

Influence of carbon towards improved lithium storage properties of $\text{Li}_2\text{MnSiO}_4$ cathodesV. Aravindan,^{abc} K. Karthikeyan,^b K. S. Kang,^d W. S. Yoon,^e W. S. Kim^f and Y. S. Lee^{*b}

Received 14th October 2010, Accepted 16th December 2010

DOI: 10.1039/c0jm03471a

Superior lithium storage in $\text{Li}_2\text{MnSiO}_4$ cathodes was observed by altering carbon content during the formulation of electrodes. Initially, $\text{Li}_2\text{MnSiO}_4$ was prepared by a conventional solid-state reaction at 900 °C under Ar flow with a fixed amount of adipic acid, which acts as a gelating agent during synthesis. The phase formation was confirmed through powder X-ray diffraction measurements. Scanning electron microscope pictures indicate the particulate morphology of synthesized $\text{Li}_2\text{MnSiO}_4$ particles. Various compositions of electrodes were formulated using the conducting carbon (ketjen black) from 3 to 11 mg along with active material. All the fabricated electrodes were cycled in a $\text{Li}/\text{Li}_2\text{MnSiO}_4$ cell configuration to evaluate its lithium storage performance at 0.05 C rate. Among the electrodes, 42% carbon in the composite electrode exhibited a very stable discharge behaviour $\sim 140 \text{ mA h g}^{-1}$ for 40 cycles at room temperature. Such storage performance was ascribed to the improved electronic conductivity of $\text{Li}_2\text{MnSiO}_4$ electrodes by incorporating carbon. This improvement was supported by electrochemical impedance spectroscopy measurements. Rate performance studies were also conducted and presented in the manuscript.

1 Introduction

Lithium orthosilicate, Li_2MSiO_4 ($\text{M} = \text{Fe}, \text{Mn}, \text{Co}$ and Ni), based cathodes were conquered in recent past due to their overwhelming advantages like high theoretical capacity ($>330 \text{ mA h g}^{-1}$ which is possible while extracting more than one Li^+ ion per formula unit), high thermal stability through strong Si–O bonding, safety issues, cost effective, environmental friendliness and ease to synthesize.^{1–15} At the same time, orthosilicate groups had been suffering from some

disadvantages like inherent conducting properties, for instance $\text{Li}_2\text{FeSiO}_4$ ($\sim 10^{-12} \text{ S cm}^{-1}$) and $\text{Li}_2\text{MnSiO}_4$ ($\sim 10^{-14} \text{ S cm}^{-1}$) when compared to other commonly available candidates like LiCoO_2 ($\sim 10^{-4} \text{ S cm}^{-1}$), LiNiO_2 ($\sim 10^{-3} \text{ S cm}^{-1}$), LiMn_2O_4 ($\sim 10^{-6} \text{ S cm}^{-1}$), LiFePO_4 ($\sim 10^{-9} \text{ S cm}^{-1}$) and LiMnPO_4 ($\sim 10^{-10} \text{ S cm}^{-1}$) at room temperature. The poor conductivity issue restricts the possibility of using orthosilicates in practical cells. The electronic conductivities of orthosilicates are three to five folds magnitude lower than the polyanionic framework LiFePO_4 .⁸ Whereas in the case of LiFePO_4 , poor conductivity problem has been circumvented by several approaches viz. cation doping, surface modification/conducting coating preferably with carbon, and creating deficient and rich phases of lithium.¹⁶ Cationic doping of either Li or Fe sites provided the conductivity enhancement about six to seven folds of magnitude than the pristine LiFePO_4 .¹⁷ Creating deficient or rich phases also yielded conductivity enhancement to about six to seven folds magnitude, but the resultant material appeared with some secondary phase materials either Li_3PO_4 or $\text{Fe}_2\text{P}_2\text{O}_7$.^{18–20} In the case of carbon coating, it not only enhanced the conductivity which also supports the faster diffusion of lithium ions into the host, but also facilitated good contact between the neighboring particles and reduction of the polarization.²¹ A similar kind of approach is desperately needed to overcome the insulating behaviour of polyanion framework orthosilicate groups. The choice of $\text{Li}_2\text{MnSiO}_4$ in the place of $\text{Li}_2\text{FeSiO}_4$ is because of its cost effective nature, environmental benign quality of Mn (similar to Fe) and higher cell voltage due to the possible oxidation of $\text{Mn}^{3+}/\text{Mn}^{4+}$ than $\text{Fe}^{2+}/\text{Fe}^{3+}$ couple.^{4–15}

To date, very few reports could be traced for the electrochemical characterization of $\text{Li}_2\text{MnSiO}_4$ materials due to their tendency to become amorphous during cycling.^{4–15} Most of the studies reported the usage of either solid state or sol–gel route followed by coating of carbon with milling. Nevertheless, those two synthesis routes are the appropriate techniques for mass production in the industrial scale. Dominko *et al.*⁷ first reported the synthesis and electrochemical performance of $\text{Li}_2\text{MnSiO}_4$ by modified Pechini sol–gel technique. In this process only 0.6 Li per formula unit could be extracted in the first cycle and 0.3 Li can be reversibly extracted during the 5th cycle at C/30 rate. Li *et al.*¹⁵ also reported the solution phase sol–gel route by using tetraethoxysilane as source material for silicon and practically demonstrated the possibility of extracting more than one Li per formula unit for few cycles (1.25 Li in 1st cycle and 0.85 Li per formula unit at 10th cycle with extremely low current density of 5 mA g^{-1}). Belharouak *et al.*¹⁴ reported the sol–gel synthesis using $\text{Li}_2\text{MnSiO}_4$,

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but failed to control the morphologies, which leads to aggregation of the resultant material. Further, ball milling was employed for carbon coating after the aggregation takes place, which in turn provides the heterogeneous coating. Also 0.81 Li per formula unit was extracted in the first cycle and 0.69 Li could be reversibly cycled at the end of the 15th cycle with a low current density of 10 mA g⁻¹, and it had also severely experienced capacity fading. Liu *et al.*¹⁰ reported the synthesis of Li₂MnSiO₄/C composites, but the cycle life of the cell was limited to 10.

So far, the reported synthesis routes for Li₂MnSiO₄ with or without carbon coating were facing the severe capacity fade during cycling which is due to the poor structural stability during cycling and inherent electronic conductivity.^{4–15} Apart from the structural stability, carbon coating alone is not sufficient to overcome the conducting issue of silicates ($\sim 10^{-14}$ S cm⁻¹), thus a large amount of carbon is necessary to alleviate this problem. In this background, an attempt has been made to stabilize the structural stability during cycling and improve the electrochemical performance of Li₂MnSiO₄ particles during cycling by altering the composition of conducting carbon during the formulation of electrode.

2 Materials and methods

Analytical grade LiOH·H₂O (Junsei 95%), MnCO₃ (Aldrich, USA, 99.9%) and SiO₂ (Aldrich, USA, 99.9%) were used as the starting materials to synthesize Li₂MnSiO₄ powders through solid state reaction method. An adipic acid (Aldrich, USA, 99%) was used as the gelating material during the synthesis and its concentration was fixed at 0.2 mol (based on the optimization). First, the stoichiometric amounts of the starting materials were fine ground using mortar and pestle with adipic acid (AA) and fired at 400 °C for 4 h in air. Then, this intermediate product was again fine ground using a mortar and placed into a tubular furnace at 900 °C for 12 h under an Ar atmosphere to get the resultant product.

Powder X-ray diffraction (XRD, Rint 1000, Rigaku, Japan) measurements were performed to study the structural properties of Li₂MnSiO₄ with Cu-K α as the radiation source. Scanning electron microscopic (SEM, S-4700, Hitachi, Japan) study was conducted to analyze the morphological features of the material synthesized. Electrochemical impedance spectroscopy (EIS) was carried out using Bio logic, USA electrochemical workstation with two electrode setup. The composite cathodes were fabricated using different amounts of active material (20, 18, 16 and 12 mg) and ketjen black (KB) (3, 5, 7 and 11 mg) with a fixed amount of conductive binder (3 mg of Teflonized acetylene black, TAB). Then, it was pressed on a 200 mm² stainless steel mesh which served as the current collector under a pressure of 300 kg cm⁻² and dried at 130 °C for 5 h in an oven. The coin cell (CR 2032) was made of a composite cathode and the metallic lithium as the anode, which was separated by a porous polypropylene film (Celgard 3401). The mixture of 1 M LiPF₆-ethylene carbonate (EC)/dimethyl carbonate (DMC) (1 : 1 v/v, Techno Semichem Co., Ltd, Korea) was used as the electrolyte. The galvanostatic cycling studies were conducted between 1.5 and 4.8 V at 0.05 to 1 C in room temperature conditions.

3 Results and discussion

A typical XRD pattern of Li₂MnSiO₄ particle is given in Fig. 1. In the diffractogram, the appearance of well defined sharp intense satellite

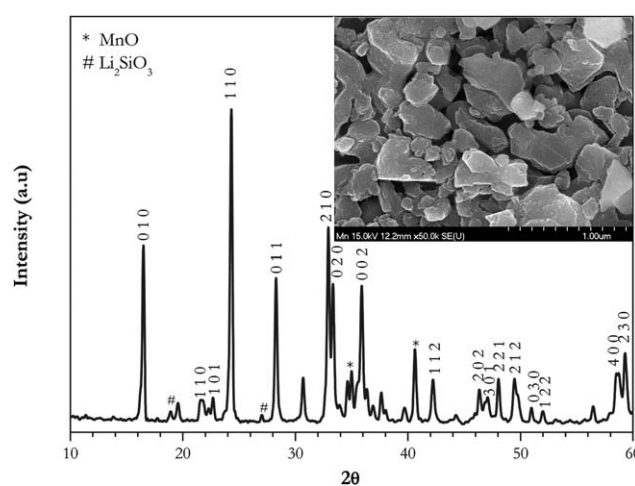


Fig. 1 Powder X-ray diffraction pattern of Li₂MnSiO₄ particles synthesized by solid state reaction method under Ar flow at 900 °C. Inset showed the scanning electron microscopic pictures of the synthesized Li₂MnSiO₄ powder.

peaks corresponds to the perfect crystalline nature of the synthesized Li₂MnSiO₄. There are no reflections corresponding to the starting materials used for this synthesis. Several authors claimed the existence of three kinds of polymorphs for Li₂MnSiO₄ which comprises *Pnm*2₁, *Pnmb* and *P2*₁/*n* space groups.²² For example, Dominko *et al.*²³ reported the Li₂MnSiO₄ having *Pnmb* space group at 900 °C (all the synthesis routes, solid-state, sol-gel, hydrothermal, *etc.*) and Politaev *et al.*²⁴ reported the existence of *P2*₁/*n* space group by solid-state reactions at 750–1150 °C. Very recently, Belharouak *et al.*¹⁴ also claimed the existence of *Pnm*2₁ space group at 800 °C by sol-gel route. In the present case, the crystalline peaks are indicative of the orthorhombic structure, which is analogous to the Li₃PO₄ pattern and exhibit the *Pnm*2₁ space group.^{1,22} The Li₂MnSiO₄ can be isostructural to certain forms of Li₃PO₄: Mn²⁺ ions are present within a [SiO₄] anionic silicate network that replaces the [PO₄] anionic phosphate network, and two Li ions are available in 3D dimensional channels. The impurity phases like MnO and less amount of Li₂SiO₃ are also unavoidably present in all the phases prepared.^{4–15,23,24} Dompablo *et al.*¹³ have succeeded to prepare the Li₂MnSiO₄ material in the absence of MnO under various pressure conditions. Nevertheless, the formation of Mn₂SiO₃ could be inevitable under such abnormal pressure conditions. In addition to that the presence of Mn₂SiO₃ phase is much prevailing than that of MnO in the conventional synthesis in either solid state or sol-gel.^{7,8,10} Based on the previous reports and present study it is confirmed that the preparation of phase pure Li₂MnSiO₄ is a complicated one.

SEM analysis has been carried out to study surface morphology of Li₂MnSiO₄ particles synthesized at 900 °C with 0.2 mol of adipic acid which is given as an inset in Fig. 1. The purpose of using gelating agent, particularly carboxylic (–COOH–) functional groups containing materials, for example carboxylic acids which act as the capping agent to prevent aggregation during synthesis, but still some sort of aggregation could be seen in the SEM pictures. It is well known that tailoring the particle morphology in solid state synthesis is quite complicated because of the experiment being conducted at high temperature, which results in irregular particulate morphology. Furthermore, the appearance of small-sized particles was also observed along with the larger-sized particles.

The electrochemical performance of the $\text{Li}_2\text{MnSiO}_4$ electrodes was carried out against metallic lithium in the presence of 1 M LiPF_6 in EC and DMC at room temperature between 1.5 and 4.8 V. The typical initial discharge curves of $\text{Li}/\text{Li}_2\text{MnSiO}_4$ cells comprising different carbon contents which were cycled at 0.05 C and the results are given in Fig. 2. The electrodes comprising 3, 5, 7 and 11 mg of carbon along with $\text{Li}_2\text{MnSiO}_4$ and the cells presented the initial discharge capacities of 79, 78, 113 and 160 mA h g^{-1} (corresponds to 0.48, 0.47, 0.68 and 0.97 Li^+ ions per formula unit) respectively. Increasing the carbon content from 3 to 11 mg provides drastic improvements in the electrochemical behavior of composite $\text{Li}_2\text{MnSiO}_4$ electrodes. Generally, in our group, the electrodes were prepared using 20 mg of active material, 3 mg of carbon content (KB) and 3 mg of binder (TAB, which comprises 2% of acetylene black and 1% of graphite) for the electrochemical studies.^{20,25,26} So, based on the total amount, we alter the active materials and carbon content according

to the fixed proportion during formulation of electrode or making composite electrode. Further, it is very difficult to make the composite electrodes comprising beyond 11 mg carbon content due to its volume effect. It is very clear to see that the higher carbon content containing electrode exhibited superior performance than other compositions compared. Fig. 2b represents the discharge capacity profile with cycle number. It is quite obvious that incorporation of higher amount of carbon content during formulation of electrode translates very stable cycle behavior, due to the enhancement of electronic conductivity. In other words, the insulating behavior of $\text{Li}_2\text{MnSiO}_4$ has been circumvented and converted as good electronically conducting material by inducting the carbon during fabrication of the electrode (validated through electrochemical impedance measurements). The inclusion of carbon not only provides the improvement in conductivity profile, but also supports the faster diffusion of Li^+ ions during charge and discharge process.^{21,27} The electrodes containing 3, 5, 7 and 11 mg of carbon along with the active material ($\text{Li}_2\text{MnSiO}_4$) demonstrated the discharge capacities of 25, 36, 60 and 140 mA h g^{-1} at the 40th cycle and corresponds to the reversible insertion of 0.15, 0.22, 0.36 and 0.85 Li^+ ions per formula unit respectively. Further, it could be seen that 42% carbon containing electrodes experienced meagre amount of capacity fade during cycling when compared to other counterparts. Conversely, from the industrial point of view, the usage of large amount of carbon in the cathodic side is not advisable for practical lithium ion cells that suppress the volumetric capacity of electrode. Meanwhile, several authors have tested and reported such polyanion framework materials using large quantity of carbon to improve the conducting properties of the material. For example, Murugan *et al.*^{28,29} tested the utilization of 50% active material (LiMnPO_4) for its poor electronic conductivity. Very recently, Oh *et al.*³⁰ also reported the electrochemical performance of $\text{LiMnPO}_4\text{-C}$ prepared by ball milling of large amount of carbon (40%) due to its insulating behaviour. In addition, during the formulation of electrode 7.5% of carbon black is also incorporated to enhance the battery performance. Kang and Ceder²¹ tested 35% of active material (LiFePO_4) for its rate capability studies. Zaghbi *et al.*³¹ employed only 33% of active materials ($\text{Li}_2\text{FeSiO}_4$) for the electrochemical measurements due to the inherent conducting properties and no cycling profiles were reported for such composition. Of late, Palomares *et al.*³² pointed out the incorporation of more carbon with active material (LiFePO_4) not only enhanced conductivity but also drastically reduced the polarization of the electrodes and which is very useful for the high current rates. Also it did not affect the electrochemical performance of the active material at any current rates tested. Here, a similar kind of strategy has been applied for the $\text{Li}_2\text{MnSiO}_4$ system. The improvement in electrochemical performance is believed due to the presence of a large amount of sp^2 hybridization (the sp^2 bonds are responsible for the conductivity enhancement). The commercially available conducting carbon promotes the faster movement electrons as well as lithium ions, whereas in the carbon coated materials comprising a less amount of sp^2 bonds provided slightly poor performance than commercial carbons comprising electrodes. Further, carbon coating alone is not capable enough to promote mere insulator ($\sim 10^{-14} \text{ S cm}^{-1}$) to a good conductor. In the present case, the binder, TAB, also comprising 1% of graphite which is having sp^2 bonds thereby enabling the support for conducting carbon resulting in the enhancement of the conductivity profile. Surprisingly, increasing the

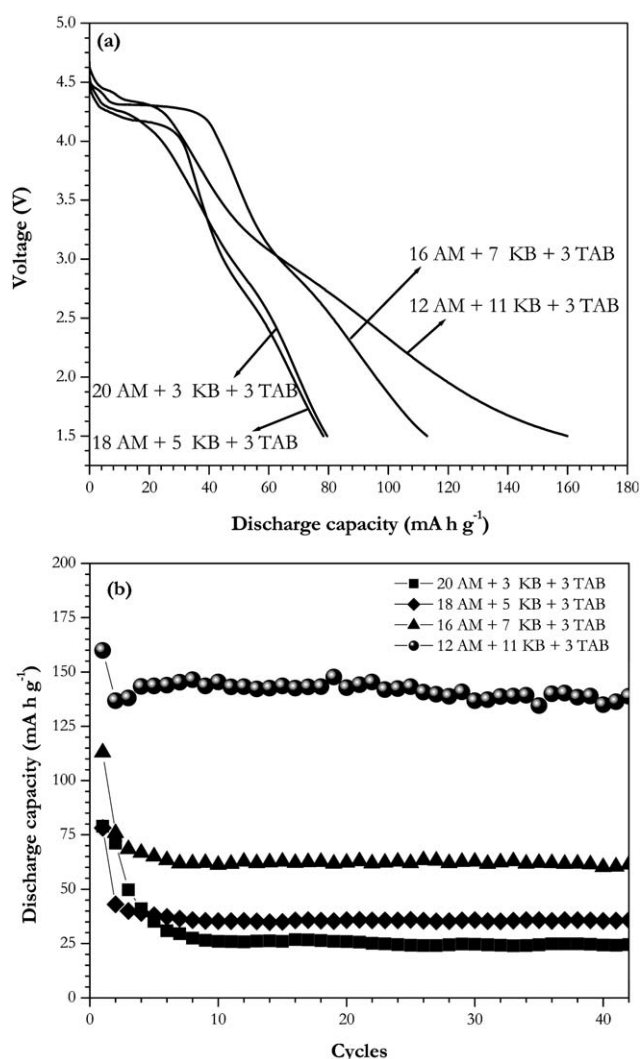


Fig. 2 Electrochemical performance of $\text{Li}/\text{Li}_2\text{MnSiO}_4$ cells at room temperature conditions, (a) initial discharge traces of $\text{Li}/\text{Li}_2\text{MnSiO}_4$ cells containing various amounts of carbon and (b) cycling profiles of $\text{Li}/\text{Li}_2\text{MnSiO}_4$ cells comprising different ratios of carbon (AM: active material ($\text{Li}_2\text{MnSiO}_4$), KB: ketjen black, TAB: tetrafluoroacetylene black).

conducting carbon not only equipped the above-mentioned issues, it also provided the retention of $\text{Li}_2\text{MnSiO}_4$ crystal structure during the cycling.

Rate capability studies were also conducted to ensure the electrochemical activity at high current densities. Fig. 3a represents the cycling profiles of 42% carbon containing electrode at various current rates from 0.05 to 1 C. The $\text{Li}/\text{Li}_2\text{MnSiO}_4$ (12 AM + 11 KB + 3 TAB) cell delivered the discharge capacity of 143, 111, 81 and 60 mA h g^{-1} , for 0.05, 0.1, 0.5 and 1 C respectively, at the end of the 25th cycle in ambient temperature. At low current rates the cells exhibited stable cycling behavior up to 25 cycles with negligible amount of capacity fade. When increasing the current rate to 0.5 C and 1 C, the cell experiencing more capacity fades than lower current rates. The stable electrochemical performances of the cells are believed to retention of crystal structure, which allows insertion and extraction of lithium ions during cycling process. However, Li *et al.*¹⁵ explained through *ex situ* XRD studies, which reveal that the crystal structure destruction occurs during cycling process. But in our case, incorporation of more amount of carbon (42%) retains the crystal structure of active material and enables improved electrochemical properties of

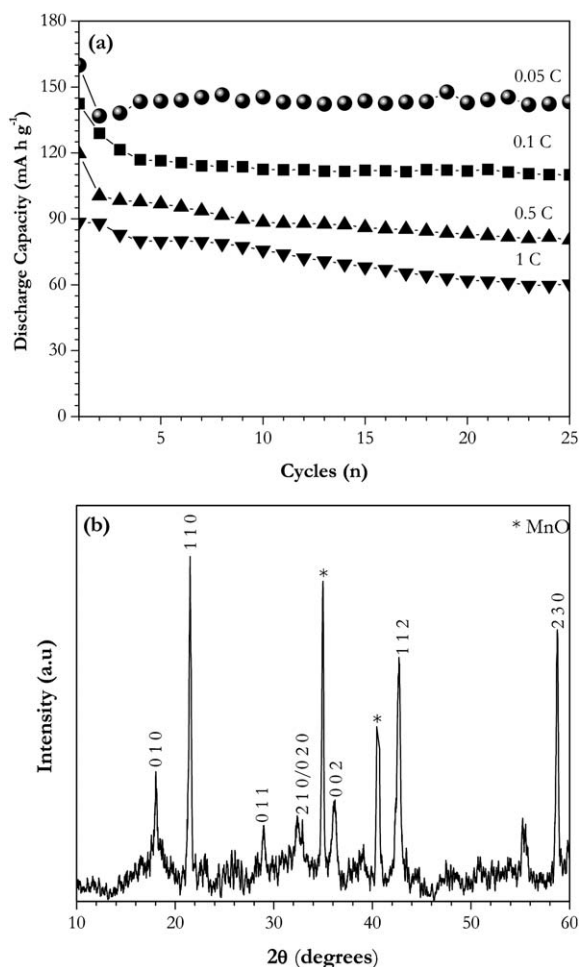


Fig. 3 (a) Rate performance studies of $\text{Li}_2\text{MnSiO}_4$ comprising electrode having 42% of carbon (12 AM + 11 KB + 3 TAB). (b) *Ex situ* X-ray diffraction pattern of 12 AM + 11 KB + 3 TAB electrode recorded after the completion of 25 cycles at 0.5 C (AM: active material ($\text{Li}_2\text{MnSiO}_4$), KB: ketjen black, TAB: tefflonized acetylene black).

$\text{Li}_2\text{MnSiO}_4$ via enhancing the electronic conductivity. This result suggested that incorporation of more carbon (42%) hampers the crystal structure destruction or suppress the formation of amorphous phase during electrochemical cycling. This may be the reason for improved performance of $\text{Li}_2\text{MnSiO}_4$ materials under more amount of carbon inclusion. The existence of crystal structure is clearly evident from the *ex situ* XRD analysis of cycled electrode (Fig. 3b) after the completion of 25 cycles at 0.5 C. However, more detailed investigations are underway to study the structural properties of $\text{Li}_2\text{MnSiO}_4$ electrodes during electrochemical cycling clearly.

To validate the effect of carbon or preparation of composite $\text{Li}_2\text{MnSiO}_4$ towards the improvement in the electrical conductivity of the electrode, EIS was utilized, which is a versatile electrochemical technique to characterize electrical properties of any material and its interface. The basis of EIS is the analysis of the impedance (resistance of alternating current) of the observed system with respect to the applied frequency and exciting signal. This analysis provides quantitative information about the conductivity, the dielectric co-efficient, the static properties of the interfaces of a system, and its dynamic change due to adsorption or charge-transfer-phenomena. The EIS uses alternating current with low amplitude signals. This provides a non-invasive observation of any sample without any or less influence on the electrochemical state. The EIS was performed to substantiate the effects of carbon coating on the electrical conductivity of the composite $\text{Li}_2\text{MnSiO}_4$ electrodes. Fig. 4 illustrates the EIS of the composite $\text{Li}_2\text{MnSiO}_4$ cathodes comprising various amounts of carbon during the formulation of the electrodes with two electrode configuration. The presence of high-frequency semicircle is ascribed to the formation of solid electrolyte interface film and/or contact resistance, the medium frequency region corresponds to the charge-transfer (CT) impedance on the electrode/electrolyte interface, and the inclined line (vertical tail) at approximately 45° angle to the real axis, which indicates the lithium diffusion kinetics towards the electrodes called Warburg tail.³³ It is obvious to notice that the diameter of semicircles in medium-frequency region for

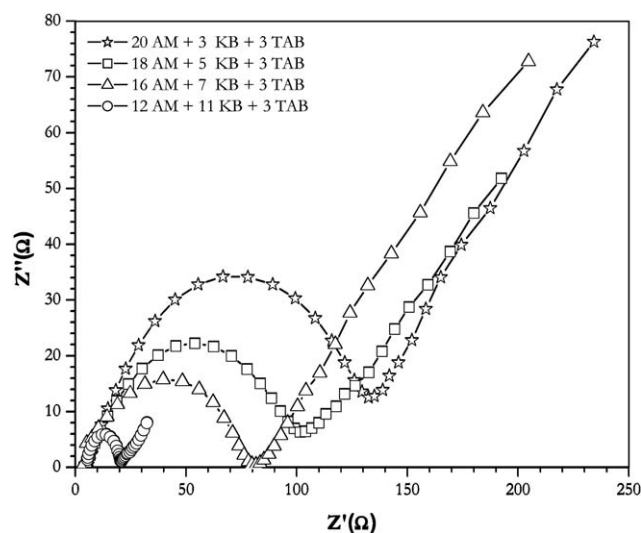


Fig. 4 Electrochemical impedance spectroscopic traces of $\text{Li}_2\text{MnSiO}_4$ electrodes comprising different proportions of carbon (AM: active material ($\text{Li}_2\text{MnSiO}_4$), KB: ketjen black, TAB: tefflonized acetylene black).

$\text{Li}_2\text{MnSiO}_4$ electrodes is in decreasing trend while increasing the carbon content which suggested lower CT impedance of electrodes. This decrease in CT resistance confirms that the electronic conductivity of $\text{Li}_2\text{MnSiO}_4$ electrodes has drastically improved while loading more and more carbon during the formation of electrode. Hence, the improvement in electrochemical performance of $\text{Li}_2\text{MnSiO}_4$ electrodes has been authenticated through the EIS studies.

4 Summary

Carbon- $\text{Li}_2\text{MnSiO}_4$ composite cathodes have been prepared during the formulation of the electrode. The composite electrodes comprising 42% of carbon demonstrated the enhanced lithium storage capabilities than the rest of the counterparts. The improved performance of carbon rich $\text{Li}_2\text{MnSiO}_4$ composites was due to the improved electronic conductivity of the electrodes fabricated. Rate performance studies were also conducted and demonstrated the capability at high current rates. *Ex situ* XRD confirms the retention of crystal structure after 25 cycles. Improvement in the electronic conductivity was verified through electrochemical impedance spectroscopy. Initially, $\text{Li}_2\text{MnSiO}_4$ particles were prepared by conventional solid state reaction method in the presence of adipic acid under Ar flow. The synthesized $\text{Li}_2\text{MnSiO}_4$ material showed the particulate morphology observed by scanning electron microscopy.

Acknowledgements

This work was supported by Energy Resources Technology R&D program (20092020100040) under the Ministry of Knowledge Economy, Republic of Korea.

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