Significant Improvement of LiMn$_2$O$_4$ Cathode Capacity by Introducing Trace Ni During Rapid Microwave-induced Solution Combustion

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ABSTRACT

LiMn$_2$O$_4$ cathodes are prepared by a rapid microwave-induced solution combustion method. Their initial discharge capacity is significantly improved by introducing trace Ni. For example, the LiMn$_{1.975}$Ni$_{0.025}$O$_4$ (LMNO-0.025) cathode shows an initial discharge capacity of 134.1 mAh g$^{-1}$ at 1 C, even 144.5 mAh g$^{-1}$ at 0.5 C, which is far higher than that of the pristine LiMn$_2$O$_4$ cathode (119.7 mAh g$^{-1}$ at 1 C) and close to its theoretical capacity of 148.2 mAh g$^{-1}$. After 1000 cycles, the capacity retention of the LMNO-0.025 sample reaches 56.53% at 1 C, and it can be presented the higher capacity retentions of 66.79% at 5 C and 66.89% at 20 C. The robust structure stability proved by XRD, SEM and HRTEM data, and the good kinetics testified by CV and EIS data of the Ni-doped material are responsible to improve the high-rate capability and long cycle properties.

1. Introduction

It is imperative for LIBs to possess cathode materials with high capacity and long-cycle life. If their specific capacity is improved 50%, the corresponding battery will increase ~28%, while the value is 13% for anodes. Spinell lithium manganite (LiMn$_2$O$_4$) is regarded as a promising cathode material, mainly owing to its high theoretical specific capacity (148.2 mAh g$^{-1}$), good thermal stability, low cost and abound resources. It is an ideal polyhedral spinel structure, in which Li$^+$ and Mn$^{3+}/$Mn$^{4+}$ occupy one eighth of all tetrahedron (8a) positions and half of octahedron (16d) positions, respectively, and form [LiO$_4$] tetrahedral skeleton and [MnO$_6$] octahedron skeleton with O atoms around 32e position, forming 8a-48f-16c three-dimensional channels for Li$^+$ to rapidly intercalation/ deintercalation in the network structure of [MnO$_6$]$_2^-$ during Li removal, the spinel structure [Mn$_2$O$_4$] skeleton is preserved. Unsurprisingly, its specific capacity rapidly declines during cycles, mainly resulting from Mn dissolution and Jahn-Teller effect. Researchers have employed lots of strategies and methods to overcome the shortcoming. High temperature solid-state, sol-gel, solution combustion, co-precipitation and so on are proposed to prepare this material. Controlling its structure and micromorphology, doping other elements and coating other matters are used to enhance its cycle performance.

Cation substitution is considered to be an important means to prolong the battery life, because it is beneficial to increase the average oxidation state of manganese cations and reduce Jahn-Teller effect. For example, Ni$^{2+}$, Mg$^{2+}$, Al$^{3+}$, Cu$^{2+}$, Cr$^{3+}$, and Co$^{3+}$ cations have been widely studied. Additionally, the shorter chemical bond between the doped cations and oxygen than the Mn-O bond improves the structure stability. The reasons for improved cycle performance by Ni element are summarized as follows: (1) higher electronegativity of Ni element (1.8) than that of Mn (1.5), (2) shorter bond length of the Ni-O bond (1.9154 Å) than that of the Mn-O bond (1.9372 Å), resulting in improving structure stability, and (3) the transformation of from ferromagnetic Mn$^{3+}$O$^{2-}$–Mn$^{4+}$ into diamagnetic Mn$^{4+}$O$^{2-}$–Mn$^{4+}$ by replacing part of Mn$^{3+}$, further improving the structure stability.

Duan et al. synthesized nickel-doped LiNi$_{0.025}$O$_4$ using a solution combustion synthesis technology. The resultant LiNi$_{0.025}$Mn$_{1.975}$O$_4$ shows a lower initial specific capacity of 101.3 mAh g$^{-1}$ at 1 C and 25°C, but a very high capacity retention of ~77% after 2000 ultra-long cycles. Azhar Iqbal et al. prepared Ni-Cu dual doping spinel LiMn$_2$O$_4$ material by a sol-gel method, exhibiting high capacity retention of 88% after 100 cycles, which is higher than that of the pristine sample of 72%. Wang et al. synthesized LiNi$_{0.055}$Mg$_{0.95}$Mn$_{1.95}$O$_4$ using a microwave irradiation sintering technique. The LiNi$_{0.055}$Mg$_{0.95}$Mn$_{1.95}$O$_4$ can deliver high initial specific capacity of 126.6, 134.9, 129.2, 128.8 and 142.5 mAh g$^{-1}$ for x = 0.0, 0.01, 0.02, 0.03 and 0.04, respectively.

In this paper, a rapid microwave-induced solution combustion method will be employed to prepare the LiMn$_2$O$_4$ cathodes with different structures. And it is found that the race Ni greatly improved its discharge specific capacity.
2. Experimental

2.1 Preparation of materials

LiMn$_{2-x}$Ni$_x$O$_4$ (x = 0.0, 0.010, 0.025, 0.050 and 0.075, named as LMO, LMNO-0.010, LMNO-0.025, LMNO-0.050 and LMNO-0.075, respectively) cathode materials were prepared by a rapid microwave-induced solution combustion. Lithium nitrate (LiNO$_3$, AR, 99.9%, Aladdin), manganese acetate (Mn(CH$_3$COO)$_2$·4H$_2$O, AR, 99.0%, Aladdin) and nickel acetate (Ni(CH$_3$COO)$_2$·4H$_2$O, AR, 99.9%, Aladdin) were accurately weighed and put into a crucible of 250 mL according 3 g theoretical mass of LiMn$_{2-x}$Ni$_x$O$_4$. Nitric acid (HNO$_3$, AR, 65.0%–68.0%, Chengdu Kelong Chemical Reagent Factory) was added into the crucible as an oxidant to keep a mole ratio of CH$_3$COO$^-$/NO$_3^-$ to 1:1. Citric acid (C$_6$H$_8$O$_7$·H$_2$O, AR, 99.5%, Aladdin) as a fuel was also added into according to a mole ratio of 100:0.75 of CH$_3$COO$^-$/C$_6$H$_8$O$_7$. After a clear solution was formed at 105°C for 15 min, it was transferred into a microwave oven (Galanz, G90F25CN3LV-Q6G0, Guangdong Glanshi Microwave Life Appliance Manufacturing Co., Ltd.). Microwave-induced solution combustion was carried out at 720 W for 5 min. As Fig. 1a shown, a fluffy black powder was obtained. It is observed that the powder have bulged the whole volume of the 250 mL crucible. The beehive-like porous structure of the powder can be seen from Fig. 1b. After it was calcined in a muffle furnace at 600°C for 4 h and then grinded by hand for about 20 minutes, a fine black powder is presented in Fig. 1c.

LiMn$_{2-x}$Ni$_x$O$_4$ powders, carbon black (conductive agent, Super P carbon, 40 nm, SCM industrial Chemical Co., Ltd.) and polyvinylidene fluoride (PVDF, adhesive) were accurately weighed at 8:1:1. A proper amount of N-Methyl pyrrolidone (NMP) was added into to form slurry by ball milling for half an hour. The slurry was coated onto an Al foil (current collector) using a automatic coating machine (AFA-III, Hefei Kejing Material Technology Co., Ltd.) was employed to characterize the charge/discharge behaviors and cycle performances of LiMn$_{2-x}$Ni$_x$O$_4$.

![Figure 1](image-url)

Figure 1. (a) As-prepared, (b) broken and (c) ground LiMn$_{2-x}$Ni$_x$O$_4$ powder prepared by microwave-induced solution combustion.

3. Results and Discussion

3.1 Structure and electrochemical performance of LiMn$_{2-x}$Ni$_x$O$_4$ (0 ≤ x ≤ 0.075)

XRD patterns of as-prepared LiMn$_{2-x}$Ni$_x$O$_4$ (0 ≤ x ≤ 0.075) are presented in Fig. 2a. All diffraction peaks of these samples are indexed to a cubic spinel structure of the LiMn$_2$O$_4$ recorded by the JCPCDS card of No. 35-07821, indicating that the low doped Ni element cannot change the crystal structure of LiMn$_2$O$_4$. The diffraction peak at about 2θ = 30.7° is not found, suggesting that Ni element substitutes for Mn at 16d site of octahedron, not Li at 8a of tetrahedron. The relationship of lattice constant (LC) and x for LiMn$_{2-x}$Ni$_x$O$_4$ is shown in Fig. 2b. It is found a linear drop of LC along with x, implying that the low doped Ni ions substituted for Mn ions with a spin state. The fitted line is as follows, where, LC is lattice constants (Å), and x is the doped Ni amount.

\[ LC = -0.1617x + 8.2450 \]

X-ray fluorescence (XRF) and energy dispersive spectrometry (EDS) are used to detect the relative content of Ni in the final
samples, and the results are shown in the Fig. 3. From the XRF spectra in Fig. 3a, it can be seen the strong peaks of Mn Ka and Mn Kb and the weak peaks of Ni. While the characteristic peaks of Ni Ka and Ni Kb can be clearly seen from Fig.3b. It is found that the two peaks become stronger along with the increase of added nickel acetate, suggesting higher Ni content in LiMn$_{2-x}$Ni$_x$O$_4$ samples. The mole ratios are shown in Fig.3a and the measured $x$ by XRF is correspond to the designed $x$, which is proofed by EDS data shown in Fig.3c.

From SEM images shown in Fig. 4, it can be seen that all samples present the polyhedron particles with clear outlines and smooth edge, being low of 200 nm. Microwave-induced solution combustion reactions are very quick and complete, which results in the formation of small particles within 5 min. Additionally, the produced gas of H$_2$O, CO$_2$ and NO$_x$ blow up the LiMn$_2$O$_4$ crystal (see Fig. 1) and the growth of partial crystals was stopped due to lacking mass diffusion, resulting in forming particles with different sizes, for example, 100–180 nm, 70–90 nm, 65–80 nm, 45–90 nm and 35–75 nm from Fig. 4a to e, respectively. Compared with the SEM images, it can be concluded that Ni-doped samples possess smaller particles and clearer polyhedron morphology. The result suggests that the growth of LiMn$_2$O$_4$ crystals can be suppressed by Ni and the smaller particles can be obtained by introduction of Ni. The similar phenomenon is also found in other combustion process.24

The initial charge-discharge curve of LiMn$_{2-x}$Ni$_x$O$_4$ ($0 \leq x \leq 0.075$) is shown in Fig. 5a. It can be seen that all samples show two charge/discharge platforms at about 4.2/4.1 V and 4.1/3.9 V, which corresponds to the two-step deintercalation/intercalation processes of LiMn$_2$O$_4$.29,30 The initial discharge specific capacities are 119.7,
125.2, 134.1, 120.1 and 111.9 mAh g⁻¹ at x = 0.0, 0.010, 0.025, 0.050 and 0.075 respectively, presenting a volcanic-like evolution. The highest point appears at x = 0.025. In addition, it can be seen that the voltage drop of Ni-doped samples at the end of the discharge curves is rapider than that of the pristine LiMn₂O₄. From Fig. 5b, it can be observed that the cycle curve of the LMNO-0.025 sample is always the top one during 1000 cycles, indicating it can always deliver the most specific capacity. Its capacity retention reaches 56.53% after 1000 long cycles at 1 C under room temperature.

3.2 Comparison of the optimized LiMn₁.₉₇₅Ni₀.₀₂₅O₄ and LiMn₀.₇O₄

The crystal shape, size and structure of LMNO-0.025 and LMO samples were further characterized by TEM and the results are shown in Fig. 6. From Fig. 6a, the particles of LMNO-0.025 exhibit a clear polyhedral morphology with a high crystallinity and uniform size distribution of about 80 nm. However, for the LMO sample, the bigger particles accompanied with fine particles were easily found, as Fig. 6b shown. Figure 6c and d demonstrates corresponding high-resolution TEM images of LMNO-0.025 and LMO, respectively. The plane space of the LMNO-0.025 sample can be measured to be 0.476 nm (Fig. 6c), which is less than that of LMO (0.478 nm, Fig. 6d). Being consistent with XRD data, the (1 1 1) crystal plane preferentially grows. It was reported that the formatted surface structures with more exposing (1 1 1) crystal planes are conductive to effectively reducing Mn dissolution, ensuring stable crystal structure. Diffraction spots at SAED patterns shown in the illustrations of Figs. 6c and d reflect the (1 1 1), (1 1 1) and (2 0 0) lattice plane of the spinel LiMn₂O₄ which corresponds to the (1 1 0) crystal ribbon axis. According to the exposed face orientations are assigned to be (1 1 1), (1 0 0) and (1 1 1) based on the established features of truncated octahedral LiMn₂O₄ with face-center cubic structure. Therefore, it can be considered that the region axis generated by these diffraction spots matches well with the truncated octahedral of LiMn₂O₄ showed a high crystallinity and single crystal skeleton. Briefly, Ni-doping enhanced electrochemical performance of LiMn₂O₄ without changing the inherent spinel structure.

The chemical states of Ni and Mn elements are analyzed by XPS, and the results are shown in Fig. 7. From Fig. 7a, it can be observed that the binding energy of Mn₂p₁/₂ and Mn₂p₃/₂ of the LMNO-0.025 sample is 654.06 eV and 642.23 eV, respectively, suggesting a slightly increased Mn valence. The Mn₂p₃/₂ peaks appear at about 641 eV, which implies the splitting of Mn with different valences. The Mn2p₃/₂ peaks were fitted using six splitting peaks of Mn³⁺ and Mn⁴⁺ with a FWHM of 1 eV according to the reference of Tang et al. and Liu et al., and the results are

Figure 5. (a) Initial charge-discharge curves and (b) cycle performance curves of LiMn₂₋ₓNiₓO₄ (0 ≤ x ≤ 0.075) samples, under conditions of 1 C and room temperature.

Figure 6. TEM images of (a) LMNO-0.025 and (b) LMO powders, and HRTEM and SAED of (c) LMNO-0.025 and (d) LMO powders.
shown in Fig. 7b. The content of Mn$^{4+}$ slightly increased after introducing Ni. The ratio of Ni$^{3+}$/Ni$^{2+}$ ions is calculated to be about 7/3 after fitting the curve of Ni$_2$P$_3$/2 (shown in Fig. 7c).

Better rate performances of the LNMO-0.025 than LMO samples can be easily distinguished from Fig. 8a. The discharge specific capacity decreases along with the rate increase, because of the high polarization during the discharge reactions under high rate. 38 Anyway, the LNMO-0.025 cathode releases more capacity under all rate conditions. Its initial discharge capacity even run up to 144.5 mAh g$^{-1}$ at 0.5 C, being close to the theoretical value of 148.2 mAh g$^{-1}$, and still reaches 105.9 mAh g$^{-1}$ at 10 C. So, it can be considered that the dynamics of the LNMO-0.025 cathode is excellent, resulting in the rapid drop at the end of charge/discharge curves (see Fig. 5a) due to the complete reactions.

In order to compare the high-rate performance, long cycle tests were carried out and the results are shown in Fig. 8b. At 5 C, the specific discharge capacity of LNMO-0.025 is about 1.45 times than that of LMO. Even at 20 C, it still releases a capacity of >70 mAh g$^{-1}$, which is even higher than that of LMO at 5 C. After 1000 cycles, the capacity retention of the LNMO-0.025 sample is 66.79% at 5 C and 66.89% at 20 C, which are all higher than the capacity retention at 1 C (Fig. 5b). The high cycle performance at high rate should be attributed to its excellent dynamics.

As Fig. 8c shown, the LMN-0.025 sample presents far better cycle performance at the elevated temperature of 55°C. After 1000 cycles, it can still release 34.9 mAh g$^{-1}$ at 55°C, while the LMO cathode releases 5.6 mAh g$^{-1}$, being close to zero. The improvement of cycle performance at high temperature can be considered resulting from the low dissolution rate of Mn, due to the improvement of its average valence in the LMNO-0.025 sample.39 However, it is found from Fig. 8c that the initial discharge specific capacity of the LMO cathode at 55°C is greatly increased to 129.5 mAh g$^{-1}$ from 119.4 mAh g$^{-1}$ at 25°C. According to Van’t Hoff rule, if the temperature of electrochemical reactions (T) is increased 10 K, their rate or rate constant (k) of the LMO cathode will be improved 2–4 times. The Arrhenius equation points out the relationship between k and activation energy ($E_a$).

$$k = A e^{-\frac{E_a}{RT}}$$  \hspace{1cm} (2)

When increasing the reaction temperature (T), the higher the $E_a$ is, the more the improvement of k is. Therefore, it can be considered that the $E_a$ of the LMO sample is higher.

To confirm their $E_a$ values, electrochemical impedance spectroscopy (EIS) was carried out at 25, 35, 45 and 55°C. As shown in Fig. 9a and b, the impedance spectra consist of two oblate...
semicircles in high-to-medium frequency region and an inclined line in lower frequency region. The two oblate semicircles are identified as surface film and charge transfer resistance respectively, and overlap together to form a large semicircle.\(^{40-42}\) The oblique line in low frequency region reflects the diffusion process of \(\text{Li}^+\). The spectra were fitted according to the equivalent circuit (the inset shown in Fig. 9b) and the corresponding charge transfer resistances \((R_{ct})\) were obtained. As we known, the \(R_{ct}\) is related to the exchange current \((i_0)\) under low-over-potential.

\[
i_0 = \frac{RT}{nF R_{ct}} \tag{3}
\]

And the \(i_0\) is also composed of \(n\) (charge-transfer number, \(n = 1\) for these two materials), \(F\) (Faraday constant), \(S\) (electrode area, \(S = 2.01 \text{ cm}^2\)), rate constant \(k\), \(C_R\) and \(C_{L0}\) (concentration of reduce and oxide, where \(C_R\) and \(C_{L0}\) is 1 due to a solid phase), as follows.

**Figure 9.** Nyquist plots of (a) LMO and (b) LMNO-0.025 samples, and the relationship between ln(\(R_{ct}\)) and \(T^{-1}\). The inset shown in Fig. 9(b) is the Equivalent circuit of all EIS spectra.

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### Table 1. Diffusion coefficients of Li\(^+\) ion (\(D_L\)) in LMO and LMNO-0.025 cathodes.

| Sample | \(D_L (\text{cm}^2\text{s}^{-1})\) | \(D_L (\text{A}_1)\) | \(D_L (\text{C}_1)\) | \(D_L (\text{A}_2)\) | \(D_L (\text{C}_2)\) |
|--------|------------------|-----------------|-----------------|-----------------|-----------------|
| LMO    | \(1.72 \times 10^{-8}\) | \(5.09 \times 10^{-9}\) | \(1.92 \times 10^{-8}\) | \(1.49 \times 10^{-8}\) | \(4.05 \times 10^{-8}\) |
| LMNO-0.025 | \(4.05 \times 10^{-8}\) | \(1.29 \times 10^{-8}\) | \(2.80 \times 10^{-8}\) | \(2.17 \times 10^{-8}\) |

\(i_0 = nF S K C_{G0}\) \(^{(4)}\)

Solving simultaneous Eqs. (3), (4) and (5), and letting \(A^* = A n F S K C_{G0}\), the Eq. (6) is obtained.

\[
\ln R_{ct} = \frac{RT}{nF} T^{-1} + \ln \left(\frac{RT}{nF} A^*\right) \tag{5}
\]

Both sides are logarithmically reduced to the following equation.

\[
\ln R_{ct} = \frac{RT}{nF A^*} T^{-1} \tag{6}
\]

The relationship between ln \(R_{ct}\) and \(T^{-1}\) of the LMO and LMNO-0.025 samples is shown in Fig. 9c. After linear fitting, the \(E_0\) of LMO and LMNO-0.025 is calculated to be 29.5895 KJ mol\(^{-1}\) and 22.7055 KJ mol\(^{-1}\) by their slopes, respectively. As expected, the \(E_0\) of the LMNO-0.025 powder does decrease after doping Ni.

The CV curves of LMO and LMNO-0.025 cathodes at different scan rates of 0.02, 0.04, 0.06, 0.08 and 0.10 mV s\(^{-1}\) are shown in Fig. 10a and b, respectively. Two pairs of characteristic redox peaks (A\(_1\)/C\(_1\) and A\(_2\)/C\(_2\)) are clearly seen from Fig. 10a and b. This indicates that the trace Ni element cannot change the two-step charge/discharge mechanism, presenting two charge/discharge voltage plateaus in Fig. 5a. It is also found that peak current \((i_p)\) of the four peaks all increases with the increase of scan rate, suggesting that these charge/discharge processes are controlled by the diffusion of \(\text{Li}^+\) ions. The diffusion behaviors are analyzed by means of the Randles-Sevcik equation.\(^{41}\)

\[
i_p = (2.69 \times 10^{3}) n^{1/2} C_{Li}^{1/2} D_L^{1/2} u^{1/2} \tag{7}
\]

Where, \(i_p\) denotes the peak current (A); \(C_{Li}\) denotes the \(\text{Li}^+\) volume concentration (\(\sim 0.02378 \text{ mol cm}^{-3}\)); \(D_L^{1/2}\) is the diffusion coefficient of \(\text{Li}^+\) (cm\(^2\) s\(^{-1}\)); \(u\) denotes the scanning rate (V s\(^{-1}\)). The relationships of the four peaks' \(i_p\) and \(u^{1/2}\) are presented in Fig. 10c and d. The linear fitting was done, diffusion coefficient of \(\text{Li}^+\) ions during each process was calculated according to the Eq. (7), and the calculated \(D_L\) values are tabulated in Table 1. As Table 1 shown, it can be considered that the doped Ni element greatly improves the \(D_L\) of A\(_1\) and C\(_1\), that is, the doped Ni is very beneficial to accelerate the first diffusion process (~3.95 times). At the same time, the doped Ni also accelerates the second diffusion process to about 1.50 times.

After 1000 cycles at 1 C under room temperature, the LMNO-0.025 cathode was characterized by XRD and SEM (Fig. 11a), and EIS and CV (Fig. 11b). From Fig. 11a, it can be clearly seen the characteristic XRD peaks of LiMn\(_2\)O\(_4\), implying that the crystal structure of spinel LiMn\(_2\)O\(_4\) is kept. The other diffraction peaks can be satisfactorily assigned to the Al current collector. From the SEM image shown in Fig. 11a, the crystal shape with polyhedrons is also retained after 1000 long cycles, although the crystal particles (about 130 nm) had slightly grown up, ascribing to an electrochemical activation and reconstruction effect during cycles. The little spheres can be distinguished to about 40 nm, which is in accord with Super P carbon.

As Fig. 11b shown, after 1000 cycles the oblate semicircle in high frequency region on the EIS curve becomes big, implying an increasing \(R_{ce}\). Compared with the CV curves in Fig. 10b and
Fig. 11b, it can be found that two pairs of redox peaks still appear after 1000 cycles ascribing to the retention of crystal structure.

4. Conclusion

A series of LiMn$_{2-x}$Ni$_x$O$_4$ (0 ≤ $x$ ≤ 0.075) black powders were successfully prepared by a facile and rapid microwave-induced solution combustion method. XRD and HRTEM data indicate that Ni substitutes for Mn in LiMn$_2$O$_4$, consequently resulting in crystal cell contraction of LiMn$_2$O$_4$. Its lattice parameter decreases linearly along with the increase of doped nickel content. XPS data suggest that the doped nickel exists in the form of bivalent (Ni$^{2+}$) and trivalent (Ni$^{3+}$) ions, with a ratio of about 3 : 7, leading to the increase of Mn$^{4+}$ in LiMn$_2$O$_4$. The crystal growth of the LiMn$_{2-x}$Ni$_x$O$_4$ powders is restrained by lack mass diffusion and suppressed by Ni, presenting a wide particle size distribution of from 30 to 200 nm and the decrease of particle size with the increase of the doped Ni. The optimized LiMn$_{1.975}$Ni$_{0.025}$O$_4$ material delivered 134.1 mAh g$^{-1}$ at 1 C and 144.05 mAh g$^{-1}$ at 0.5 C, and retained 74.4, 87.5 and 60.2 mAh g$^{-1}$ after 1000 cycles at 1 C, 5 C and 20 C, respectively. Such good cycle and rate performances can be contributed to the improved structure stability, the low apparent activation energy of 22.7055 KJ/mol and large lithium ions diffusion coefficient of $1.29 \times 10^{-9}$ cm$^2$ s$^{-1}$ and $2.80 \times 10^{-8}$ cm$^2$ s$^{-1}$ for the first and second discharge processes, respectively. The initial discharge capacity of the pristine LMO sample is improved to 134.1 mAh g$^{-1}$ at 55°C from 119.7 mAh g$^{-1}$ at 25°C, due to high apparent activation energy of 29.5895 KJ/mol.

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