Transition metal chlorides \( \text{NiCl}_2, \text{KNiCl}_3, \text{Li}_6\text{VCl}_8 \) and \( \text{Li}_2\text{MnCl}_4 \) as Alternative Cathode Materials in Primary Li Thermal Batteries

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Transition metal chlorides \( \text{NiCl}_2, \text{KNI} \text{C}l_3, \text{Li}_6\text{VCl}_8 \) and \( \text{Li}_2\text{MnCl}_4 \) were synthesized by solid state reaction in sealed quartz tubes and investigated as candidate cathode materials along with \( \text{NiCl}_2 \) in Li thermal batteries. The structure and morphology were studied and electrochemical properties probed at high temperatures (400°C–500°C) against \( \text{Li}_1\text{Si}_4 \) by galvanostatic discharge and galvanostatic intermittent titration technique (GITT). All the transition metal chlorides reduced to metal and the products of the discharge mechanism were confirmed by powder X-ray diffraction. \( \text{NiCl}_2 \) was tested at 500°C and a capacity of 360 mAh g\(^{-1}\) was achieved. \( \text{KNI} \text{C}l_3 \) was tested at different current densities from 15 mA cm\(^{-2}\) to 75 mA cm\(^{-2}\) and a high voltage profile 2.30 V was achieved at 425°C with a capacity of 262 mAh g\(^{-1}\). \( \text{Li}_6\text{VCl}_8 \) was tested at 500°C and a 1.80 V plateau at a current density of 7.5 mA cm\(^{-2}\) was achieved with a capacity of 145 mAh g\(^{-1}\). \( \text{Li}_2\text{MnCl}_4 \) was tested at the same current density at 400°C and a capacity of 254 mAh g\(^{-1}\) was achieved. These transition metal chlorides exhibit higher voltage against \( \text{Li}_1\text{Si}_4 \) and, hence, provide more specific power compared to the well-known metal disulfides \( \text{MS}_2 \) (M = Fe, Co, Ni) and may be promising cathode materials for Li thermal batteries.

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Thermal batteries were first designed by German scientists during World War II for V2 rockets as a military application.1 Thermal batteries are electrochemical systems and convert directly the chemical energy into electrical energy as the anode is oxidized and the cathode is reduced utilizing a molten salt electrolyte at high temperature (>300°C). These batteries are useful due to their ability to be stored for decades before being used.2 Currently, the most studied thermal batteries use a lithium alloy as an anode, a halide salt eutectic in an insulating porous material as an electrolyte, and a transition metal sulfide as a cathode.3 To the best of our knowledge, few transition metal chlorides have been studied as components of Li thermal batteries. Some transition metal chlorides such as \( \text{NiCl}_2, \text{FeCl}_2 \) and \( \text{SbCl}_3 \) have been used for study as cathodes for thermal batteries in the Na/NaAlCl\(_4\) system which used a liquid-Na anode and a NaAlCl\(_4\) electrolyte.4–11 \( \text{FeCl}_3 \) was tested as cathode at temperatures where the electrolyte was solid. 12 \( \text{CuCl}_2, \text{FeCl}_2 \) and \( \text{MoCl}_5 \) were studied in the Li-alloy/LiF-KF/MFx system or Li-alloy/LiF-NaF system.4–11 \( \text{FeCl}_3 \) was tested as cathode at temperatures where the electrolyte was solid. 12 \( \text{CuCl}_2, \text{FeCl}_2 \) and \( \text{MoCl}_5 \) were studied in the Li-alloy/LiF-KF/MFx system or Li-alloy/LiF-NaF system.4–11

This work uses the \( \text{Li}_1\text{Si}_4 \) alloy as an anode because it has the highest Li content and exhibits minimum oxidation under dry-room conditions.16 The discharge mechanism of \( \text{Li}_1\text{Si}_4 \) to \( \text{Li}_2\text{Si}_2 \) at a potential of 0.157 V against Li metal at 415°C corresponds to a capacity of 485 mA h g\(^{-1}\).16 The Li-IKCl eutectic (melting at point of around 354°C) is used as the electrolyte and requires minimum 35 wt% MgO as the separator.

This work focuses on \( \text{NiCl}_2, \text{KNiCl}_3, \text{Li}_6\text{VCl}_8 \) and \( \text{Li}_2\text{MnCl}_4 \) as alternative cathode materials for use in Li thermal batteries. These materials have not been reported as cathodes in the past against \( \text{Li}_1\text{Si}_4 \). \( \text{NiCl}_2 \) crystallizes in hexagonal \( \text{P6}_3\text{mc} \) with cell dimensions \( a = b = 11.795 \) Å and \( c = 5.926 \) Å as shown in Figure 1a.17 \( \text{Li}_2\text{MnCl}_4 \) adopts an inverse spinel structure (Fd\(_3\)m, \( a = 10.502 \) Å) with half of the lithium ions tetrahedrally coordinated by chloride ions and the remaining Li atoms, together with the Mn ions, are distributed statistically over the occupied octahedral sites as shown in Figure 1b.18 \( \text{Li}_6\text{VCl}_8 \) crystallizes in cubic \( \text{Fm\text{3m}} \) with cell parameter \( a = 10.294 \) Å and the structure is shown in Figure 1c.19 \( \text{NiCl}_2 \) crystallizes in trigonal \( \text{R}3\text{m} \) with cell parameter \( a = b = 3.483 \) Å and \( c = 17.40 \) Å as shown in Figure 1d.20

Experimental

Transition metal chlorides were synthesized by solid state reactions in sealed evacuated quartz tubes to ensure they were not oxidized. 0.73 g of KCl (Aldrich, 99%) and 1.27 g of \( \text{NiCl}_2 \) (Alfa Aesar, 99%) powders were used to synthesize \( \text{KNI} \text{C}l_3 \). 0.81 g of LiCl (Alfa Aesar, 99%) and 1.19 g of MnCl\(_2\) (Strem, 97%) powders were used to synthesize \( \text{Li}_2\text{MnCl}_4 \). 1.18 g of VCl\(_3\) (VCl\(_2\), Aldrich, 97%) and 0.82 g of LiCl (Alfa Aesar, 99%) powders were used to synthesize \( \text{Li}_6\text{VCl}_8 \). VCl\(_2\) was prepared through the decomposition of VCl\(_3\) to VCl\(_2\) under nitrogen flow at 797°C followed by a further firing of VCl\(_3\) at 827°C for 12 hours with in a quartz tube. The powders were weighed out in the required stoichiometry for \( \text{KNI} \text{C}l_3, \text{Li}_6\text{VCl}_8 \) or \( \text{Li}_2\text{MnCl}_4 \) and mixed in a mortar and pestle in an argon filled glove box, then sealed into evacuated quartz tubes (10\(^{-3}\) mbar). The samples were heated in a tube furnace, with a heating and cooling rate of 1°C min\(^{-1}\). \( \text{KNI} \text{C}l_3 \) was fired at 675°C, \( \text{Li}_2\text{MnCl}_4 \) was fired at 600°C and \( \text{Li}_6\text{VCl}_8 \) was fired at 800°C for 1 week. Room temperature powder X-ray diffraction data were collected using a Panalytical Empyrean diffractometer in Bragg-Brentano geometry with a Ge (220) monochromator and Cu K\(_\alpha\) radiation (\( \lambda = 1.5406 \) Å). Data were collected from 5° to 70° 20 for 1 hour with a step size of 0.017° and a time per step of 0.94 seconds. WinXPOW software was used for indexing and refining the unit cell parameters. Scanning electron microscopy was carried out using a Jeol JSM-5600 model microscope. Composite cathode pellets for high temperature electrochemical investigations were made by mixing 75 wt% \( \text{NiCl}_2, \text{KNI} \text{C}l_3, \text{Li}_6\text{VCl}_8 \) or \( \text{Li}_2\text{MnCl}_4 \) (0.15 g) with 25 wt% Super P Carbon (0.05 g) and pressing in a 13 mm diameter die. The anode pellet was made by mixing 75 wt% \( \text{Li}_1\text{Si}_4 \) (Lithium Rockwood) (0.15 g) and 25 wt% LiCl-KCl eutectic (Sigma Aldrich 99.99%) electrolyte (0.2 g) onto an anode pellet and then placing the cathode pellet on the top. To prevent movement all three pellets were contained in a ceramic cup. Graphite foil was used as the top and bottom current collectors. The resulting cell was placed into a Swagelok sample holder, allowing the measurements to be carried out sealed under argon. The resulting assembly (comprising of...
Figure 1. Crystal structure of (a) KNiCl$_3$, (b) Li$_2$MnCl$_4$, (c) Li$_6$VCl$_8$ and (d) NiCl$_2$. Purple atoms are potassium, green atoms are chlorine, gray atoms are nickel, blue atoms are lithium, orange atoms are manganese and red atoms are vanadium.

Figure 2. PXRD data of (a) KNiCl$_3$, (b) Li$_2$MnCl$_4$, (c) Li$_6$VCl$_8$ and (d) NiCl$_2$. Experimental patterns are shown by the red line and the simulated diffraction patterns using published crystallographic models are shown by the black line.
the cell within the Swagelok sample holder) was heated, and during this procedure the electrolyte melts and the voltage starts to rise. The thermal batteries were tested at high temperatures (NiCl₂ and Li₆VCl₈ at 500°C, KNiCl₃ at 425°C and Li₂MnCl₄ at 400°C) using a Maccor battery tester (model 5300) by galvanostatic discharge and galvanostatic intermittent titration technique (GITT). In the GITT method, galvanostatic discharge pulses, each 10 minutes long, followed by 5 minutes of relaxation time, with no current passing through the cell show the potential which drops between the pulses and the relaxation until a potential of 0.5 V is reached. The experimental capacity was calculated using the Maccor software and then this was converted to x, the moles of lithium ions per moles of formula unit.

Results and Discussion

**Cathode materials characterization.**—NiCl₂, KNiCl₃, Li₆VCl₈ and Li₂MnCl₄ were analyzed by powder X-ray diffraction and the resulting diffraction patterns are shown in Figure 2. In the synthesis of Li₆VCl₈ the main phase corresponded to Li₆VCl₈ but there is also a V₂O₃ impurity (a = 4.948(7) Å, c = 13.989(20) Å). As the synthesis of Li₆VCl₈ was in a sealed quartz tube we suggest that the V₂O₃ arises as an impurity in the synthesis of the VCl₂ reagent during the decomposition VCl₃ to VCl₂. KNiCl₃ was identified as the main phase but there is also a KCl impurity (a = 6.280(25) Å). Li₂MnCl₄ was identified as the main phase but there is a LiCl impurity (α = 5.140(10) Å). NiCl₂ (Alfa Aesar, 99%) was identified as the main phase. The unit cell parameters of NiCl₂, KNiCl₃, Li₂MnCl₄ and Li₆VCl₈ are given in Table I. All the materials were studied electrochemically with the impurities (LiCl and KCl) as the electrolyte LiCl–KCl eutectic which is used, consists of KCl and LiCl. The morphology and the elemental composition of the materials was investigated by SEM and EDX before and after discharge and results are shown in Figures 3 and 4. The SEM images show that the morphology has been changed after the discharge and the size of the crystallites differs for each material. EDX confirms K 19 at%, Ni 19 at% and Cl 62 at% as expected for KNiCl₃ and Ni 30 at%, Cl 70 at% as expected for NiCl₂ before testing. The elemental analysis of both KNiCl₃ and NiCl₂ cathodes after testing (K 14 at%, Ni 5 at%, Cl 81 at% and Ni 62 at%, Cl 38 at%, respectively) means different products of the electrochemical mechanism as Ni metal, KCl and LiCl.

**Electrochemical investigation of transition metal chlorides at high temperature.**—Galvanostatic discharge curves for measurements carried out at 425°C and a galvanostatic intermittent titration technique curve for a measurement at 425°C for KNiCl₃ are presented in Figure 5. Galvanostatic discharge was performed at different current densities from 15 mA/cm² to 75 mA/cm². At current densities of 15, 30 and 60 mA/cm² there is a high cell voltage (over than 2.0 V) but a flat voltage plateau could not be obtained as we are getting an insertion reaction rather than a conversion reaction. A voltage plateau is preferred as this gives a better voltage control during the discharge reaction. A capacity of 262 mAh g⁻¹ was measured for KNiCl₃ and this corresponds to a value of x = 2 for the number of lithium atoms transferred during the discharge process. At current densities of 68 and 75 mA/cm² the cell voltage is lower which is probably due to a higher cell resistance. The electrochemical mechanism corresponds to

\[
\text{KNiCl}_3 + 2\text{Li} =\rightarrow \text{KCl} + 2\text{LiCl} + \text{Ni}
\]

This electrochemical Reaction 1 is expected as it is analogous to the system Na/NaAlCl₄/NiCl₂.⁶ The galvanostatic intermittent titration technique measurements (GITT) show the IR drop is 125 mV at the beginning of discharge and 375 mV at the end of the measurement, which indicates that the cell resistance is increasing during the reduction of the cathode, from a resistance of 16 Ω at the beginning of the measurement to 50 Ω after the cell discharge, which suggests that it is more difficult for the lithium ions to transfer from the anode to the cathode electrode.

Galvanostatic discharge curves for measurements carried out at 400°C and the galvanostatic intermittent titration technique curve for measurements carried out at 400°C for Li₂MnCl₄ are presented in Figure 6. Galvanostatic discharge was performed at different current densities from 15 mA/cm² to 75 mA/cm². At a current density of 15 mA/cm² there is a high cell voltage (2.50 V) similar to KNiCl₃ but again a flat voltage plateau could not be obtained. Li₂MnCl₄ exhibits a

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**Table I. Refined unit cell parameters of transition metal chlorides.**

| Unit cell [Å] | Experimental | Published |
|---------------|--------------|-----------|
| a and c KNiCl₃ | 11.800(11) and 5.926(4) | 11.795 and 5.926¹⁷ |
| a Li₂MnCl₄ | 10.495(7) | 10.502¹⁸ |
| a Li₆VCl₈ | 10.294(5) | 10.294¹⁹ |
| a and c NiCl₂ | 3.468(21) and 17.30(7) | 3.483 and 17.40²⁰ |
Figure 4. SEM images of Li$_2$MnCl$_4$ and Li$_6$VCl$_8$ before and after discharge.

Figure 5. (a) Galvanostatic discharge of KNiCl$_3$ at current densities of 15, 30, 60, 68 and 75 mA/cm$^2$ at 425$^\circ$C and (b) galvanostatic intermittent titration technique of KNiCl$_3$ at current density of 7.5 mA/cm$^2$ at 425$^\circ$C.

Figure 6. (a) Galvanostatic discharge of Li$_2$MnCl$_4$ at current densities of 15, 30, 45 and 75 mA/cm$^2$ at 400$^\circ$C and (b) galvanostatic intermittent titration technique of Li$_2$MnCl$_4$ at current density of 7.5 mA/cm$^2$ at 400$^\circ$C.
Figure 7. (a) Galvanostatic discharge of Li₆VCl₈ at current densities of 7.5, 23, 30 and 45 mA/cm² at 500 °C and (b) galvanostatic intermittent titration technique of Li₆VCl₈ at current density of 7.5 mA/cm² at 500 °C. The maximum capacity of 254 mA h g⁻¹. The electrochemical mechanism corresponds to

\[
\text{Li}_2\text{MnCl}_4 + 2\text{Li} \rightarrow 4\text{LiCl} + \text{Mn} \quad [2]
\]

The IR drop is 100 mV at the beginning of discharge and 625 mV at the end of the measurement, which indicates that the cell resistance is increasing from a resistance of 13 Ω at the beginning of the measurement to 83 Ω after the cell discharge.

Galvanostatic discharge curves for measurements were carried out at 500 °C and the galvanostatic intermittent titration technique curve for a measurement carried out at 500 °C for Li₆VCl₈ is presented in Figure 7. Galvanostatic discharge was performed at different current densities from 7.5 mA/cm² to 45 mA/cm². At a current density of 7.5 mA/cm² there is a flat voltage profile at 1.80 V and a capacity of 145 mA h g⁻¹ was achieved. At current densities of 23 and 30 mA/cm², Li₆VCl₈ shows a lower but again flat voltage plateau at 1.50 V. However at a current density of 45 mA/cm² a flat voltage plateau could not be obtained. Therefore, at low current densities, the behavior of Li₆VCl₈ is different to that of Li₃MnCl₄ and KNiCl₃ as Li₆VCl₈ is the only material which exhibits a flat voltage plateau in the discharge profile. The electrochemical mechanism corresponds to

\[
\text{Li}_6\text{VCl}_8 + 2\text{Li} \rightarrow 8\text{LiCl} + \text{V} \quad [3]
\]

The cell resistance increases during the reduction of the cathode from 6 Ω at the beginning to 33 Ω at the end of discharge.

Galvanostatic discharge curves for measurements carried out at 500 °C and the galvanostatic intermittent titration technique curve for a measurement carried out at 500 °C for NiCl₂ are presented in Figure 8. Galvanostatic discharge was performed at different current densities from 22 mA/cm² to 75 mA/cm². At a current density of 22 mA/cm² there is a high voltage profile at 2.25 V and a capacity of 360 mA h g⁻¹ was achieved. At current densities of 60 and 75 mA/cm², NiCl₂ shows a lower voltage profile but still at around 2.0 V. The electrochemical mechanism corresponds to

\[
\text{NiCl}_2 + 2\text{Li} \rightarrow 2\text{LiCl} + \text{Ni} \quad [4]
\]

The cell resistance increases during the reduction of the cathode from 13 Ω at the beginning to 33 Ω at the end of discharge.

The advantage of transition metal chlorides is that they provide more specific power and exhibit higher voltage against Li₁₃Si₄ at high temperatures compared to that of the well-known metal disulfides FeS₂, CoS₂ and NiS₂ as shown in Table II. The thermal stability and the overall capacity of transition metal chlorides in the voltage range from OCV 3.0 V to 1.50 V are also comparable to that of the most commonly used disulfides.

PXRD data were collected after discharge for all of the cathodes as shown in Figure 9. The product of the electrochemical reaction of KNiCl₃ is KCl (a = 6.292(3) Å), Ni metal (a = 3.524(7) Å) and LiCl as shown in Figure 9a. There are some peaks of the starting material KNiCl₃ (a = 11.805(4) Å and c = 5.935(12) Å) and some peaks of NiO (a = 4.177(4) Å).
Table II. Overall capacity, thermal stability, voltages vs Li$_{13}$Si$_4$, and specific power of transition metal chlorides compared to transition metal disulfides FeS$_2$, CoS$_2$ and NiS$_2$.

| Sulfides | Overall Capacity (mA h g$^{-1}$) | Thermal Stability °C | Voltages vs Li$_{13}$Si$_4$ | Capacity (mA h g$^{-1}$) in the voltage range (OCV – 1.5 V) | Specific power (Wh g$^{-1}$) |
|----------|---------------------------------|-----------------------|----------------------------|-------------------------------------------------|-----------------------------|
| FeS$_2$  | 558$^{3}$                       | 580$^{24,25}$         | 1.77 V, 1.64 V, 1.13 V$^{21}$ | 357                                             | 0.14$^{26}$                 |
| CoS$_2$  | 598$^{3}$                       | 650$^{22}$            | 1.75 V, 1.40 V, 1.25 V$^{21}$ | 348                                             | 0.11$^{27}$                 |
| NiS$_2$  | 545$^{3}$                       | 600$^{23}$            | 1.76 V, 1.60 V, 1.40 V, 1.25 V$^{21}$ | 349                                             | ≥ 0.11$^{28}$              |
| Chlorides |                                |                       |                            |                                                 |                             |
| NiCl$_2$ | 360                             | 500                   | 2.25 V                     | 326                                             | 0.80                        |
| KNiCl$_3$| 262                             | 675                   | 2.25 V                     | 215                                             | 0.51                        |
| Li$_6$VCl$_8$ | 145                         | 800                   | 1.80 V                     | 136                                             | 0.26                        |
| Li$_2$MnCl$_4$ | 254                         | 600                   | 2.50 V                     | 214                                             | 0.54                        |

The product of the electrochemical reaction of Li$_2$MnCl$_4$ is LiCl ($a = 5.142(17)$ Å) and Mn metal ($a = 8.948(2)$ Å) as shown in Figure 9b. There are some peaks of the electrolyte KCl and peaks of Mn$_2$O$_3$ ($a = 9.44(5)$ Å, $b = 9.55(4)$ Å and $c = 9.28(3)$ Å) and Mn$_3$O$_4$ ($a = 5.747(3)$ Å and $c = 9.444(6)$ Å).

The product of the electrochemical reaction of Li$_6$VCl$_8$ is LiCl ($a = 5.139(12)$ Å) with some residual V$_2$O$_3$ ($a = 4.944(15)$ and $c = 14.020(4)$ Å) as shown in Figure 9c. There are also peaks of KCl ($a = 6.289(3)$ Å) and MgO ($a = 4.209(12)$ Å) and some other peaks that were difficult to identified and indexed to the known PDF database.

The product of the electrochemical reaction of NiCl$_2$ is LiCl ($a = 5.129(5)$ Å) and Ni metal ($a = 3.524(7)$ Å) as shown in Figure 9d. There are some peaks of the starting material NiCl$_2$ ($a = 3.468(21)$ Å and $c = 17.302(7)$ Å), some peaks of NiO ($a = 4.180(12)$ Å) and some peaks of KCl ($a = 6.299(18)$ Å).

Figure 9. PXRD data of the cathode after galvanostatic discharge of (a) KNiCl$_3$, (b) Li$_2$MnCl$_4$, (c) Li$_6$VCl$_8$ and (d) NiCl$_2$. 

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We attribute the small amount of oxide impurity in each of the diffraction patterns after discharge to a small amount of oxidation of the sample prior to and during the collection of PXRD data.

**Conclusions**

The high temperature discharge behavior of transition metal chlorides NiCl₂, KNiCl₃, Li₂MnCl₄ and Li₆VCl₈ synthesized by solid state reaction (except NiCl₂) is presented in this work. At temperatures of 400–500 °C the value of the working voltage profile was recorded at different current densities. KNiCl₃ exhibits a high cell capacity of 145 mA h g⁻¹ was recorded at different current densities. KNiCl₃ exhibits a high cell voltage against Li₁₃Si₄ compared to that of the transition metal chlorides. Li₁₃Si₄ has a capacity of 254 mA h g⁻¹ was achieved. Li₂MnCl₄ was tested at 400 °C and a capacity of 254 mA h g⁻¹ was achieved. Li₆VCl₈ exhibits a flat voltage plateau of 1.80 V at a current density of 7.5 mA cm⁻² with capacity of 262 mA h g⁻¹. These transition metal chlorides provide more specific power and exhibit higher voltage against Li₁₃Si₄ compared to that of the well-known metal disulfides so we suggest transition metal chlorides as alternative promising candidate materials for Li thermal battery applications.

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