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Effects of Nickel Particle Size and Graphene Support on the Electrochemical Performance of Lithium/Dissolved Polysulfide Batteries

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Abstract

The electrocatalytic effect of nickel (Ni) nanoparticle sizes on the lithium polysulfide conversion reactions in dissolved lithium sulfur battery configuration is investigated. The Ni particles of 20 nm with the higher cathode surface area show a superior capacity of 1066 mAh g⁻¹ sulfur compared to Ni particles of 40 and 100 nm for the first cycle. In addition, to further improve the capacity retention and discharge capacity of the cell, the effect of the graphene support on Ni nanoparticle dispersion and cycling performance is investigated. The results show a significant improvement in the discharge capacity compared to the other electrodes. This could be explained by the homogeneous distribution of Ni nanoparticle within the carbon matrix, which suppress the agglomeration and surface area loss of the Ni nanoparticle after cycling; as well as a synergetic effect of graphene structure and Ni nanoparticle.

Keywords

Lithium sulfur battery; Polysulfide; Electrocatalyst; Cathode material; Dissolved polysulfide

1. Introduction

Advances in portable electronic devices and electric vehicles requires advanced electrical energy storage systems, such as rechargeable batteries with high energy density and long lasting cycle performance. Among the most promising energy storage systems, lithium sulfur (Li/S) batteries have received increasing attention due to their high energy density of 2600 Wh kg⁻¹ and theoretical capacity of 1675 mAh g⁻¹. [1] In addition, sulfur is environmentally friendly and has a low cost. [1-3] However, the development of lithium sulfur batteries presents some obstacles such as poor cyclability, lower practical capacity and high self-discharge rate. [1-3] The poor conductivity of sulfur and its final discharge products, Li₂S₂ and Li₂S, limits the specific capacity of Li/S batteries. Furthermore, the dissolution of lithium polysulfide intermediates in the liquid electrolyte during the charge-discharge process causes the polysulfide shuttle process and lithium corrosion, which results in low cyclability, charging inefficiency and high self-discharging rate of batteries [4, 5].

In recent years, efforts have been made to improve the performance of Li/S batteries and overcome the above challenges. Much of the research has focused on the development of new cathode materials to enhance the electrical conductivity, to accommodate and absorb polysulfide and active materials within the pores or layers of the cathode structure. In order to improve cathode material performance, conductive carbon additives such as: mesoporous and nano-structured carbon [6-8], porous hollow carbon spheres [9, 10], carbon multi-walled nano-tubes [11, 12], graphene [13, 14], conductive polymers [15-17], and carbon interlayers have been used. Several studies have been conducted on the design of alternative current

collectors such as Ni foam as an interlayer, cathode conductive structure [18], and a protective layer [19], which improves the active material utilization, cycle life, and battery performance due to its metallicity and 3-D network structure.

It has been reported that the reaction kinetics of aqueous polysulfide can be enhanced by using electrocatalytic electrodes in photoelectrochemical solar cells [20] and redox flow battery cells [21]. Metal oxides such as CeO_2 [22, 23], MnO_2 [24-26], have been demonstrated to be promising cathode catalysts for rechargeable batteries electrochemical reactions. In addition, some metal oxides such as TiO_2 [27], Al_2O_3 [28], SiO_2 [29] and MnO_2 [30] have been shown to enhance Li/S discharge capacities and cycling stability. This can be attributed to their strong ability to adsorb sulfur species, thus effectively suppressing the diffusion of polysulfide species into the electrolyte. Ti_4O_7 has also been reported to enhance the Li/S batteries redox chemistry due to its sulphiphilic surface and good electron conductivity [5]. In our recent study, carbon-free electrocatalysts such as Pt, Au and Ni has been found to enhance lithium polysulfide conversion reactions and improve Li/S battery performance [31]. Among these electrocatalysts, Ni showed a promising behavior due to its high conductivity along with electrocatalytic activity toward polysulfide reduction reaction. [31] Very few studies have been conducted on lithium polysulfide dissolved configuration with electrocatalytic electrodes. Babu et al. [31] found that with a 200 nm thick Ni electrode and 10 μl of 0.2 M Li_2S_8 catholyte, a capacity of 420 mAh g^{-1} sulfur was observed after 40 cycles; while Zhang et al. [32] measured a capacity of 490 mAh g^{-1} sulfur with a super-p carbon electrode and 20 μl of 0.25 m Li_2S_9 catholyte, also after 40 cycles. In the present study, a series of Ni nanoparticles with nominal particle size of 20, 40, and 100 nm have been used as electrocatalysts, and the effect of particle size on Li/S battery performance has been

investigated. Furthermore, graphene has been chosen as a support to anchor the Ni nanoparticles and to investigate the synergetic effect of carbon material and Ni nanoparticles for the lithium polysulfide conversion reactions. The results indicated there is a strong particle size effect, and Ni/graphene electrode exhibits a capacity of 753 mAh g⁻¹ sulfur after 40 cycles which is significantly higher than similar studies [31, 32].

2. Experimental

2.1. Preparation of electrocatalysts

Nickel nanoparticles (Ni, 99.9% with sizes of 20 nm, 40 nm and 100 nm, US Research Nanomaterial Inc.) were activated under hydrogen for 3 h at 150 °C. To prepare Ni/graphene hybrids, 5 grams of graphene (Angstrom Materials) were refluxed with 250 mL of 70% HNO₃ at 110 °C for 3h to functionalize and also remove metallic impurities. The material was then washed with water and dried at 70 °C for 12 h. 0.8 g of the functionalized graphene was then stirred with 300 mL of ethylene glycol, and nickel chloride hexahydrate (NiCl₂·6H₂O, Sigma Aldrich) was added to the resulting suspension. Ni metal loading on graphene support can be controlled by changing the amount of Ni precursor (nickel chloride hexahydrate NiCl₂·6H₂O) during the preparation. In the present work, we have used 0.81 g of nickel chloride hexahydrate (NiCl₂·6H₂O) to achieve Ni metal loading of 20 wt.% on graphene. The resulting suspension was then heated to 140 °C and held for 10 min. Thereafter, 0.65 g sodium borohydride (NaBH₄, Sigma Aldrich) dissolved in 20 mL of ethylene glycol was slowly added and refluxed for 2 h. Finally, the solution was filtered, washed with water/ethanol, and dried overnight.

2.2. Fabrication of electrodes and electrochemical measurements

The cathode slurry was prepared by adding 10 wt% of poly(acrylonitrile-methyl methacrylate) (Polysciences Inc) AN/MMA=94:6, as binder and N-methyl pyrrolidinone (NMP) as solvent to the electrocatalyst materials (Ni nanoparticles, Ni/graphene, or graphene). The slurry was coated on Al foil and dried at 80 °C under vacuum for 10 h.

Elemental sulfur S_8 , lithium sulfide Li_2S , Bis(trifluoromethane)sulfonimide lithium salt $LiN(SO_2CF_3)_2$, LiTFSI, Triethylene glycol dimethyl ether (TG_3), were purchased from Aldrich and used as received. A catholyte solution with 0.2 M Li_2S_8 , 0.1 M LiTFSI, and 1 M $LiNO_3$ was prepared by stirring appropriate amounts of S_8 and Li_2S into TG_3 at 80 °C for 6 h. 10 μ L of 0.2 M Li_2S_8 catholyte solution containing 0.54 mg sulfur was added onto positive electrodes with 8 mg $Ni\ cm^{-2}$ loading. In addition, a Polypropylene separator (Celgard 2400), and lithium foil anode were used to assemble coin cells (CR2032) inside an argon filled glove box. The effect of catholyte concentration on Ni catalyst has been investigated in our recent study on a 200 nm Ni film, with 100, 200 and 600 mM of Li_2S_8 catholyte concentration at 0.1 C rate [31]. The results shows a decrease in specific capacity with increase in the concentration of polysulfide due to increase in the electrolyte viscosity. Therefore, 0.2 M electrolyte was used in the present study.

2.3. Characterization and electrochemical measurements

Phase purity of the positive electrode materials was characterized using a Rigaku Miniflex 600 X-Ray Diffractometer. Morphological features of the cathodes before and after cycling

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4 were observed with field emission scanning electron microscopy (JEOL 7600F, FESEM). The
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6 specific surface area analyses were measured by Braunauer-Emmet-Teller (BET)
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8 multimolecular adsorption method (Micromeritics Tristar II surface area/porosimeter).
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10 Galvanostatic discharge-charge tests were conducted using a Maccor Model 4200
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12 Automated Test System between the voltage range of 1.5 to 3 V (vs. Li/Li⁺) at room
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14 temperature. Cyclic voltammetry experiments were performed using a Gamry potentiostat
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16 reference 3000 at different scan rates ranging from 0.05 to 1 mV s⁻¹ in the voltage range of 3
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18 to 1.5 V (vs. Li/Li⁺).
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28 **3. Results and discussion**

29 **3.1. Structure and morphology**

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33 SEM images of the Ni nanoparticles, graphene and graphene supported Ni nanoparticles
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35 were recorded at high magnification and show the uniform distribution of the spherical
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37 shaped Ni nanoparticles (Figure 1a-c). The average particle size was calculated from the
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39 measurement of about 250 particles found in an arbitrarily chosen area of the enlarged
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41 images. It was found to be about 17, 38, and 92 nm for the nominal 20, 40, and 100 nm Ni
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43 nanoparticles, respectively. In the case of Ni/graphene, average size of about 11 nm Ni
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45 nanoparticles are homogeneously distributed within the graphene matrix (Figure 1d). It was
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47 also confirmed from the corresponding EDS mapping images shown in Fig. S1
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49 (supplementary info).
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55 The surface area of Ni nanoparticles was measured by BET sorptometry and results are
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57 provided in (Figure 1e). As expected, the surface area of 20 nm size Ni nanoparticles is 28.9
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$\text{m}^2 \text{g}^{-1}$ which is higher than 3.6 and $2.7 \text{ m}^2 \text{g}^{-1}$ for the 40 and 100 nm Ni nanoparticles, respectively. Crystal structure of the nanostructured electrocatalysts is analyzed by XRD. Figure 1f shows the XRD pattern of Ni nanoparticles and the graphene supported Ni nanoparticles. A face-centered cubic phase Ni diffraction pattern without any other peaks was observed for all of the samples, which indicates that the Ni nanoparticles are single-phase fcc. Ni crystallite size is determined using Scherrer's equation and considering the full width at half maximum (FWHM) of all the Ni diffraction peaks, the average Ni crystallite sizes are calculated to be 10, 20, 39, and 58 nm for the Ni/graphene, 20, 40, and 100 nm Ni nanoparticles, respectively.

3.2. Electrochemical performances

In order to have a better understanding of Ni electrocatalyst activity towards polysulfides conversion reaction, cyclic voltammograms were performed at different scan rates from 0.05 to 1 mV s^{-1} . All cycles present one anodic oxidation peak at 2.54 V (vs. Li/Li^+) and two cathodic reduction peaks at 2.0 and 2.4 V (vs. Li/Li^+). The higher voltage cathodic peak corresponds to the conversion of sulfur to higher order lithium polysulfide (Li_2S_n $n > 4$) and the lower voltage cathodic peak represents the transformation of dissolved higher order lithium polysulfide to insoluble lower order lithium polysulfide (Li_2S_n $n < 4$) [1]. (Figure 2). The 20 nm Ni nanoparticle electrode shows a more stable behavior for polysulfide conversion reaction during the first 4 cycles (Figure 2a). In addition, Graphene electrode without Ni also exhibited similar redox behavior (Fig. S2). Figure 3 shows the cyclic voltammograms at different scan rates. Anodic and cathodic peak positions shift toward higher and lower voltage, respectively,

as scan rate increases, which indicates the quasi-reversible nature of polysulfide reactions [33]. Furthermore, the Randlese-Sevcik are shown a linear relationship of the cathodic peak height as a function of the square root of the scanning rate, which clearly indicates that polysulfide conversion reaction are diffusion controlled [34].

Figure 4a-c presents the charge and discharge voltage profile of Ni electrodes at a 0.1 C rate. All of the discharge curves present two plateaus in the voltage range of 2.0 to 2.4 V (vs. Li/Li⁺), which are in good accordance with the two cathodic peaks in the charge voltage curves (Figure 2). It is known that one of the factors determining electrocatalytic activity is the accessible surface area [35]. Therefore, the 20 nm Ni particles electrode with higher surface area displays a high initial discharge capacity of 1067 mAh g⁻¹ sulfur, contrasting with the 580 and 496 mAh g⁻¹ sulfur discharge capacity of the 40 nm and 100 nm electrodes, respectively. In addition, after 40 cycles, the electrode with 20 nm shows the highest discharge capacity of 583 mAh g⁻¹ sulfur, compared to the 493 and 298 mAh g⁻¹ sulfur capacity of the 40 nm and 100 nm electrodes, respectively. In order to further improve the capacity retention and discharge capacity of the cell, the effect of the graphene support to anchor the Ni nanoparticle has been investigated. The capacity performance of the cell with Ni/graphene electrode is significantly improved to a high initial capacity of 1216 mAh g⁻¹ sulfur compared to 766 mAh g⁻¹ sulfur capacity of graphene electrode. Ni/graphene electrode and graphene electrode capacities decreased to 753, and 408 mAh g⁻¹ sulfur after 40 cycles (Figure 4d). In addition, capacity retention of the Ni/graphene electrode is around 10 percent higher than graphene electrode during 40 cycles. Moreover, we have demonstrated Ni electrochemical activity by investigating the effect of polysulfide concentration and temperature on Li/S battery performance in our recent study [31]. Therefore, the superior Ni/graphene cell performance

can be attributed to the synergetic effect of both Ni nanoparticle catalyst and graphene structure. Moreover, the homogeneous distribution of Ni nanoparticle within the carbon matrix can minimize the agglomeration of the Ni nanoparticle which decreases the surface area loss after cycling.

Regarding the quasi-reversible nature of polysulfide reactions and the formation of passivation layer on positive electrode and lithium surface, the original mass of active sulfur on the positive electrode can become lower during cycling which is one of the main reasons of capacity fade after cycling. Although the capacity of all electrodes decreases with cycling, the Ni/graphene electrode has the highest capacity after 40 cycles compared to all of the other electrodes (Figure 5a). The rate capability of the Ni electrodes is presented in Figure 5b. The C rate is based on the theoretical capacity of sulfur ($C=1675 \text{ mAh g}^{-1}$ sulfur). All of the electrodes 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 operated at 0.1 C for more 6 cycles. The capacity of all of the Ni electrodes decreases with increasing cycle numbers. The Ni/graphene cell shows a higher capacity performance of 1170, 827, 629, and 489 mAh g^{-1} sulfur, compared to the other electrodes at 0.1, 0.2, 0.5, and 1.0 C rates, respectively. All of the cells recovered most of their capacity when the current rate was returned back to 0.1 C.

3.3. Morphological changes of the cathodes

The cathode electrode was completely washed with TG3 prior to SEM measurements to remove the soluble polysulfides. Figure 6 shows the SEM images of the Ni nanoparticle, graphene, and graphene supported Ni nanoparticle electrodes before and after cycling. After

the 40th full charge process, a passivation layer is observed on the particle surface, which appears to be thinner in the 40 and 100 nm nanoparticle electrodes. The formation of this layer, which is reported to be mostly lithium sulfide Li_2S [36-41], may reduce the cell performance in several ways. It diminishes the interfacial property between the electrodes and electrolyte [40]. In addition, while the polysulfide reactions occur at the surface of the electrode, the insulating nature of the passivation layer may cause a capacity fade [38]. Furthermore, this passivation layer decreases the electrochemical active surface area of the electrode. More importantly, the precipitated Li_2S in the cathode matrix at fully charged state does not contribute to discharge capacity and can be regarded as irreversible loss of active material [41]. There may be a possibility for the formation of NiS_x during the charge-discharge process. However, the formation of NiS_x was not reported in Nickel foam and Ni film that have been used in Li/S batteries. [18, 31]

Therefore, the capacity fade in the cases of the Ni 20 nm and Ni/graphene electrodes are more significant compared to the other electrodes. These results are in a very good agreement with the electrochemical measurement.

4. Conclusions

The effects of Ni particle size and graphene support on the lithium polysulfide conversion reactions and Li/S battery performance have been studied. The results indicate the 20 nm Ni electrode with higher surface area has good electrochemical performance. Moreover, the 40 nm Ni electrode shows more superior stability, which is possibly because of thinner passivation layer formation and less morphological changes of the positive electrode. Ni/graphene electrode exhibited higher initial capacity and capacity retention compared to the

graphene electrode. This is probably due to the better dispersion of Ni nanoparticles on graphene support, large surface-volume ratio and synergetic effect of graphene and Ni.

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List of Figure Captions

Figure 1. SEM images of Ni nanoparticles: (a) 20 nm, (b) 40 nm, (c) 100 nm, (d) Ni/Graphene, (e) BET surface area of Ni nanoparticles, and (f) XRD patterns of all of the nanoparticles.

Figure 2. Voltammograms for first 4 cycles: (a) Ni 20 nm, (b) Ni 40 nm, (c) Ni 100 nm, and (d) Ni/Graphene

Figure 3. Cyclic voltammograms at different scan rates (0.05 to 1 mV s^{-1}): (a) Ni 20 nm, (b) Ni 40 nm, (c) Ni 100 nm, and (d) Ni/Graphene.

Figure 4. Voltage vs specific capacity profiles at different cycles: (a) Ni 20 nm, (b) Ni 40 nm, (c) Ni 100 nm, (d) Ni/Graphene, and (e) Graphene.

Figure 5. Effect of particle size and graphene support on cycling performance: (a) Capacity performance, and (b) Rate capability at different current rates.

Figure 6. Images of electrodes before cycling (left column), and after 40 cycles (right column): (a) Ni 20 nm, (b) Ni 40 nm, (c) Ni 100 nm, and (d) Ni/Graphene.

Figure 1

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Figure 6