. As shown in Fig. 2(a) with our previous work [35], the binding energy of the S2p electron in the elemental S₈ was observed 164.09 eV. However, the S2p electron in the toluene-washed Ta₂O₅/S composite shifts from 164.09 eV to 162.57 eV shown in Fig. 2(b). This shift can be ascribed to the increased electron density around the S atoms, as shown in the various metal sulfides [54]. Consequently, Ta₂O₅ is expected to outperform other host materials like TiN (−0.99 eV) [35]

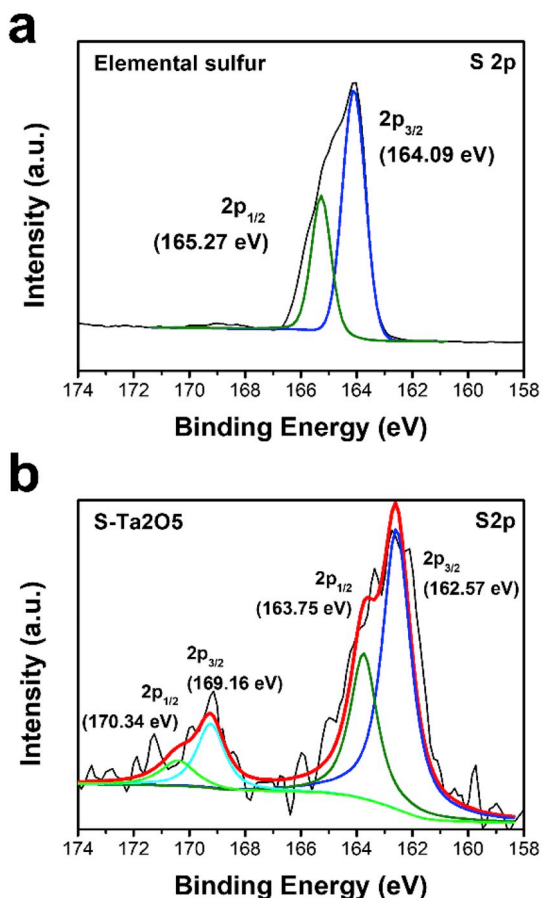


Fig. 2. XPS 2p spectra of (a) elemental sulfur and (b) S_8 on Ta_2O_5 .

and WC (-0.72 eV) [55] in our previous works. Furthermore, the peak around 169 eV is commonly known as the S–O band [56,57], which was produced by the interaction between S and O from Ta_2O_5 . This may be another evidence that Ta_2O_5 and sulfur interact strongly, associated with other experimental results. Hence, this result strongly suggests that the surface-bound S_8 rings are fully disrupted forming chemical bonds between sulfur and Ta_2O_5 , indicating the formation of passivation layer. Thereby Ta_2O_5 might played an important role as heterogeneous catalysts similar to the TiN. On the contrary, the intensity of the spectra for sulfur on carbon (Fig. S4) was much lower than that for Ta_2O_5 , and was hard to detect the peak shift. This indicates that the formation of passivation layer between carbon and sulfur is negligible compared to Ta_2O_5 and sulfur, thus the unique interaction in the sulfur passivated Ta_2O_5 surface plays an essential role in enhancing the battery performance.

Besides, XPS for Ta_2O_5 -polysulfide mixture shows that the S2p peak was shifted -1.91 eV compared to elemental sulfur (Fig. S5). Also comparing the intensity of 169 eV, it is much stronger in Ta_2O_5 -polysulfide than in Ta_2O_5 -S, means that much stronger S–O band is formed in the case of Ta_2O_5 -polysulfide. Thus, it confirmed that Ta_2O_5 forms ultra-strong chemical bonding not only with sulfur but also with polysulfide and has especially stronger interaction with polysulfide.

The heterogeneous catalysis on Ta_2O_5 surfaces was clearly verified with the in-situ UV–Vis spectroscopy. Li_2S_4 was synthesized according to the previous literature and was dissolved in the electrolyte [35,49]. Then, a chronoamperometric (CA) measurement was performed at 2.0 V vs. Li/Li^+ for a given period of time with a RDE setup potentiostat. GC and Ta_2O_5 pellet were used as a working electrode as Fig. 1, and the lithium metal was used as both the reference and counter electrodes. As shown in Fig. 3, while the peak intensity at around $\lambda = 410$ nm (corresponding to the Li_2S_4 concentration) for the GC showed little

difference with reaction time, the Ta_2O_5 exhibited a notable decrease of peak height as well as the color change of the electrolyte. Also, in the case of Ta_2O_5 , yellow-white powder precipitate was formed inside the electrolyte and on the electrode surface. It was found to be sulfur (Fig. S6), which was formed by the disproportionation reaction of Li_2S_4 , implying that Ta_2O_5 promotes the polysulfide disproportionation reaction. As a result, the heterogeneous catalysis on Ta_2O_5 surface was clearly confirmed with two strong evidences like the sulfur binding energy shift in XPS and the absorption peak intensity decrease in UV–Vis spectroscopy.

In our previous studies, we demonstrated that the combination of heterogeneous catalysis with polysulfide capture techniques like carbon interlayers having a large electrochemically active surface area is an effective approach to enhance the performance of LSB and to decrease the production cost of LSB with a simple insertion of the catalyst and carbon coated separator [30,35]. To maximize the cell performance, we prepared the Ta_2O_5 /C separator via a simple casting and drying of ink composed of Ta_2O_5 and carbon in the PvdF-contained solvent onto the PE separator. The morphology of Ta_2O_5 powder and Ta_2O_5 /C separator with scanning electron microscopy (SEM) and energy dispersive spectrometer (EDS) are shown in Fig. S7. The particle size of Ta_2O_5 is around 1 μ m from the SEM images and the Ta_2O_5 and carbon are homogeneously mixed on the separator from the EDS spectra. Electrochemical impedance spectroscopy (EIS) measurements were performed on bare and Ta_2O_5 electrodes from 100 mHz to 1 MHz region to verify the catalytic promotion of chemical disproportionation by Ta_2O_5 is responsible for the superior performance of LSB (Fig. S8). At the high frequency region, the impedance response shows a semicircular loop, which is relevant to the charge transfer resistance, a measure of the charge transfer kinetics. As a result, it was clearly observed that the charge transfer resistance of the cell with Ta_2O_5 decreases dramatically and is lower than that of the cell of the bare electrode. This indicates that the catalysis of the Ta_2O_5 can improve the electrochemical kinetics of LSB [58].

In order to confirm the effect of Ta_2O_5 catalysts in the Ta_2O_5 /C separator, we compared the battery performances among the LSBs with Ta_2O_5 /C separator, carbon coated separator (C separator) and conventional polyethylene separator (PE separator). Fig. 4 shows the charge-discharge profiles and the cycle performances on different C-rates, and CV for the cells having different kinds of separators. All the cells showed typical voltage profiles for LSB having two plateaus at around 2.4 V and 2.0 V, which was corresponding to the formation of dissolvable lithium polysulfide (Li_2S_n , $4 \leq n \leq 8$) and perceptible lithium sulfide (Li_2S_n , $n \leq 2$), respectively [14,59,60]. Compared to the PE separator, C and Ta_2O_5 /C separator showed an enhanced battery performance. The discharge capacities of PE, C and Ta_2O_5 /C separator were 606, 951, 1108 $mAh\ g^{-1}$ at 0.5 C (Fig. 4(a)) and 129, 755, 914 $mAh\ g^{-1}$ at 5 C (Fig. 4(b)). Generally, at high C-rate, the iR resistance increases, so compared to the curve at 0.5C, the ohmic loss is serious at 5 C, so that the second plateau does not appear in PE separator. Also, during the discharging process, since the very sluggish chemical disproportionation reaction requires an enough time to proceed the reaction, however, under the high C-rate like 5 C, there is not enough time to form the second plateau by supplying polysulfide intermediate due to the chemical disproportionation, which increase the effect of the ohmic loss. In the case of C separator, it is obvious that the resistance is reduced by the effect of reaction area increase due to carbon particles on the separator. Hence, the second plateau in the discharge curve can be observed in contrast with the PE separator. In particular, for the Ta_2O_5 /C separator, since the catalyst also promotes the sluggish chemical disproportionation, the second plateau is clearly observed. The results for other C-rates like 1 C or 2 C are shown in Fig. S9. This indicates that the modified separator is obviously effective to enhance the battery performance and particularly the rate capability. Indeed, there have been several reports that modified separator such as carbon coated separator resulted in the performance enhancement of LSB. In the previous literature, it was already reported that the carbon coated separator

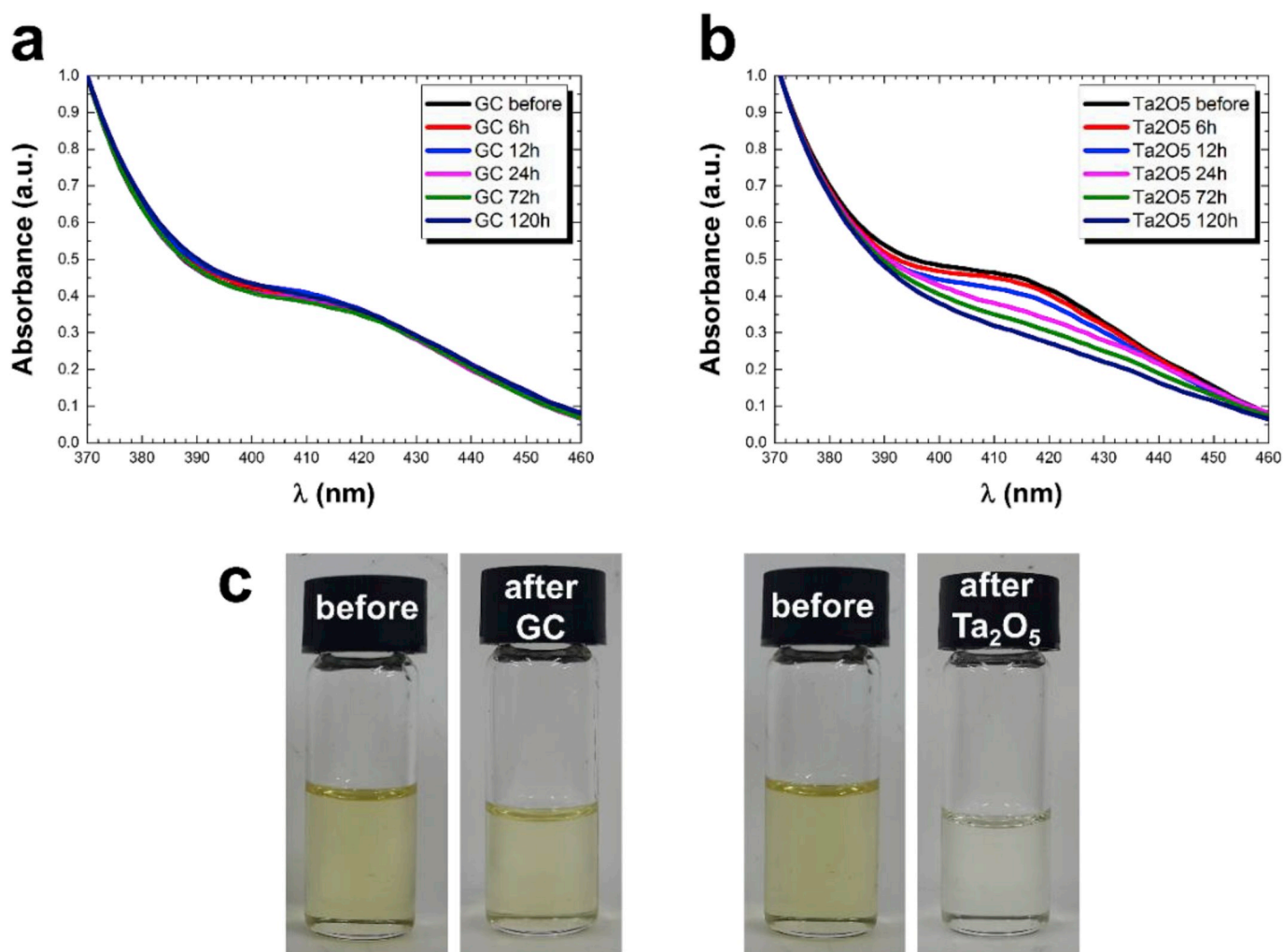


Fig. 3. UV/Vis spectra measured in operando mode using a rotating disk electrode with (a) carbon-pellet and (b) Ta₂O₅-pellet in the electrolyte containing 30 mM Li₂S₄. (c) Visual confirmation of polysulfide disproportionation by concentration change of electrolyte with Li₂S₄ before and after test with GC and Ta₂O₅.

could capture the polysulfide dissolved in electrolyte [61]. It is however interesting to note here that the separator with Ta₂O₅ demonstrated markedly enhanced battery performance at all the tested C-rates. In particular, the capacity difference between Ta₂O₅/C separator and others became greater with the increase of C-rate, implying that the rate capability was drastically enhanced by the addition of Ta₂O₅. Also, Ta₂O₅/C separator showed smaller polarizations than the other samples at a high C-rate. On the side of cyclability, the Ta₂O₅/C separator exhibited good capacity retention (Fig. 4(c)). After 100 cycles, the capacities of PE, C and Ta₂O₅/C separator were 375, 786 and 964 mAh g⁻¹, which the capacity retention of 54.3%, 76.6% and 81.9% based on the 10th cycle, and Ta₂O₅/C separator also show a good cycle performance in higher C-rate like 2C (Fig. S10). Moreover, in high sulfur loading (5.91 mg/cm²), the 0.2C cycle characteristics result in high coulombic efficiency of 99.9% at 5th cycle, and also 92.8% was maintained even in the 50th cycle (Fig. S11). Therefore, it shows that Ta₂O₅ is also capable for high sulfur loading.

In order to clearly manifest the origin of markedly enhanced rate capability by Ta₂O₅ addition, we carried out the CV measurements with the battery cells. As shown in Fig. 4(d), the CV curves for the cells with PE, C and Ta₂O₅/C separator demonstrated a typical characteristic of LSB having two peaks in both positive and negative sweep. The negative peaks at 2.4 V and 2.0 V were widely recognized to be corresponding of the transformation of sulfur to long-chain soluble lithium polysulfide and reduction of lithium polysulfide to insoluble lithium sulfide,

respectively. The positive peak at 2.5 V indicated the formation of sulfur from the discharge products (Li₂S), which was well consistent with the charge-discharge voltage profiles. Even though the CV for Ta₂O₅/C separator showed also typical redox peaks, there is a notable point in the negative sweep that the intensity of second wave and the ratio of second wave to first wave are much higher than any other cells. In C separator, there will be no kinetic enhancement or catalytic effect to promote cell performance because it was used only carbon and no catalyst to make modified separator. Therefore, only the increase of the intensity of the CV area was occurred by the increase of the reaction area, while in Ta₂O₅/C separator shows not only a considerable increase in the capacity consistent with the higher discharge capacity but the peak shift compared to other electrodes. Such difference indicates that LSB with Ta₂O₅/C separator has a better ability to reduce polysulfide than C and PE separator, because the Ta₂O₅ in the Ta₂O₅/C separator acted as a heterogeneous catalyst to promote the chemical disproportionation reaction of reaction intermediates like Li₂S₄ which requires a relatively long time to proceed and therefore can be attributed to the main origin of poor rate capability of LSBs. Similar phenomenon also occurred with the CV curve using a composite cathode cell containing 10 w% Ta₂O₅ shown in Fig. S12, indicating Ta₂O₅ lowers the activation energy and thus increases the kinetics of reactions.

Also, a simple comparison was made with our previously reported TiN under the same conditions. In Fig. S13, Ta₂O₅ shows similar or better performance than TiN, indicates that Ta₂O₅ also possesses

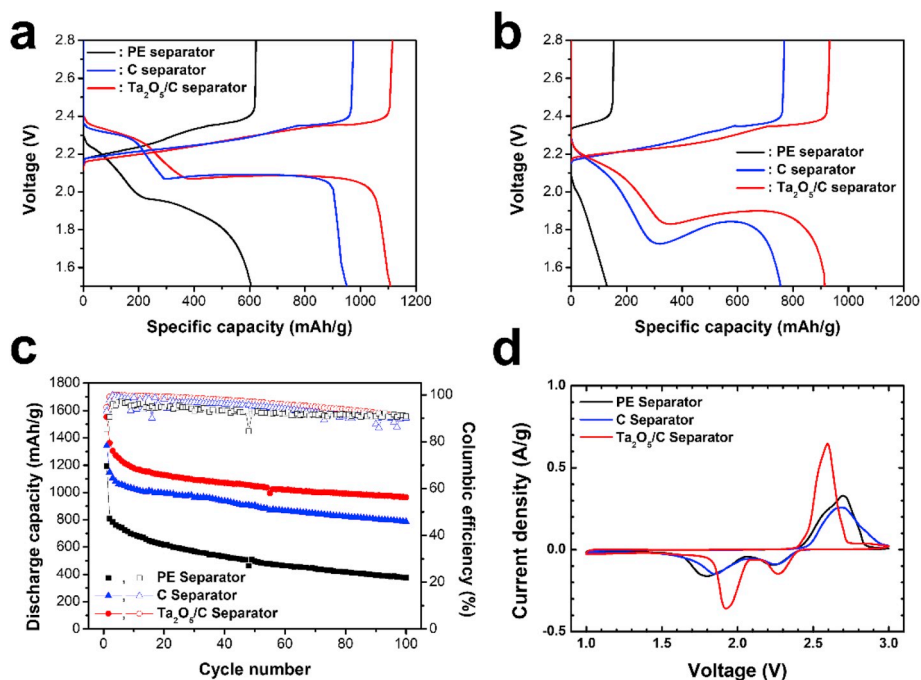


Fig. 4. Charge-discharge profiles at (a) 0.5 C, (b) 5 C. (c) Cyclability of the PE, C, Ta₂O₅/C separator at 0.2 C. (d) CV curves of PE, C and Ta₂O₅/C separator at a scan rate of 0.1 mV/s.

excellent catalytic activity for chemical disproportionation. Hence, we strongly suggest that the employment of heterogeneous catalysts possessing an activity for chemical disproportionation of polysulfides as reaction intermediates is essential for battery performance enhancement and particularly the Ta₂O₅ is one of the most promising materials for the heterogeneous catalysts in LSBs.

3. Conclusions

In summary, we have suggested a simple and unique approach to enhance the electrochemical properties of LSB using the heterogeneous catalyst coated separator. The catalyst coated separator possessed many useful characteristics with synergistic effects that were responsible for the enhanced capacities and cyclic stability. LSB with Ta₂O₅ coated separator displayed an excellent discharge capacity of 964 mAh g⁻¹ and a good cycle retention of 81.9% after 100 cycles. It also delivered an excellent discharge capacity of 914 mAh g⁻¹ at 5 C. We discovered that heterogeneous catalysis to promote the fragmentation of polysulfides, based on the ultra-strong adsorption on Ta₂O₅ can markedly enhance the discharge capacity and rate capability of LSB. The catalytic properties of Ta₂O₅ were revealed to be the ultra-strong chemical bonding between S and the Ta₂O₅ surfaces using the experimental analysis. This simple strategy of coating separator could aid in achieving long cycle life and enhanced rate capability for future commercialization of LSB.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jpowsour.2019.226707>.

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