Short communication

Synthesis of Li_xMnO_2 by chemical lithiation in an aqueous media

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ABSTRACT

Li_xMnO_2 ($x = 0.302$) was synthesized by chemical lithiation, using a formaldehyde reducing agent and a LiOH lithium source in an aqueous media. The electrochemical properties and structural stability of the product were characterized by X-ray diffraction and charge–discharge measurements. The chemically lithiated Li_xMnO_2 had a first charge and discharge capacity of 86.2 and 265 mAh/g, respectively, with good cycling behavior. Based on the electrochemical results of the first charge, a two-step mechanism of Li_xMnO_2 lithiation is proposed. γ-MnO₂ is first oxidized by formaldehyde, and then Li diffuses into the γ-MnO₂ lattice.

1. Introduction

Lithiated MnO₂ known as composite dimensional manganese oxide (CDMO) has been a promising cathode material for rechargeable lithium batteries for its relatively high specific capacity of up to 200 mAh/g. This material is obtained by lithiation reaction with LiOH (or LiNO₃) of γ-MnO₂ (chemical manganese dioxides (CMD) or electrolytic manganese dioxide (EMD)) mixture with a Li:Mn ratio of 3:7 at 300–400 °C in air [1–8]. These CDMO products have been shown to provide improved electrochemical cycling compared to their parent γ-MnO₂ structures.

During the lithiation/calcination process, the phase transitions occurring still remain obscure. It was reported that the reaction between LiNO₃ and γ-MnO₂ produced a composite material composed of γ-MnO₂ and Li₂MnO₃, followed by the phase change to spinel LiMn₂O₄ due the higher thermodynamically stability of the spinel phase than the layered Li₂MnO₃ for the temperature range of 300–400 °C and the Li:Mn ratio used [9,10]. Moreover, it was also reported that the heat-treated γ-MnO₂ (HEMD) shows a two-phase reaction during reduction with two different tetragonal sublattices ($a = 4.39$ Å, $c = 2.86$ Å, $a' = 4.9$ Å, $c' = 2.82$ Å) between $0.3 < x < 0.5$ in Li_xMnO_2 followed by an homogeneous phase reaction with constant increase of a' and c' when the sample was prepared at 400 °C from an EMD, but that was not the case for the HEMD prepared at 250 °C from the same EMD [11]. The transformation from a more ramsdellite type to pyrolusite type was observed during the thermal treatment leading to poor cycling behavior of EMD sample and removal of proton using oxidant in non-aqueous solvent was shown to be effective in order to avoid the phase transformation [12]. Bowden et al. reported a lithiated EMD made in aqueous sulphuric acid by ionic exchanged with aqueous LiOH showing good performance for Li primary batteries [13]. Considering the above investigations, thermal treatment of γ-MnO₂ with or without lithium sources should give rise to phase transitions of the parent structure of γ-MnO₂. Alternative synthetic methods for the preparation of lithiated Li_xMnO_2 leading to high capacity with good cycling behavior materials are more than desirable.

In this study, Li_xMnO_2 was synthesized from γ-MnO₂ chemical lithiation in an aqueous solvent was performed using a reducing agent, the relationship between the depth of lithiation and electrochemical performance was examined. For comparison, the cyclic behavior of samples that were chemical lithiation in an organic media was also examined, using lithium iodide (LiI) in acetonitrile and n-butyllithium (n-BuLi) in n-hexane.

2. Experimental

Chemically oxidized γ-MnO₂ was synthesized as follows. Electrolytic manganese dioxides (TKV-B, Mitsui Mining and Smelting Co., Ltd.) were heated in vacuum at 100 °C for 12 h to remove water. After heat treatment, the powder was mixed with an oxidant (nitronium tetrafluoroborate, NO₂BF₄) in acetonitrile solution and stirred for 24 h under an Ar gas atmosphere. After filtering and vacuum drying at 120 °C for 12 h, the final product was kept under an Ar atmosphere for several days prior lithiation.

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Table 1
Molar ratios of γ-MnO$_2$, lithium salt (LiOH), buffer salt (NaOH), and reducing agent (HCOH) for sample preparation.

Sample	γ-MnO$_2$	LiOH	NaOH	HCOH
Li-1	1	10	–	–
Na-1	1	–	10	–
LiNa-1	1	2	10	–
HCOH-1	1	1	–	1
HCOH-2	1	4	–	1
HCOH-3	1	4	–	4
HCOH-4	1	7	–	4
HCOH-5	0.1	4	–	4

To produce chemically lithiated γ-MnO$_2$ in an aqueous media, a formaldehyde reducing agent (37% solution in water) and a lithium hydroxide (LiOH) Li source were employed. γ-MnO$_2$ was added to the LiOH solution (see Table 1 for molar ratio) and stirred. Formaldehyde solution (see Table 1 for molar ratio) was added dropwise to the solution, which was then stirred for 24 h. Finally, the samples were filtered with deionized water, dried at 120 °C, and then kept under an Ar atmosphere for several days.

To prepare chemically lithiated γ-MnO$_2$ in an organic media, γ-MnO$_2$ was chemically oxidized to remove protons from the structure. TKV-B was then heated in vacuum at 100 °C for 12 h to remove water. After heat treatment, the powder was mixed with an oxidant (NO$_2$BF$_4$) in acetonitrile solution, and then stirred for 24 h under an Ar atmosphere. Lithiation was obtained by treatment of the chemically oxidized samples with LiI or n-BuLi reducing agents. In the chemical lithiation using LiI, the chemically oxidized γ-MnO$_2$ powder was mixed with an equimolar amount of LiI in acetonitrile solution, and then stirred for 24 h at room temperature under an Ar atmosphere. The product was filtered and vacuum dried at 120 °C for 12 h, and then kept under an Ar atmosphere for several days. In the chemical lithiation using n-BuLi, chemically oxidized γ-MnO$_2$ powder was mixed with an equimolar amount of n-BuLi in n-hexane solution, and then stirred for 24 h at room temperature under an Ar atmosphere. After vacuum drying at 60 °C for 6 h to remove impurities and n-hexane, the products were kept under an Ar atmosphere for several days.

To characterize the electrochemical and structural properties, coin-type "2032" cells were assembled as follows. The cathode materials were prepared by mixing the Li$_x$MnO$_2$ with acetylene black and Teflon powder with a weight ratio of 80:16:4, and then disk shape pellet with an area of 1 cm^2 was cutted. Cells were constructed by stacking a cathode pellet between two pieces of Al mesh as current collectors, lithium metal anode, polypropylene separator and 1 M LiPF$_6$ in EC:DEC = 3:7 vol.%) were used. The cells were assembled in a glove box under an Ar atmosphere. The charge–discharge experiments (multi-channel galvanostat TOSCAT-3100, TOYO SYSTEM Co., Ltd.) were conducted over a voltage range from 2.0 to 4.5 V versus Li/Li$^+$, with a current density of 0.1 mA/cm^2 at 25 °C.

X-ray diffraction analysis (XRD, Cu Kα radiation, λ = 1.54 Å, 50 kV, 150 mA, Rigaku RU200B) was used for the structural characterization of γ-MnO$_2$. Patterns were recorded over the 2θ range from 10° to 80° with a step size of 0.03° and a count time of 3.0 s.

3. Results and discussion

3.1. Structural characterization and charge–discharge performance of γ-MnO$_2$ lithiated in an organic solvent

Fig. 1 shows X-ray diffraction patterns of chemically oxidized γ-MnO$_2$ and γ-MnO$_2$ after chemical lithiation by the reducing agents LiI or n-BuLi. As the lithiation level was increased by chemical reduction, the diffraction peaks shifted to lower angles (shown in

Fig. 1(b) and (c)), which indicates an insertion of lithium into the γ-MnO$_2$. Notably, the shift of the 1 1 0 diffraction peak ($2\theta \cong 22°$) indicates the expansion of 1 × 1 and 1 × 2 channels along the c-axis. The shift of the 1 1 0 diffraction peak ($2\theta \cong 22°$) could be used as a parameter to tailor the insertion of Li ions using reducing reaction, consequently it will also be used to tailor the insertion of Li ions for the reduction in aqueous media.

Fig. 2 shows charge–discharge profiles of chemically lithiated γ-MnO$_2$, formed using a LiI reducing agent in acetonitrile solution and n-BuLi in an n-hexane solution. The γ-MnO$_2$ lithiated by LiI had a first charge capacity of 94.5 mAh/g, which corresponds to an initial composition of $x = 0.332$ in Li$_x$MnO$_2$ from the result of theoretical capacity of 285 mAh/g for LiMnO$_2$, and showed a first discharge capacity of 240 mAh/g with reversible cyclic behavior. On the other hand, the γ-MnO$_2$ lithiated by n-BuLi had a much larger charge capacity of 291.3 mAh/g, corresponding to a lithium content of $x = 1.0$ in Li$_x$MnO$_2$. This difference in depth of lithation between the samples was caused by the different redox potentials of the reducing agents. Although reversible cyclic behavior was obtained, with two plateaus around 3.0 and 3.4 V from the second cycle on, the charge–discharge capacity of the γ-MnO$_2$ lithiated by n-BuLi decreased from 175 (first discharge) to 130 mAh/g (second discharge). This capacity fade in the first two cycles was due to a structural change during chemical lithiation. The X-ray diffraction patterns of the sample lithiated by n-BuLi showed lower crystallinity than the other two samples, as shown in Fig. 2.

3.2. Structure characterization and charge–discharge performance of γ-MnO$_2$ lithiated by a reducing agent in an aqueous media

Lithiation conditions were optimized for a formaldehyde reducing agent in an aqueous media. Table 1 summarizes the molar ratios of γ-MnO$_2$, lithium salt (LiOH), buffer salt (NaOH), and reducing agent (HCOH) for the different sample preparation. A buffer salt of NaOH was employed to investigate the effect of the [OH]$^-$ concentration during the chemical lithiation of samples Na-1 and LiNa-1. The effects of the concentration of the lithium salt LiOH and/or the formaldehyde reducing agent were then examined for the samples HCOH-2–HCOH-5.
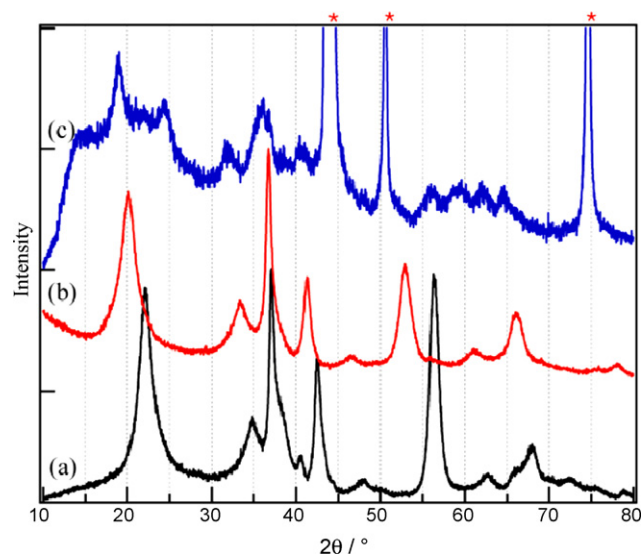

Fig. 1. X-ray diffraction patterns of γ-MnO$_2$: (a) chemically oxidized, (b) chemically lithiated by LiI, and (c) chemically lithiated by n-BuLi (asterisks are due to sample holder).
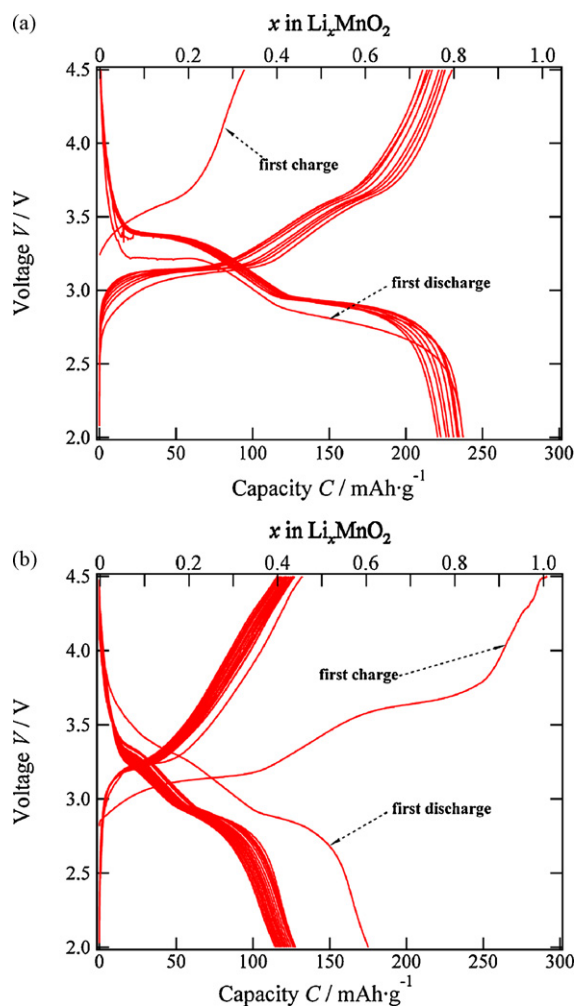
Fig. 2. Charge–discharge profiles of lithiated γ-MnO₂: (a) using LiI in acetonitrile solution and (b) using n-BuLi reducing agent in n-hexane.
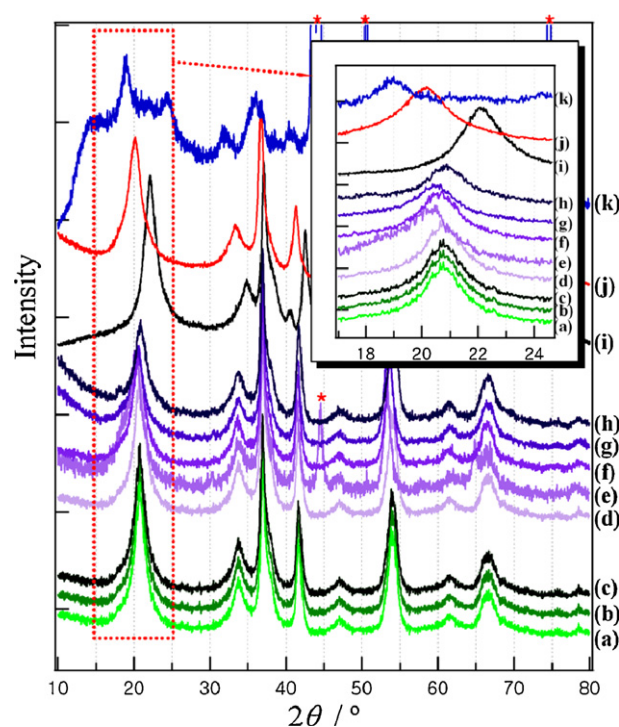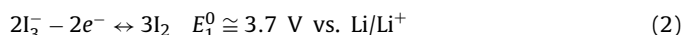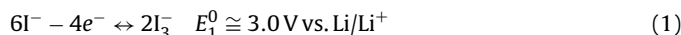

Fig. 3. X-ray diffraction patterns of lithiated γ-MnO₂ in aqueous solution: (a) sample Li-1, (b) sample Na-1, (c) sample LiNa-1, (d) sample HCOH-1, (e) sample HCOH-2, (f) sample HCOH-3, (g) sample HCOH-4, (h) sample HCOH-5, (i) chemically oxidized γ-MnO₂, (j) γ-MnO₂ chemically lithiated by LiI, and (k) γ-MnO₂ chemically lithiated by n-BuLi (asterisks are due to sample holder).

Fig. 3 shows the X-ray diffraction patterns of lithiated γ-MnO₂ in aqueous solution. The 1 1 0 diffraction peaks ($2\theta \cong 22°$) shifted to lower angles due to Li insertion into γ-MnO₂, without any significant host structure changes. The HCOH-2 sample, treated with a molar ratio of γ-MnO₂:LiOH:HCOH = 1:4:1 showed the largest peak-shift, corresponding to the largest amount of Li insertion. Moreover, the concentration of buffer salt and formaldehyde reducing agent proved to have no influence on the depth of lithiation.

Fig. 4 shows the charge–discharge profiles of the sample HCOH-2. The cell showed first charge and discharge capacities of 86.2 and 265 mAh/g, respectively, and reversible cyclic behavior with two plateaus in the charge–discharge curves. This first charge capacity of lithiated γ-MnO₂ gave a composition of $x = 0.302$ in Li$_x$MnO₂. The lithium content was slightly lower than the $x = 0.35$ in Li$_x$MnO₂ obtained for γ-MnO₂ chemically lithiated by LiI in organic solution, because of the difference in the redox potentials between formaldehyde and LiI, which are $E = 3.235$ and 2.8 V versus Li/Li⁺, respectively. As a result, γ-MnO₂ could be chemically lithiated up to a depth of discharge of 30.2% ($x = 0.302$ in Li$_x$MnO₂) using a formaldehyde reducing agent in aqueous solution.

3.3. Lithiation mechanism in an aqueous media and comparison of reducing agent redox potentials

Although the redox potential of LiI is 2.8 V versus Li/Li⁺, only a narrow range of potential above 3.4 V versus Li/Li⁺ in γ-MnO₂

was reduced, which was corresponding to be $x = 0.332$ in Li$_x$MnO₂. The chemistry of LiI as a reducing agent in acetonitrile was previously studied in detail [14]. The oxidation of I⁻ to I₂ occurs in two reversible steps as follows:

$$6I^- - 4e^- \leftrightarrow 2I_3^- \quad E_1^0 \cong 3.0 \text{ V vs. Li/Li}^+ \tag{1}$$

$$2I_3^- - 2e^- \leftrightarrow 3I_2 \quad E_1^0 \cong 3.7 \text{ V vs. Li/Li}^+ \tag{2}$$

γ-MnO₂ has two redox potentials of Mn⁴⁺/Mn³⁺. Mn⁴⁺/Mn³⁺ at 3.4 V versus Li/Li⁺ is related to either the octahedral sites around Mn³⁺ inner channels of pyrolusite and ramsdellite, and/or Mn⁴⁺/Mn³⁺ at 3.0 V versus Li/Li⁺ is associated with sites around
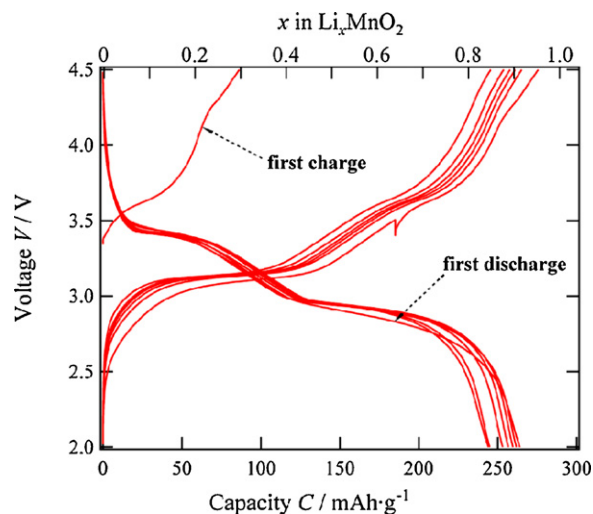

Fig. 4. Charge–discharge profiles of lithiated γ-MnO₂ using a formaldehyde reducing agent in aqueous solution.

Mn^{4+} vacancies, "Ruetschi" protons, where vacancy clustering occurs. However, the potential of 3.0 V versus Li/Li^+ became lower during lithium insertion (or the discharge state). Therefore, only reaction 1 was considered for γ-MnO_2 with Mn^{4+}/Mn^{3+} at 3.4 and 3.0 V versus Li/Li^+, which could explain the lack of lithiation in the potential range below 3.0 V versus Li/Li^+.

The reduction of transition metal oxides and chalcogenides using n-BuLi as a reducing agent in hexane has been widely investigated [15,16]. This reaction is accompanied by the insertion of Li ions into the lattice structure of transition metal oxides and chalcogenides. The reaction occurs as follows:

$$MO_2 + m(n\text{-}C_4H_9)Li \rightarrow Li_mMO_2 + \frac{m}{2}C_8H_{18} \qquad (3)$$
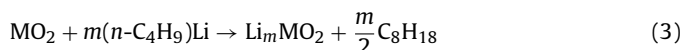
where M is a transition metal. n-BuLi is a very strong reducing agent, with a redox potential of 1.0 V versus Li/Li^+, which could lithiate 1 mole of Li in γ-MnO_2. However, lithiation with LiI or n-BuLi in organic solvent should be performed after the chemical oxidation, because "Coleman" protons and "Ruetschi" protons cannot be extracted in an organic solvent.

On the other hand, formaldehyde solution is a powerful reducing agent, especially under alkaline conditions. In aqueous solutions, formaldehyde can exist in several different forms [17,18]. Under alkaline conditions, the overall reaction of formaldehyde oxidation is described as follows:

$$HCOH + 3OH^- \rightarrow HCOO^- + 2H_2O + 2e^- \qquad (4)$$
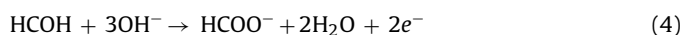
As formaldehyde has no Li^+ cation, the addition of Li is necessary. Formaldehyde is more effective in high pH medias, so lithium hydroxide (LiOH) salt, which is very strongly alkaline in aqueous solution, was introduced.

Based on the electrochemical results with a first charge capacity of 86.2 mAh/g (shown in Fig. 4), the lithiation mechanism of Li_xMnO_2 using formaldehyde can be separated in a two steps process. In the first step, formaldehyde was oxidized to formic acid (Eq. (4)), which reduced γ-MnO_2 to form MnO_2^- anions. In the second step, Li^+ cations diffused into the γ-MnO_2 lattice, forming a bond with MnO_2^- anions, which then form Li_xMnO_2 (Eq. (5))

$$xLi^+ + xe^- + MnO_2 \rightarrow Li_xMnO_2 \qquad (5)$$

Fig. 5 shows a schematic drawing of the lithiation mechanism in aqueous media using the formaldehyde reducing agent described above. The removal of some of the "Ruetschi" and "Coleman" protons from the host structure during lithiation was unlikely, because
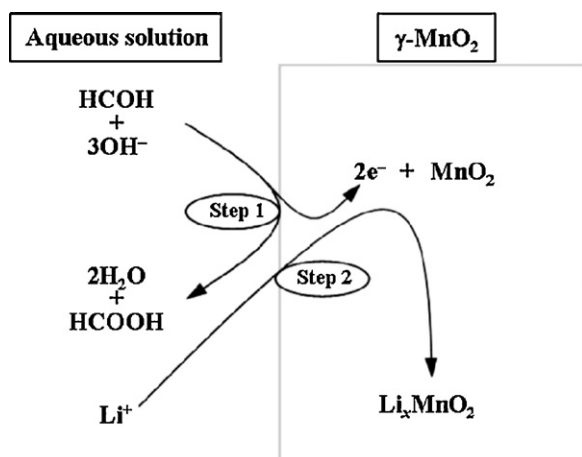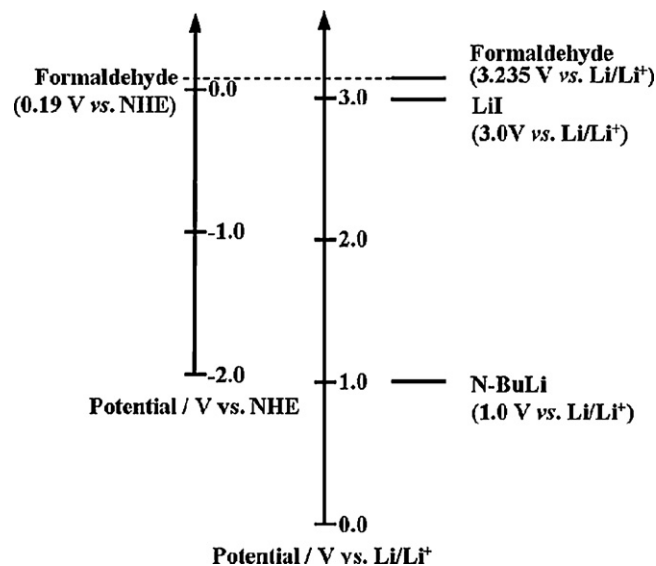
Fig. 6. Comparison of redox potential for the different reducing agents: LiI, n-BuLi and formaldehyde.

of the aqueous media. However, the electrochemical results indicated that the depth of lithiation reached a value of $x = 0.302$ in Li_xMnO_2 for the chemically lithiated γ-MnO_2 in aqueous media.

Fig. 6 shows a comparison of redox potentials for the different reduction agents: LiI, n-BuLi, and formaldehyde. In an aqueous media, formaldehyde has a redox potential of 0.19 V versus NHE, thus giving a redox potential of 3.235 V versus Li/Li^+ ($E(Li/Li^+) = E(NHE) + 3.045$ V) [17]. Moreover, the redox potential becomes lower when the pH of the solution is increased. Compared to LiI, formaldehyde has a slightly higher redox potential, which is sufficient to reduce γ-MnO_2 and to lithiate the γ-MnO_2 at the higher potential of 3.4 V.

4. Conclusion

Chemical lithiation was examined using formaldehyde as a reducing agent in an aqueous media, and lithiated Li_xMnO_2 was synthesized using a γ-MnO_2 host material. Lithiation was optimized at a molar ratio of γ-MnO_2:LiOH:HCOH = 1:4:1, which indicated a composition of $x = 0.302$ in Li_xMnO_2, and showed a first charge capacity of 86.2 mAh/g. This depth of lithiation was lower than the lithiated sample with $x = 0.332$ in Li_xMnO_2 obtained using LiI in organic solution. Lithiation with formaldehyde in an aqueous media is a comparatively simple process, which improved the cycling characteristics of γ-MnO_2, and achieved the highest discharge capacity of 265 mAh/g. Our new lithiation reaction using aqueous media is a simple and suitable process to improve the charge–discharge capacity of manganese dioxides, previously reported only 160 mAh/g for non-treated γ-MnO_2. The capacity obtained by the reaction is extremely high compare with the conventional lithium cathode materials such as lithium cobalt oxides (150 mAh/g). The new reaction process is applicable for other positive electrode materials containing protons, which is easily introduced into the structures by exchange reactions between lithium and proton even for lithium containing cathode materials.

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Fig. 5. Schematic drawing of the lithiation mechanism in an aqueous media using a formaldehyde reducing agent.

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