

Optimization of synthesis condition and electrode fabrication for spinel LiMn_2O_4 cathode

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Received 23 November 2001; received in revised form 18 January 2002; accepted 18 January 2002

Abstract

We used cyclic voltammetry (CV) and galvanostatic cycling test to optimize the synthesis condition and electrode composition for spinel LiMn_2O_4 cathode. Based on a synthetic approach of solid reaction, the most appropriate Li–Mn source for the synthesis of LiMn_2O_4 was found to be LiOH/MnO_2 and the optimum synthesis condition was to react at 750°C in air for 18 h. The LiMn_2O_4 such obtained has an initial specific capacity of 120–130 mAh/g between 3.5 and 4.2 V. In the electrode films, the carbon that was used as a conducting agent significantly affects performance of the LiMn_2O_4 electrode. Among the carbons examined in this work, we found that carbon black from Alfa Aesar was a better conducting agent and its appropriate content was around 10% in the LiMn_2O_4 electrode. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Spinel LiMn_2O_4 ; Cyclic voltammetry; Capacity fading; Carbon black; Li-ion battery

1. Introduction

High demand for larger lithium-ion battery applications such as hybrid electric vehicles (HEV) and electric vehicles (EV) has intensified the search for lower cost, safer, and less toxic cathode materials. To address these issues, much research has focused on the development of spinel LiMn_2O_4 cathode material [1–3]. Drawbacks of the LiMn_2O_4 that have been reported include: (i) irreversible capacity loss upon an over-discharge below 3.5 V in relation to a Jahn–Teller distortion [4], (ii) capacity loss associated with the dissolution of manganese ions (Mn^{3+}) into electrolyte, especially in the presence of acids such as HF that exists in the LiPF_6 -based electrolytes [5,6], (iii) capacity loss due to structural degradation during lithiation and delithiation cycle [7], and (iv) relatively high self-discharge rate as observed during storage [8,9]. Therefore, much effort was devoted previously to resolving these problems such as stabilization of spinel structure by doping cation [10] or anion [11] into LiMn_2O_4 structure. Synthesis approaches of the spinel LiMn_2O_4 are various, including solid reaction [1–3], sol–gel reaction [12,13], and Pechini process [14]. However, specific capacity of the LiMn_2O_4 seems to be independent of the synthesis approaches, which typically is around 120 mAh/g between 3.5 and 4.3 V. Compared to sol–gel and Pechini approaches, in which additional starting

materials and synthetic procedures are generally needed for preparation and separation of the targeted Li–Mn precursors, solid reaction is simpler and easier handled. Therefore, in this work we selected solid reaction to synthesize spinel LiMn_2O_4 . Synthesis conditions of the spinel LiMn_2O_4 will be optimized in the terms of Li–Mn source, reaction temperature and time, and the effect of carbon conducting agents on the performance of the LiMn_2O_4 will also be discussed.

2. Experimental

All starting materials for the synthesis of LiMn_2O_4 were purchased from Aldrich. Detailed conditions of the synthesis will be described in Section 3. A general procedure is as follows. A 2:1 (mol) stoichiometric mixture of Mn and Li starting materials was ball-milled for 16 h, followed by solid reaction in a Lindberg furnace (general signal). After reacting at a certain temperature in air for a desirable period, the mixture was allowed to cool naturally by turning off the electric power of the furnace. The resulted solids were ground and sieved through a 200-mesh sieve. According to the literature [1–3], the LiMn_2O_4 such obtained is of a spinel structure. No structural characterization was performed in this work.

Electrode films were made by mixing of LiMn_2O_4 powder and conducting agent (carbon) with 1 wt.% of Teflon (Du Pont) binder, and then pressing the resultant paste onto an

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aluminum foil. Composition of the electrode films will be specified in Section 3. Size of the electrodes was 0.64 cm^2 ($8 \text{ mm} \times 8 \text{ mm}$) and the thickness was $20 \pm 5 \mu\text{m}$ with a LiMn_2O_4 loading of 3–4 mg. The electrodes were dried at 120°C under vacuum overnight before use. All operations (electrolyte preparation, cell assembly, and electrochemical test) were carried out in an argon-filled glove box. Salts LiClO_4 (99.99%, Aldrich) and LiPF_6 (Stella Chemifa Corporation), and solvents ethylene carbonate (EC, 99.95%, Grant Chemical), dimethoxyethane (DME, 99.99%, EM Industries Inc.), and EMC (99.9%, EM Industries Inc.), were used as received. In most cases, the electrolyte was 1 M LiClO_4 solution in 1:1 (w/w) EC/DME mixed solvent unless specified otherwise. A three-electrode cell was used for all electrochemical measurements, in which Li foils were served as a counter electrode and a reference electrode, respectively. An EG&G PAR Potentiostat/Galvanostat Model 273A controlled by a personal computer was used to conduct cyclic voltammetry (CV). Scanning rate for cyclic voltammetry was at 0.1 mV/s. For cycling test, Li/ LiMn_2O_4 cell with an electrode area of 1.27 cm^2 was assembled by using Rayovac's BR2335 button cell hardware and a 1 M LiPF_6 3:7 (w/w) EC/EMC electrolyte. The cell was cycled on a Maccor Series 4000 tester at a current density of 0.5 mA/cm^2 between 3.6 and 4.3 V.

3. Results and discussion

3.1. Effect of Li–Mn sources

We first compared the data of discharge capacity and cycling efficiency, obtained from CV and galvanostatic cycling test, respectively, of the LiMn_2O_4 electrode, and found that they were in good consistence as scan rate of the CV was 0.1 mV/s or slower. Therefore, we herein used CV to evaluate the effect of Li–Mn sources on the performance of LiMn_2O_4 by fixing reaction temperature at 780°C and reaction time for 25 h. In this experiment, composition of the electrodes was 90% LiMn_2O_4 , 9% carbon black and 1% Teflon. Usually, Coulombic efficiency (CE) for the first cycle of the LiMn_2O_4 electrode is relatively low (80–85%) and gradually goes up in the subsequently cycles. This is mainly ascribed to the formation of surface layer, or called solid electrolyte interface (SEI) film, on LiMn_2O_4 electrode [15,16], and to the decomposition of electrolyte solvents probably catalyzed by the fresh surface of conducting carbon [6]. Therefore, all CVs in this work were selected from the second cycle. Table 1 summarizes discharge capacity and CE of the LiMn_2O_4 materials that were made from different starting materials. We found that all these LiMn_2O_4 materials have a CE of more than 90%, with negligible dependence on the Li–Mn sources. However, specific capacity of the LiMn_2O_4 significantly varies with the Li/Mn sources. Under the synthesis conditions described, the LiMn_2O_4 made from either $\text{LiOH/Mn}_2\text{O}_3$ or LiOH/MnO_2

Table 1

Comparison of the LiMn_2O_4 materials made from different Li–Mn sources

Li–Mn source	Discharge capacity (mAh/g)	Coulombic efficiency (%)
$\text{LiOH/Mn}_2\text{O}_3$	100	97
LiOH/MnO_2	122	96
LiOH/MnCO_3	71	95
$\text{LiOH/Mn}(\text{CH}_3\text{COO})_2$	68	93
$\text{Li}_2\text{CO}_3/\text{Mn}_2\text{O}_3$	82	94
$\text{Li}_2\text{CO}_3/\text{MnCO}_3$	85	97

Note: the Li–Mn mixture was reacted at 780°C for 25 h and the electrode was composed of 90% LiMn_2O_4 , 9% carbon black and 1% Teflon. The data were recorded from the CV of the second cycle at 0.1 mV/s.

exhibits a reasonable capacity ($>100 \text{ mAh/g}$). While other four Li–Mn sources listed in Table 1 lead to a low capacity ($<90 \text{ mAh/g}$). We noticed that, of the other four Li–Mn starting materials, at least one such as MnCO_3 , $\text{Mn}(\text{CH}_3\text{COO})_2$, or Li_2CO_3 , could release CO_2 during its thermal decomposition. However, it is uncertain whether the low capacity observed here is in relation to the formation of CO_2 . Now, we focused our attention on these two LiMn_2O_4 materials starting from $\text{LiOH/Mn}_2\text{O}_3$ and LiOH/MnO_2 mixture, respectively. Their CVs are shown in Fig. 1, which indicates two pairs of reversible oxidization and reduction current peaks at 4.0 and 4.1 V, respectively with a CE higher than 96%. It is known that these two pairs of current peaks originate from two reversible phase–phase transitions of the LiMn_2O_4 during lithiation and delithiation processes, $\text{LiMn}_2\text{O}_4 \leftrightarrow \text{Li}_{0.5}\text{Mn}_2\text{O}_4 \leftrightarrow \lambda\text{-MnO}_2$ [17]. Larger capacity (122 mAh/g) of the LiMn_2O_4 obtained from LiOH/MnO_2

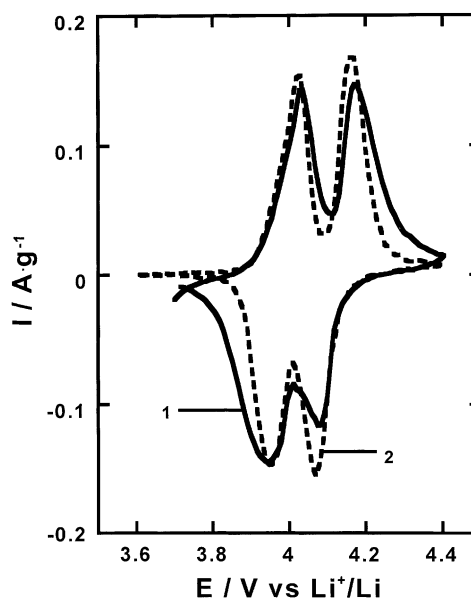


Fig. 1. Cyclic voltammogram of the LiMn_2O_4 made by heating Li–Mn starting materials at 780°C for 25 h. Electrode composition was 90 LiMn_2O_4 /9 carbon black/1 Teflon and scan rate was 0.1 mV/s ((1) $\text{LiOH/Mn}_2\text{O}_3$ and (2) LiOH/MnO_2).

mixture suggests that LiOH and MnO₂ would be a better combination for the synthesis of spinel LiMn₂O₄.

3.2. Effect of reaction temperature

It is known that reaction temperature is important in determining performance of the LiMn₂O₄. Therefore, we choose LiOH/Mn₂O₃ and LiOH/MnO₂ starting materials to examine the effect of reaction temperature. In this experiment, we first prepared a large amount of reacting mixture and then split it into several equal portions, followed by heating them for a fixed time of 25 h at various temperatures in 50 °C increments from 400 to 950 °C. Fig. 2 selectively

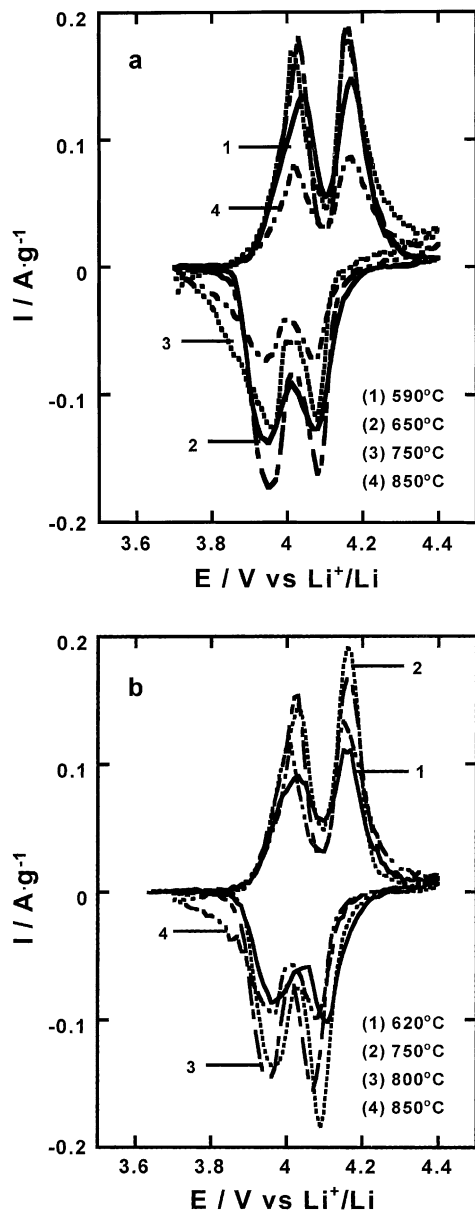


Fig. 2. Cyclic voltammogram of the LiMn₂O₄ made by heating Li–Mn starting materials at various temperatures for 25 h. Electrode composition was 90 LiMn₂O₄/9 carbon black/1 Teflon and scan rate was 0.1 mV/s ((a) LiOH/Mn₂O₃ and (b) LiOH/MnO₂).

plots CVs of the LiMn₂O₄ thus made in an electrode composition of 90 LiMn₂O₄/9 carbon black/1 Teflon. It appears that the optimum reaction temperature for the synthesis of the LiMn₂O₄ is related to the Li–Mn sources materials. Fig. 2 indicates that the optimum reaction temperature for LiOH/Mn₂O₃ mixture is 650 °C and that for LiOH/MnO₂ is 750 °C. Similar results were also obtained from galvanostatic cycling tests. In general, high temperature will increase crystallinity and grain size of the LiMn₂O₄, both of which result in a decline of the capacity [18]. Furthermore, the LiMn₂O₄ will be thermally decomposed at high temperatures (for example LiMn₂O₄ → O₂ + LiMn₂O_{4-δ}), which may cause degradation of the spinel structure and lead to loss of the capacity [19]. On the contrary, low temperature is unfavorable for increasing capacity as it may cause an incomplete reaction between starting materials. As a result of these two reverse trends, an optimum reaction temperature is formed. It is determined that initial specific capacity of the LiMn₂O₄ made at the optimum reaction temperature from LiOH/Mn₂O₃ and LiOH/MnO₂, respectively is in a range of 120–130 mAh/g between 3.5 and 4.3 V.

3.3. Effect of reaction time

Based on the results described, we choose LiOH/MnO₂ starting materials to study the effect of reaction time on the performance of LiMn₂O₄. Fig. 3 compares CVs of the LiMn₂O₄ prepared by reacting a LiOH/MnO₂ mixture at 750 °C for different times. It is calculated that, when being shorter than 25 h, the reaction time hardly affects capacity of the LiMn₂O₄. Comparison of CV 2 and CV 3 in Fig. 3

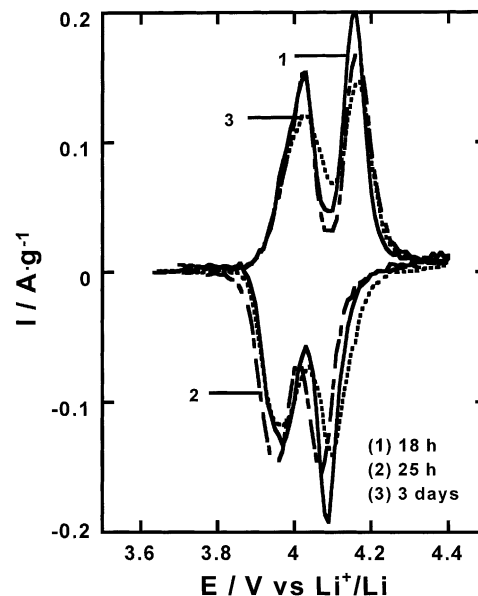


Fig. 3. Effect of the reaction time on cyclic voltammogram of the LiMn₂O₄ made by heating LiOH/MnO₂ mixture at 750 °C for different times. Electrode composition was 90 LiMn₂O₄/9 carbon black/1 Teflon and scan rate was 0.1 mV/s.

indicates that the capacity is decreased as the reaction time is further extended. This observation is likely associated with the change in crystallinity and grain size of the LiMn_2O_4 . At the reaction temperature, the grain size gradually grows with the time, which increases diffusion length of the lithium ions within LiMn_2O_4 particles and results in a decrease of the capacity.

3.4. Comparison of conducting agents in LiMn_2O_4 electrode

To retain sufficiently electronic conductivity of the electrode, it is necessary to mix appropriate amount of conducting agents (carbon powder) into the electrode film. There are number of carbons commercially available for this purpose and their conductivity and specific surface area vary from one carbon to another carbon. To select an appropriate carbon for fabrication of the LiMn_2O_4 electrode, we comparatively evaluated five carbons by fixing electrode composition as 90% LiMn_2O_4 , 9% carbon and 1% Teflon. Brief physical properties of these five carbons together with the initial capacities and CEs of the LiMn_2O_4 electrodes using them are summarized in Table 2, in which the initial capacity and CE data were recorded from the second cycle of a chronopotentiometry measurement at 0.5 mA/cm^2 between 3.6 and 4.3 V. It is seen that these five carbons have comparable particle size (10–35 nm in diameter) but much different surface area. Of them, graphite has the lowest specific surface area ($11 \text{ m}^2/\text{g}$) and relatively high gravity density. Table 2 shows that the LiMn_2O_4 electrode using graphite has the lowest capacity of 85 mAh/g. This means that 9 wt.% of graphite is not enough to electronically bridge LiMn_2O_4 particles. Carbon aerogel is very porous (porosity > 50%, pores diameter < 100 nm) and black pearl has the highest specific surface area ($1500 \text{ m}^2/\text{g}$). As a result, capacities of the LiMn_2O_4 electrodes using these two carbons are not satisfactory (<110 mAh/g) and fade rapidly with the cycle number (not presented here, which was observed after many repeated cycles). According to the early literature [6], fresh surface of the conducting carbons could catalyze decomposition of electrolyte solvents and higher surface area generally causes low CE. Therefore, the rapid capacity fading with carbon aerogel and black pearl is probably associated with their high surface area. XE-2 and carbon black, which are highly conductive

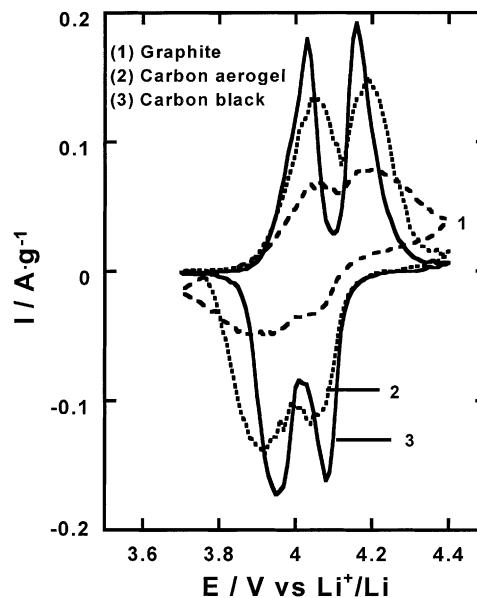


Fig. 4. Effect of the carbon type on cyclic voltammogram of the LiMn_2O_4 electrodes. Electrode composition was 90 LiMn_2O_4 /9 carbon black/1 Teflon and scan rate was 0.1 mV/s .

and have relatively low specific surface area, provide reasonable initial capacity of >120 mAh/g. However, it is seen that, with an increase of the cycle number, the LiMn_2O_4 electrode using XE-2 fades its capacity faster than that using carbon black.

Fig. 4 selectively plots CVs of the LiMn_2O_4 electrodes using different carbons. Two pairs of oxidation and reduction current peaks of the LiMn_2O_4 electrode using graphite could not be clearly distinguished, and furthermore the current peaks were small and broad. This is a characteristic of the high polarization, caused by low electronic conductivity of the electrode. In contrast, the current peaks of the electrode using carbon black were sharp and distinctly separated, which corresponds to a high capacity (122 mAh/g) and high CE (96%). These CVs result are in good agreement with those obtained from the chronopotentiometry test as mentioned.

3.5. Optimization of carbon content

While providing electronic conductivity, carbon black brings some negative effects into the electrode. First, it

Table 2

Brief physical properties of the carbons used in the electrode and initial capacities of the LiMn_2O_4 electrodes

Carbon	Supplier	Surface area (m^2/g)	Particle size (nm)	Capacity (mAh/g)	Efficiency (%)
Graphite	Aldrich	11	33	85	89
Carbon aerogel	Ocellus	400	–	108	88
Black pearl	Cabot	1500	12	101	93
XE-2	Dugussa	162	35	124	96
Carbon black	Alfa Aesar	80	35	128	94

Note: specific surface area and particle size were cited from MSDS of the suppliers.

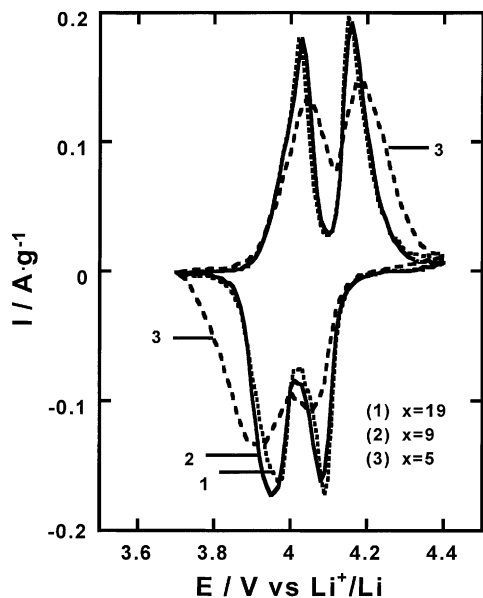


Fig. 5. Cyclic voltammogram of the LiMn_2O_4 electrodes containing different amount of carbon black. Electrode composition was $(99-x)\text{LiMn}_2\text{O}_4/x$ carbon black/1 Teflon and scan rate was 0.1 mV/s.

occupies the limited volume of the electrode within the battery. Second, it potentially catalyzes decomposition of the electrolyte solvents due to some active sites on its fresh surface during the initial few cycles. Therefore, it is important to find the optimum content of carbon black in the LiMn_2O_4 electrode. Fig. 5 compares CVs of the LiMn_2O_4 electrodes containing different carbon content. The LiMn_2O_4 electrodes having 9 and 19%, respectively of carbon black display nearly same CV profile, which corresponds to a similar capacity. This result shows that 9% of carbon black is already enough to maintain electronic conductivity of the composite electrode as required for the operation of the LiMn_2O_4 electrode. Excess carbons cannot increase utilization of the active cathode materials but reduce energy density of the battery by occupying more volume of the electrode. As the content of carbon black is lowered to 5%, the oxidation and reduction current peaks of the LiMn_2O_4 electrode become lower. This reveals that 5% of carbon black could not be enough to electronically connect LiMn_2O_4 particles.

Fig. 6 illustrates voltage–composition curves of the $\text{Li}/\text{LiMn}_2\text{O}_4$ cells containing different content of carbon black, which was recorded at 0.5 mA/cm² during the fourth cycle. One may find that the LiMn_2O_4 electrode containing 5% of carbon black has slightly higher charge voltage and slightly lower discharge voltage. This is an indicative of high polarization, which here must be caused by low electronic conductivity of the electrode film. As the content of carbon black increases to 9% or higher, electronic conductivity of the electrode film becomes high enough to ensure electrode reaction. Therefore, these two electrodes containing 9 and 19%, respectively, of carbon black have very similar voltage–composition correlation and show a similar discharge

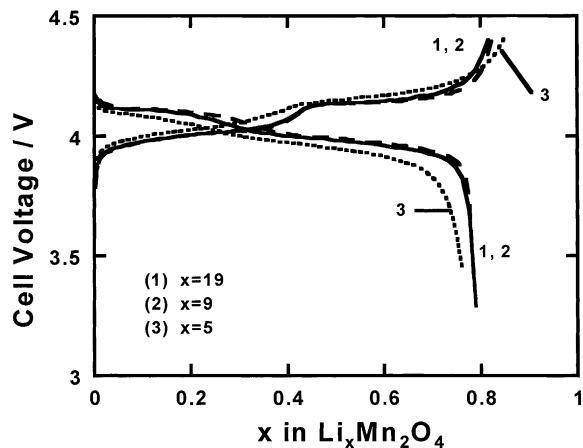


Fig. 6. Voltage–composition curves of the LiMn_2O_4 electrodes containing different amount of carbon black. Electrode composition was $(99-x)\text{LiMn}_2\text{O}_4/x$ carbon black/1 Teflon and current density was 0.5 mA/cm².

capacity. This observation is in accordance with the CV results as described.

The electrolytes based on LiPF_6 , EC, and linear carbonate such as dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethylmethyl carbonate (EMC) are most widely used in the state-of-the-art lithium-ion batteries mainly because these electrolytes passivate Al (current collector of the cathode) well [20] and help form a stable SEI film on the graphite electrode [21]. Therefore, we here used 1 M LiPF_6 3:7 EC/EMC electrolyte to evaluate the optimized LiMn_2O_4 electrode. Fig. 7 displays charge and discharge capacities of the $\text{Li}/\text{LiMn}_2\text{O}_4$ cell with this electrolyte, which were obtained by cycling the cell at 0.5 mA/cm² between 3.6 and 4.3 V. It is observed from Fig. 7 that the initial few cycles have rather fast capacity fading. This is likely due to the relatively low CE (about 95%) of the initial few cycles, which gradually increased to near 100% with an increase of the cycle number. The low CE of the initial few cycles is believed to be associated with these two known

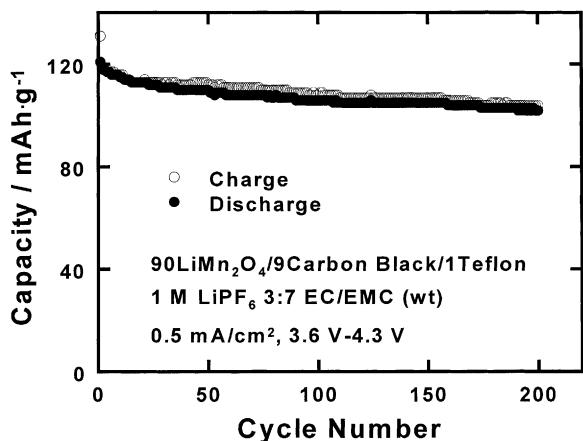


Fig. 7. Charge and discharge capacities of the LiMn_2O_4 , which were obtained by cycling $\text{Li}/\text{LiMn}_2\text{O}_4$ button cell at 0.5 mA/cm² between 3.6 and 4.3 V. Electrode composition was 90 $\text{LiMn}_2\text{O}_4/9$ carbon black/1 Teflon and electrolyte was 1 M LiPF_6 3:7 (w/w) EC/EMC.

phenomena of the LiMn_2O_4 electrodes: formation of surface layer on the LiMn_2O_4 electrode [15,16] and catalytic decomposition of electrolyte solvents on the fresh surface of conducting carbons [6]. Because of intrinsic features of the spinel LiMn_2O_4 as described in Section 1 [4–9], both charge and discharge capacities of the cell are gradually faded with the cycling number although the CE remains at $\sim 100\%$.

4. Conclusion

We empirically evaluated six couples of Li–Mn starting materials for the synthesis of spinel LiMn_2O_4 , of which LiOH/MnO₂ couple was found to be the most appropriate. The optimized synthesis condition for this couple is to react at 750 °C in air for 18 h. The resulting LiMn_2O_4 has an initial specific capacity of 120–130 mAh/g. For fabrication of the electrode films, the type and content of the conducting carbons are very important for the operation of the LiMn_2O_4 active materials. We observed that appropriate content of the carbon black in the LiMn_2O_4 electrode was around 10%.

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