Characterization and Electrochemical Activities of Nanostructured Transition Metal Nitrides as Cathode Materials for Lithium Sulfur Batteries

Negar Mosavati, Steven O. Salley and K. Y. Simon Ng

Department of Chemical Engineering and Materials Science, Wayne State University, Detroit,
MI 48202

* ***Corresponding author:*** K. Y. Simon Ng;

E-mail address: sng@wayne.edu; Fax: +1 313 577 8171; Tell: +1 313 577 3805

Abstract

The Lithium Sulfur (Li-S) battery system is one of the most promising candidates for electric vehicle applications due to its higher energy density when compared to conventional lithium ion batteries. However, there are some challenges facing Li-S battery commercialization, such as: low active material utilization, high self-discharge rate, and high rate of capacity fade. In this work, a series of transition metal nitrides: Tungsten nitride (WN), Molybdenum Nitride (Mo_2N), and Vanadium Nitride (VN) was investigated as cathode materials for lithium polysulfide conversion reactions. Capacities of 697, 569, and 264 mAh g^{-1} were observed for WN, Mo_2N , VN, respectively, with 8 mg cm^{-2} loading, after 100 cycles at a 0.1 C rate. WN higher electrochemical performance may be attributed to a strong reversible reaction between nitrides and polysulfide, which retains the sulfur species on the electrode surface, and minimizes the active material and surface area loss. X-ray photoelectron spectroscopy (XPS) analysis was performed to gain a better understanding of the mechanism underlying each metal nitride redox reactions.

Keywords: Lithium Sulfur Battery, Cathode Material, Tungsten nitride, Molybdenum Nitride, Vanadium Nitride

1. Introduction

Advances in electric vehicles (EV), hybrid electric vehicles (HEV), and portable electronic devices require more robust electrical energy storage systems, with high energy density and long cycle life performance. Li-S batteries are one of the most promising systems for moving beyond lithium ion battery technologies due to their high theoretical specific capacity of 1,675 mAhg⁻¹, high theoretical energy density of 2,600 Wh kg⁻¹, nontoxicity, and low-cost [1]. However, despite their remarkable superiority, there are some intrinsic limitations facing Li-S battery performance, such as: limited active material utilization due to the insulating nature of sulfur and discharge products, high self-discharge products due to the dissolution of lithium polysulfide (LPS) intermediates in liquid electrolyte and redox shuttle reactions, and high rate of capacity fade attributed to the cathode structural degradation as a result of the volumetric changes that happens during charge and discharge [2, 3].

In order to address the above issues, a wide variety of strategies including development of new electrolytes and additives to electrolytes [4, 5], cathode material development [1, 6-9], and anode modifications [10, 11], have been explored extensively. Among these strategies, suppressing polysulfides from dissolution by trapping polysulfides with physisorption or chemisorption are promising approaches for long life Li-S batteries [12, 13]. Metal oxides and hydroxide additives such as: TiO₂, Ti₄O₇, Al₂O₃, SiO₂, ZnO, and ZrO₂, Ni(OH)₂; as well as metal sulfides, such as TiS₂ and ZrS₂, have been investigated as polysulfide adsorbents [14-18]. They have been reported to reduce redox shuttle reactions, and exhibit a better cycle stability and capacity performance. On the other hand, transition metal nitrides are well known for supercapacitors and lithium-ion battery applications. Various types of metal nitrides such as: TiN [19], VN [20], Mo₂N [21, 22], Zn₃N₂ [23], Ni₃N [24], NbN [25], revealed high

reversible insertion and extraction of ionic species and the capability of storing lithium by the intercalation mechanism [26-31]. Our group investigated titanium nitride (TiN), as a new class of cathode materials and demonstrated its superior performance of 726 mAhg⁻¹ after 100 cycles at 0.1 C rate [32]. Thus, we expand our studies to different transition metal nitrides to gain a better understanding of the role of surface composition and morphology in enhancing the electrochemical performance of Li-S batteries.

In this work, WN, Mo₂N, and VN were synthesized and the electrochemical performance and surface composition of cathodes electrodes composed of these metal nitrides were investigated for lithium sulfur batteries. In addition, the mechanism underlying (LPS) conversion reactions of metal nitrides were investigated. The WN cathode exhibited a higher capacity of 697 mAh g⁻¹, compared to 573 and 264 mAh g⁻¹ for VN and Mo₂N, respectively. This capacity which is in the range of the reported capacities for lithium/dissolved polysulfide systems, such as capacity of 789 mAh g⁻¹ and 600 mAh g⁻¹ after 100 cycles for Pt/graphene cathode with 0.2 M Li₂S₈ catholyte concentration [33], and vertically-aligned carbon nanotubes with 0.3 M Li₂S₆ concentration [34], respectively. However, with a higher loading of WN cathode (9.5 and 12.5 g cm⁻²), higher capacities of 980 and 1,283 mAh g⁻¹ sulfur after 100 cycles at 0.1 C rate, were observed.

2. Experimental Details

2.1 Material Nitride Preparation

2.1.1 Tungsten Nitride Preparation

Ammonium tungstate ((NH₄)₁₀H₂(W₂O₇)₆, Aldrich, 99.99 %), used as a precursor, was

dissolved in 5 M hydrochloric acid solution (HCl Aldrich, 35%) and stirred at 25 °C for 1 h. The solution kept at 120 °C for 2 h, then cooled to room temperature, washed several times with ethanol and distilled water, and then filtered. The obtained yellow tungsten oxide powder was dried at 50 °C in a vacuum oven overnight. In order to produce tungsten nitride structures, it was heated up in a furnace under NH₃ flow to 700 °C over 11 h, held at 700 °C for 3 h and cooled down to room temperature, and subsequently passivated for 2 h in flowing Ar gas overnight.

2.1.2 Molybdenum Nitride Preparation

Ammonium molybdate tetrahydrate (Sigma Aldrich) was dissolved in 5 M HNO₃ (Sigma Aldrich) and stirred at room temperature for 1 h, following by a reaction in an autoclave at 160 °C for 3 h. The resulting molybdenum oxide was washed with water and ethanol and then dried at 80 °C in a vacuum oven overnight. Subsequently, it was heated up in a furnace under NH₃ flow to 700 °C over 12 h, maintained at 700 °C for 1 h and cooled down to room temperature, followed by flowing Ar gas overnight.

2.1.3 Vanadium Nitride Preparation

1.7 g ammonium metavanadate (NH₄VO₃ Sigma Aldrich), and 1.82 g oxalic acid dihydrate (C₂H₂O₄·2H₂O Alpha Aesar) were dissolved in 60 mL distilled water at room temperature with constant stirring for 12 h. The solution was then heated in an autoclave at 180 °C for 24 h. After centrifuging and washing several times with distilled water, the resulting product was dried at 80°C in a vacuum oven overnight. The dried material was then heated to 800 °C under NH₃ flow and maintained at 800 °C for one hour.

2.2 Fabrication of electrodes and Cell assembly

The cathode slurry was prepared by adding 10 wt% of Poly (vinylidene fluoride) PVDF, as binder and N-methyl pyrrolidinone (NMP) as solvent to the electrocatalyst materials (WN, VN, and Mo₂N). The slurry was coated on Al foil and dried at 80 °C under vacuum for 12 h. Elemental sulfur S₈, lithium sulfide Li₂S, Bis(trifluoromethane)sulfonimide lithium salt LiN(SO₂CF₃)₂, LiTFSI, Triethylene glycol dimethyl ether (TG₃), were purchased from Aldrich and used as received. Catholyte solutions with 0.2 M Li₂S₈, 0.1 M LiTFSI, and 1 M LiNO₃ were prepared by stirring appropriate amounts of S₈ and Li₂S into TG₃ at 80 °C overnight. 8 μ L of catholyte solution was added on the positive electrodes. Coin cells (CR2031) were assembled inside an Ar filled glove box, using a polypropylene separator (Celgard 2400), and lithium foil anode.

2.3 Characterization and electrochemical measurements

Phase purity of the positive electrode materials was characterized using a Rigaku Miniflex 600 X-Ray Diffractometer. Cathode material morphology was observed with field emission scanning electron microscopy (JEOL 7600F, FESEM). The average particle size was calculated using about 100 particles found in an arbitrarily chosen area of the enlarged microscopic images. The specific surface areas of the electrode materials were measured by Braunauer-Emmet-Teller (BET) multimolecular adsorption method (Micromeritics Tristar II surface area/porosimeter). Galvanostatic discharge-charge tests were conducted using a Maccor Model 4200 Automated Test System between the voltage range of 1.5 to 3 V (vs. Li/Li⁺) at room temperature. Cyclic voltammetry measurements were made using a Gamry potentiostat reference 3000. The voltammogram was performed at a scan rate of 0.05 mV s⁻¹, and voltage range of 3 to 1.5 V (vs. Li/Li⁺).

3. Results and discussion

3.1 Structural Characterization

3.1.1 Tungsten Nitride

Morphology and structure of the prepared WN was analyzed using SEM (Fig. 1a), TEM (Fig. 1d), and XRD (Fig. 1g). The WN material exhibited a fairly uniform nano-plate structure with regular mesopores. The average size and thickness of nano-plates was measured to be 290 and 23 nm, respectively. The XRD of the WN sample indicates a face-centered cubic (fcc) structure having diffraction peaks at 2θ values of 37.6° , 43.8° , 63.7° , 76.4° and 80.5° corresponding to the (111), (200), (220), (311), and (222) planes, respectively (JCPDS # 75-1012). The d-spacing from inner to outer can be indexed to the same planes of WN cubic phase, which is in a good agreement with the XRD results (Fig. 1g). The calculated crystal size according to the Scherrer equation is 73.8 Å. The BET surface area of WN was measured to be $16.7 \text{ m}^2 \text{ g}^{-1}$ using BET sorptometry.

3.1.2 Vanadium Nitride

The prepared VN exhibited pea shape nanoparticles, with the average particle diameter and length of 47 and 85 nm, respectively (Fig. 1b, 1e). X-ray diffraction spectroscopy (XRD) pattern of the as-prepared VN materials (Fig. 1h) shows diffraction peaks of 37.5° , 43.7° , 63.5° , 76.0° , and 80.0° . These peaks can be ascribed to the (111), (200), (220), (311), and (222) crystal planes with an fcc structure (JCPDS # 73-2038). The average crystallite sizes using Scherrer equation was determined to be 81.97 Å. The BET surface area of VN was measured to be $13.3 \text{ m}^2 \text{ g}^{-1}$ using BET sorptometry.

Fig. 1. SEM image of (a) WN, (b) VN, (c) Mo_2N . TEM images and SAED patterns of (d) WN, (e) VN, (f) Mo_2N . Powder XRD pattern of (a) WN, (b) VN, (c) Mo_2N .

3.1.3 Molybdenum Nitride

Fig. 1c and 1f show the SEM and TEM images of the fairly uniform mesoporous nano rod shaped porous Mo_2N , respectively. The average particle diameter and length of nano rods was calculated to be 850 and 75 nm, respectively. In the XRD pattern of the as-synthesized sample, the diffraction peaks of Mo_2N (JCPDS # 25-1366) at 2θ values of 37.4° , 43.4° , 63.1° , 75.7° , and 79.2° corresponds to an fcc Mo_2N structure with (111), (200), (220), (311), and (222) planes, respectively (Fig. 1i). The average crystallite sizes using Scherrer equation was

determined to be 112.5 Å. BET surface area of Mo₂N was measured to be 10.2 m² g⁻¹ using BET sorptometry.

Although all materials show face centered cubic structure, they have varied size, shape, and surface area. WN has the smallest thickness and crystalline size. Moreover, WN and Mo₂N have a porous structure surface, while VN has a quite smooth surface. In addition, the BET surface area of WN is higher than VN and Mo₂N.

3.2 Electrochemical performance and morphological changes of cathodes

In order to have a better understanding of nitride electrodes activity towards the polysulfide conversion reactions, cyclic voltammetry was performed for cells with a 0.2 M Li₂S₈ catholyte concentration, at a scan rate of 0.05 mV s⁻¹ (Fig. 2). In general, reduction of Li₂S₈ to Li₂S occurs through a series of intermediate Li₂S_x species (2<x<8) at different potentials [2]. The higher voltage cathodic peak corresponds to the reduction of dissolved Li₂S₈ on the surface of the cathode to soluble higher order LPS Li₂S_x (4<x<6), and the lower voltage cathodic peak represents the further reduction of LPS to insoluble lithium sulfides (Li₂S₂ and Li₂S) [2].

The typical sulfur redox reactions with one oxidation and two reduction peaks were observed for cells with WN and VN cathodes. However, the cell with WN shows two overlapping oxidation peaks after first cycle, which implies stages reversible transition between lower and higher order polysulfide during the charge process. In addition, the Mo₂N cathode revealed much broader redox peaks compared to the other nitrides, which suggests a slower redox behavior toward lithium sulfide redox shuttle reactions. This could be due to the lower Mo₂N surface area and a morphology that causes higher polarization on the electrode surface. Furthermore, under the same experimental conditions, the current density of the cell with the WN electrode is clearly higher than VN and much higher than Mo₂N. According to the

Randles-Sevcik equation: $i_p = (2.69 \times 10^5) n^{3/2} A C D^{1/2} \nu^{1/2}$, where i_p is the peak current, n is electron stoichiometry, A is electrode area, D is diffusion coefficient, C is concentration, and ν is scan rate, this maybe attributed to the higher diffusion coefficient of Li ion in WN cathode which can be due to WN porous surface structure and higher surface area.

Another noticeable point that was observed is the potential difference between anodic and cathodic peaks of VN, which increases by cycling and Mo_2N , which is almost stable after the first cycle (unlike WN, that decreases). This potential increase, which is due to the higher polarization on the electrode surface is associated with the LPS accumulation on the VN and Mo_2N electrodes. Thus, redox reactions are less inclined to occur on the surface of these two electrodes. In general, the CV results demonstrated a better reversibility and lower polarization for the cell with the WN cathode.

Fig. 2. Cyclic voltammograms at 0.05 mV s^{-1} recorded for (a) WN, (b) VN, (c) Mo_2N .

Fig. 3. depicts the galvanostatic discharge-charge (GDC) profiles of the different electrodes at a 0.1 C rate, with 0.2 M Li_2S_8 catholyte concentration. They all demonstrated two reduction plateaus (conversion of Li_2S_8 to higher and lower order LPS). In the case of WN, first and second plateaus started to form at 2.43 and 1.96 V for the 10th cycle, respectively. Also, the VN cathode demonstrated two plateaus at around 2.2 and 1.7 V for the 10th cycle, respectively. The Mo_2N cathode barely shows any plateaus after the 10th Cycle.

Fig. 3. GDC profiles in the voltage limit 1.5-3.0 V for (a) WN, (b) VN, (c) Mo_2N .

It appears that the capacity and cycle performance of the Li-S battery can be influenced by the type of nitride cathode (Fig. 4.a). A high initial capacity of 1,768 mAh g^{-1} sulfur was observed for the WN cathode with a 8 mg cm^{-2} electrode loading. This could be due to the high surface area of WN electrode and reversible insertion and extraction of ionic species.

However, this capacity was deactivated to 700 mAh g⁻¹ sulfur within 100 cycles. The Mo₂N and VN cathodes also revealed initial capacities of 1,001 and 1,068 mAh g⁻¹ sulfur for the same loading of 8 mg cm⁻², which dropped to 573 and 264 mAh g⁻¹ sulfur after 100 cycles, respectively. Therefore, in order to get a better understanding of capacity fading, all metal nitride electrodes were separated from the coin cell and washed thoroughly with TG₃ solvent several times and subjected to SEM analysis. Fig. 4b-h. presents the SEM image of the nitride electrodes surface after 100 charges. A passivation layer, which is reported to mainly consist of insoluble LPS (Li₂S and Li₂S₂), can be observed for all cathodes. This layer appears to cover a few sections of WN and Mo₂N, and almost the majority of the VN cathode surface. In addition, the WN cathode particle size is bigger as a result of particle agglomeration or cathode morphological change due to redox reactions. In general, three major reasons appear to influence metal nitride capacity fade. First, an increase in internal resistance on the cathode surface due to the non-conductive nature of Li₂S and Li₂S₂ which reduces the Li ion diffusion into the cathode electrode. Second, surface area loss due to particle agglomeration, size change, and passivation layer formation; third, active material loss due to the quasi-reversible nature of polysulfide conversion reaction, which was shown by the existence of Li₂S and Li₂S₂ at the charge state.

Fig. 4. a) Cycling performance at 0.1 C rate, and SEM images of electrodes before cycling (b) WN, (e) VN, (g) Mo₂N. and after cycling (c) WN, (f) VN, (h) Mo₂N.

Fig. 5a, shows the rate capability and coulombic efficiency of WN, VN, and Mo₂N electrodes at different C rates, and their efficiency. The C rate is based on the theoretical capacity of sulfur ($C = 1,675 \text{ mAh g}^{-1} \text{ sulfur}$). The cells were first subjected to a low 0.1 C rate to obtain stable nominal capacity. Subsequent cycling was performed at higher current rates of 0.2, 0.5, and 1.0 C each for 5 cycles. Finally, it was reverted to 0.1 C for 6 additional cycles. Interestingly, cell capacity fading decreases as the C rate increases. This could be due to a change in reaction path, which decreases the amount of insoluble polysulfide precipitation on cathode surface. The capacity fading of WN decreased to 7.5% at 1.0 C rate, compared to 28.5% at 0.1 C rate.

The results reveal the higher capacity performance for WN electrode for all rates. The cells with WN, Mo₂N, and VN cathodes revealed a capacity of 665, 347, and 145 $\text{mAh g}^{-1} \text{ sulfur}$ at 1.0 C rate respectively. The specific capacity decreases with increasing cycle numbers.

However, the cell recovered most of its capacity when the current rate was returned back to 0.1 C. Although, changing the C rate affects coulombic efficiency for a cycle, it remains constant at almost 98% for the rest of cycles and different C rates.

Fig. 5. a) Rate capability and coulombic efficiency of metal nitrides at different C rates, b) Capacity performance of WN cathode with different loadings.

The effect of cathode material loading on battery performance was studied for WN cathode (Fig. 5b). Cathode loadings of 8, 9.5, 12.5 mg cm⁻² were prepared and the capacity performance and cycleability of Li-S cells were examined with 8 μ l of 0.2 M Li₂S₈ at 0.1 C rate. Increase in the loading of electro-active material results in higher active surface area for polysulfide conversion reaction. It should be mentioned that reported capacity in Li-S systems are based on the amount of active sulfur (polysulfides) in the system. The cell with lower loading (8 mg cm⁻²) presented lower capacity performance and lower capacity deactivation compared to the cells with 9.5 and 12.5 mg cm⁻² loadings. However, cells with 9.5 and 12.5 mg cm⁻² loadings revealed very high initial capacities of 3,907 and 4,355 mAh g⁻¹ sulfur, which deactivated to 980 and 1,283 mAh g⁻¹ sulfur after 100 cycles, respectively. In order to

investigate any possible reactions between electrolyte material and WN cathode that may result to such a high capacity, WN cells with different loadings and electrolyte solution were prepared and examined at 0.1 C rate. The results show the capacity is affected by WN loadings in (Fig. S1 of the Electronic Supplementary Information). In addition, the cell with catholyte solution presents both lower and higher voltage plateaus during discharge profile, indicating the reduction reaction of Li_2S_8 to lower order polysulfides, and one oxidation plateau associated with oxidation of lower order polysulfide to sulfur (Fig. S2a). However, the cell with electrolyte solution doesn't show any plateaus, which indicate any redox reaction (Fig. S2b). The high capacity of WN cathode could be as a result of Li-ion intercalation.

5.4. Surface composition changes of the cathodes

In order to obtain a better understanding of the underlying mechanism of lithium sulfide redox reactions, surface chemical environment of the electrodes was investigated by X-ray photoelectron spectroscopy (XPS). XPS was conducted on electrodes extracted from cells after first charged and discharged state and the deconvoluted spectra in the S2p region are presented in Fig. 6a-c. In order to have a direct comparison, the scanning rate and number of scans to improve the signal to noise ratio were maintained the same across all samples. Peak binding energies of 160.5 and 161.75 eV suggested Li_2S and Li_2S_2 were formed both in charge and discharge status of all electrodes [35, 36]. However, the presence of these peaks in charged state indicates poor reversibility of LPS redox reactions [33]. The higher intensity for the Li_2S and Li_2S_2 peaks of VN and Mo_2N suggests their lower reversibility compared to the WN electrodes. It is also in very good agreement with the detected passivation layer (Fig. 4f). Furthermore, the presence of Li_2S_n ($n \geq 4$) at 162.7 ± 0.1 eV [37-39] at discharge status of VN

and Mo_2N electrodes is consistent with incomplete redox reactions of these two electrodes, which was suggested earlier by cyclic voltammetry results (Fig. 2).

Fig. 6. Post-mortem analysis of the electrodes in charge and discharge states: deconvoluted XPS S2p spectra of the (a) WN, (b) VN, (c) Mo_2N . Original and fitted XPS data are represented with gray and orange lines respectively.

Interestingly, in addition to the long chain polysulfides detected in the S2p spectrum of WN, a strong peak was detected at 163.5 eV of the discharged state. This peak, which was not detected in VN and Mo_2N S2p spectrum, is sited within the range of W-S binding energy [40, 41], and can be attributed to the S-W-N bond. The existence of S-W-N upon discharge, which converts back to WN during charge, suggests the ability of WN to trapped polysulfides during discharge. This minimizes the active material and surface area loss, which happen due to insoluble LPS precipitation. The peaks with the binding energy of 167 ± 0.2 eV were found in all samples, and can be attributed to the -S-O bonding in $-\text{SO}_3$ and $-\text{SO}_2$ species. These species are originated from the electrolyte [37, 42].

5. Conclusions

In summary, we prepared different transition metal nitrides (WN, VN, and Mo₂N) as cathode materials for the lithium sulfur battery. We also investigate the mechanisms underlying these cathodes polysulfide conversion reactions using XPS analysis. Among these materials, WN demonstrated the most promising cycling performance and a high capacity of 700 mAh g⁻¹ sulfur after 100 cycles. By increasing the WN cathode loading to 9.5 and 12.5 mg m⁻² an improved capacity of 980 and 1,283 mAh g⁻¹ sulfur after 100 cycles were observed. The superior performance of WN could be due the existence of S-W-N bonding at electrode surface, which indicates a strong interaction between LPS and WN. This could effectively alleviate the insoluble LPS formation on cathode surface, active material and surface area loss, and improve the overall performance of the battery cell. This result is comparable with our previous study on using a TiN cathode with 16 nm spherical shape nanoparticles and a face centered cubic face structure. TiN revealed a high capacity of 726 mAh g⁻¹ sulfur for 7 mg cm⁻² cathode loading after 100 cycles. Although these results indicate that WN is a highly promising candidate for high performance Li-S batteries, other structural modification could be made to further improve its cycling stability.

Acknowledgment

Financial support from the Department of Energy (Grant DEEE0002106) is gratefully acknowledged. We also thank Dr. C.V Rao for his helpful discussions.

References

- [1] S.-H. Chung, A. Manthiram, *Electrochim. Acta*, 107 (2013) 569-576.
- [2] S.S. Zhang, *J. Power Sources*, 231 (2013) 153-162.

- [3] J. Wang, S.Y. Chew, Z.W. Zhao, S. Ashraf, D. Wexler, J. Chen, S.H. Ng, S.L. Chou, H.K. Liu, *Carbon*, 46 (2008) 229-235.
- [4] J. Guo, Z. Wen, M. Wu, J. Jin, Y. Liu, *Electrochem. Commun.*, 51 (2015) 59-63.
- [5] F. Wu, Q. Zhu, R. Chen, N. Chen, Y. Chen, Y. Ye, J. Qian, L. Li, *J. Power Sources*, 296 (2015) 10-17.
- [6] L. Yuan, H. Yuan, X. Qiu, L. Chen, W. Zhu, *J. Power Sources*, 189 (2009) 1141-1146.
- [7] Y. Fu, A. Manthiram, *J. Phys. Chem. C*, 116 (2012) 8910-8915.
- [8] M. Xu, Z. Zhang, X. Wang, L. Jia, L. Yang, *Energy*, 80 (2015) 303-317.
- [9] M. Xu, Z. Zhang, X. Wang, L. Jia, L. Yang, *J. Power Sources*, 256 (2014) 233-243.
- [10] X.-B. Cheng, R. Zhang, C.-Z. Zhao, F. Wei, J.-G. Zhang, Q. Zhang, *Advanced Science*, 3 (2016) n/a-n/a.
- [11] S. Liu, G.-R. Li, X.-P. Gao, *ACS Appl Mater Interfaces*, 8 (2016) 7783-7789.
- [12] M.K. Song, Y. Zhang, E.J. Cairns, *Nano Lett.*, 13 (2013) 5891-5899.
- [13] D.V. Esposito, K.D. Dobson, B.E. McCandless, R.W. Birkmire, J.G. Chen, *J. Electrochem. Soc.*, 156 (2009) B962-B969.
- [14] C.J. Hart, M. Cuisinier, X. Liang, D. Kundu, A. Garsuch, L.F. Nazar, *Chemical Communications*, 51 (2015) 2308-2311.
- [15] J.R. SMITH, F.C. WALSH, *J. Appl. Electrochem.*, 28 (1998) 1021-1033.
- [16] X. Ji, S. Evers, R. Black, L.F. Nazar, *Nat Commun*, 2 (2011) 325.
- [17] Q. Pang, D. Kundu, M. Cuisinier, L.F. Nazar, *Nat. Commun.*, 5 (2014) 4759.
- [18] Z.W. Seh, J.H. Yu, W. Li, P.-C. Hsu, H. Wang, Y. Sun, H. Yao, Q. Zhang, Y. Cui, *Nat. Commun.*, 5 (2014).
- [19] X. Lu, G. Wang, T. Zhai, M. Yu, S. Xie, Y. Ling, C. Liang, Y. Tong, Y. Li, *Nano Lett.*, 12 (2012) 5376-5381.
- [20] Q. Sun, Z.-W. Fu, *Electrochim. Acta*, 54 (2008) 403-409.
- [21] D.K. Nandi, U.K. Sen, D. Choudhury, S. Mitra, S.K. Sarkar, *ACS Appl Mater Interfaces*, 6 (2014) 6606-6615.
- [22] H.-C. Park, K.-H. Lee, Y.-W. Lee, S.-J. Kim, D.-M. Kim, M.-C. Kim, K.-W. Park, *J. Power Sources*, 269 (2014) 534-541.
- [23] N. Pereira, L.C. Klein, G.G. Amatucci, *J. Electrochem. Soc.*, 149 (2002) A262.
- [24] F. Gillot, J. Oró-Solé, M.R. Palacin, *J. Mater. Chem.*, 21 (2011) 9997.
- [25] D. Choi, P.N. Kumta, *J. Am. Ceram. Soc.*, 94 (2011) 2371-2378.
- [26] H. Zheng, S. Fang, Z. Tong, G. Pang, L. Shen, H. Li, L. Yang, X. Zhang, *J. Mater. Chem. A*, 3 (2015) 12476-12481.
- [27] M.-S. Balogun, M. Yu, C. Li, T. Zhai, Y. Liu, X. Lu, Y. Tong, *J. Mater. Chem. A*, 2 (2014) 10825.
- [28] B. Das, M.V. Reddy, G.V.S. Rao, B.V.R. Chowdari, *J. Mater. Chem.*, 22 (2012) 17505.
- [29] M.-S. Balogun, W. Qiu, W. Wang, P. Fang, X. Lu, Y. Tong, *J. Mater. Chem. A*, 3 (2015) 1364-1387.
- [30] K.H.T. Raman, T.R. Penki, N. Munichandraiah, G.M. Rao, *Electrochim. Acta*, 125 (2014) 282-287.
- [31] S. Dong, X. Chen, X. Zhang, G. Cui, *Coord. Chem. Rev.*, 257 (2013) 1946-1956.
- [32] N. Mosavati, V.R. Chitturi, S.O. Salley, K.Y.S. Ng, *J. Power Sources*, 321 (2016) 87-93.
- [33] H. Al Salem, G. Babu, C. V. Rao, L.M.R. Arava, *J. Am. Chem. Soc.*, 137 (2015) 11542-11545.

- [34] S. Liatard, K. Benhamouda, A. Fournier, J. Dijon, C. Barchasz, *Electrochim. Acta*, 187 (2016) 670-676.
- [35] L. Madec, R. Petibon, K. Tasaki, J. Xia, J.P. Sun, I.G. Hill, J.R. Dahn, *Physical Chemistry Chemical Physics*, 17 (2015) 27062-27076.
- [36] N. Azimi, Z. Xue, I. Bloom, M.L. Gordin, D. Wang, T. Daniel, C. Takoudis, Z. Zhang, *ACS Appl Mater Interfaces*, 7 (2015) 9169-9177.
- [37] Z. Jin, K. Xie, X. Hong, Z. Hu, *J. Power Sources*, 242 (2013) 478-485.
- [38] X. Liang, A. Garsuch, L.F. Nazar, *Angew Chem Int Ed Engl*, 54 (2015) 3907-3911.
- [39] Y.S. Su, Y. Fu, T. Cochell, A. Manthiram, *Nat. Commun.*, 4 (2013) 2985.
- [40] T. Alphazan, A. Bonduelle-Skrzypczak, C. Legens, A.-S. Gay, Z. Boudene, M. Girleanu, O. Ersen, C. Copéret, P. Raybaud, *ACS Catalysis*, 4 (2014) 4320-4331.
- [41] S.M. Tan, M. Pumera, *ACS Appl Mater Interfaces*, 8 (2016) 3948-3957.
- [42] X. Liang, C. Hart, Q. Pang, A. Garsuch, T. Weiss, L.F. Nazar, *Nat. Commun.*, 6 (2015).