Experimental studies of transition metal chloride electrodes in undivided cells using molten NaAlCl$_4$ electrolyte

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Abstract

An undivided cell, using NaCl–saturated AlCl$_3$–NaCl molten electrolyte, was used to study the behaviour of MCl$_2$/M electrodes made by co-sintering metal powders M with NaCl (M = Ni, Fe, Mn, V) The aluminium electrode exhibits reversible redox behaviour in this melt, and thus serves as a useful counter electrode The cell avoids the use of either Na metal or β″-alumina, and provides a simple and convenient way of testing the charging and discharging of these electrodes The charge/discharge behaviour of electrodes where M = Mn or V was much inferior to the Ni and Fe systems Extended cycling of all MCl$_2$/ M electrodes was accompanied by steady loss of electrode capacity Dissolution and transport of solid electrode reagents (e g, NiCl$_2$) to the bulk electrolyte may be a contributing factor, but is not the only cause of diminished capacity

Introduction

High energy density cells which utilize a liquid sodium anode and a transition metal chloride as the cathode reagent have received considerable attention in recent years [1–11] The overall reaction in these cells is

$$2Na(l) + MCl_2(s) \rightleftharpoons 2NaCl(s) + M(s) \tag{1}$$
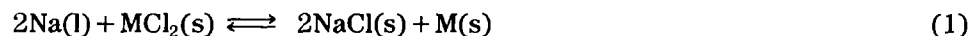
where M is commonly Fe or Ni The cells incorporate a solid electrolyte, β″-alumina, to separate the sodium from the other reagents The cathode is a porous matrix of the three solid reagents in (1), the relative amounts depending on the state of charge An excess of metal over the stoichiometric quantity of M is needed to ensure adequate electronic conductivity in the cathode even when it is fully charged In the case of nickel, for example, utilization of the metal is usually kept below about 40% [4] A liquid electrolyte, NaCl–saturated NaAlCl$_4$, floods the pores of the cathode

Cells of this type have been successfully tested over many deep discharge cycles [4, 5], and have also been demonstrated in batteries for vehicle propulsion [5]. However, in the research laboratory, construction and testing of such complete cells can be both time-consuming and costly. This paper proposes a cell design in which transition metal chloride electrodes can be

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tested without the burden of the Na electrode and the β''-alumina separator In such cells the focus would be on the charge/discharge behaviour of individual electrodes according to the reaction

$$M(s) + 2NaCl(s) \rightleftharpoons MCl_2(s) + 2Na^+ + 2e^- \tag{2}$$
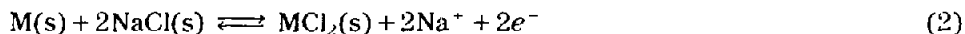
Given a suitable cell design, the evaluation of different metals M and different compositions of both electrodes and melt could be rapidly and conveniently achieved We report here on some early results from such a cell, containing neither Na nor β''-alumina

Experimental

Aluminium chloride and sodium chloride were purified and mixed to give NaCl–saturated $NaAlCl_4$ as described previously [12]

Electrochemical measurements were carried out using about 50 g of NaCl–saturated molten $NaAlCl_4$ together with a small excess of solid NaCl, in a Pyrex cell sealed with three 'Ace-Thred' adapters and Teflon bushings and ferrules These bushings held Pyrex tubes in which were sealed tungsten wires which connected to the current collectors on the electrodes The cell design is shown in Fig 1. The lower part of the cell fitted into the well of a furnace, so that the Teflon components were above the heated zone All the electrochemical studies were carried out at $250\ 0 \pm 0\ 3\ °C$

To construct the MCl_2/M electrodes, a weighed amount of a mixture of the metal powder M and NaCl was placed in a mould in contact with a

Labels:
- Wire leading to potentiostat
- Teflon bushing
- 'Ace–Thred'' adapter
- Tungsten wire
- Glass holder for Tungsten wire
- Wire connection joint
- Thermocouple well
- Al counter electrode
- NaCl–saturated $NaAlCl_4$
- Al reference electrode
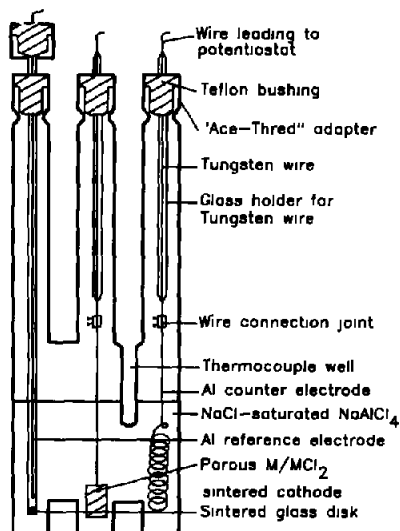- Porous M/MCl_2 sintered cathode
- Sintered glass disk

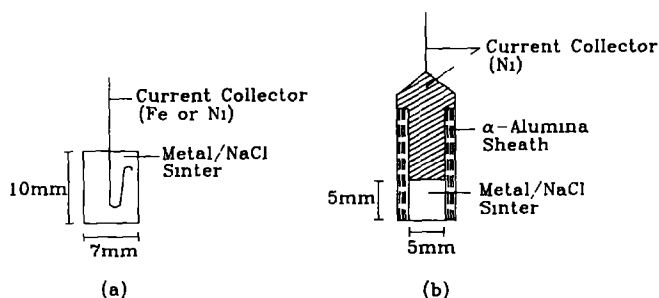Fig 1 Undivided cell design used in studies of various cathodes

Fig 2 Cross sections of the type (a) and (b) designs of MCl_2/M electrodes

current collector, and sintered under hydrogen at between 750 and 800 °C
Two electrode designs were used (see Fig 2), in both cases the electrodes
were cylindrical in shape In type (a) electrodes the entire surface of the
cylinder was exposed to the melt, while in type (b) only the lower end face
contacted the melt These electrodes were fabricated with capacities typically
in the region of 50 to 100 mA h, based on the mass of the limiting reagent,
normally NaCl The sintered electrodes, after impregnation of the pores with
molten $NaAlCl_4$, were then cycled against each other or against Al wire
counter electrodes

Electrochemistry was carried out in either a purge-type glove box, under
purified nitrogen, or a high integrity glove box (Faircrest) under recirculating
argon An IBM PC XT-compatible computer, linked to a home built potentiostat-
galvanostat via an IBM Data Acquisition and Control Adapter card (12 bit
A to D and D to A), controlled and monitored the charging and discharging
of the electrochemical cell All charging and discharging was carried out in
galvanostatic mode

Source and purity of chemicals

Aluminium chloride (Fluka, puriss., anhydrous, iron-free), aluminium
wire (Johnson Matthey, 1 mm diam , 99 999%), iron powder (GAF, type C,
carbonyl iron, 99 5%, particle size 6–8 μm); iron wire (Johnson Matthey,
0.5 mm diam., 15 ppm total metal impurities); manganese powder (Aldrich,
99 9%, particle size ~149 μm), nickel powder (INCO, type 287, 99 6%,
particle size 2 6–3 3 μm); nickel wire (Johnson Matthey, 0 5 mm diam ,
99 8%), sodium chloride (Merck, Guaranteed Reagent, > 99.5%), sulfur powder
(Merck, sublimed, 99.5%, particle size < 44 μm); tungsten wire (Alfa 0 5
mm diam , 99 98%), vanadium powder (Fluka, puriss > 99 5%)

Results and discussion

The electrode reaction at an aluminium electrode in equimolar $AlCl_3$ NaCl
(i e $NaAlCl_4$) melts may be written [13, 14]

$$AlCl_4^- + 3e^- \longrightarrow Al + 4Cl^- \tag{3}$$

Since the present melt is saturated with respect to NaCl, much of the Cl^- product in (3) is likely to precipitate on the aluminium surface as NaCl Thus, if an aluminium electrode is cycled anodically and cathodically according to reaction (3), the only species which will be introduced into the melt are $AlCl_4^-$ and Cl^-, which are in fact the dominant anions present in the melt [14] Thus the bulk composition of the melt will remain unchanged, since it is also in contact with excess solid NaCl

When an aluminium wire electrode of about 7 cm^2 in area was anodically oxidized at 20 mA, using Al counter and reference electrodes having similar areas to the working electrode, the overpotential remained in the range 20 ± 10 mV for over 4 h With a 20 mA cathodic current, the overpotential was even smaller and steadier, at -10 ± 2 mV The small and relatively constant polarization at an aluminium electrode indicates that it can serve as a practical counter electrode for the study of MCl_2/M electrodes in either two- or three-electrode cells In the studies described below, extensive use was made of aluminium wire counter electrodes of this type

Figure 3 shows the performance of a type (a) $NiCl_2/Ni$ electrode charged and discharged against an aluminium counter electrode The excellent characteristics of the nickel electrode are clearly demonstrated — polarization losses are small and the charge/discharge plateaus are long and flat. The
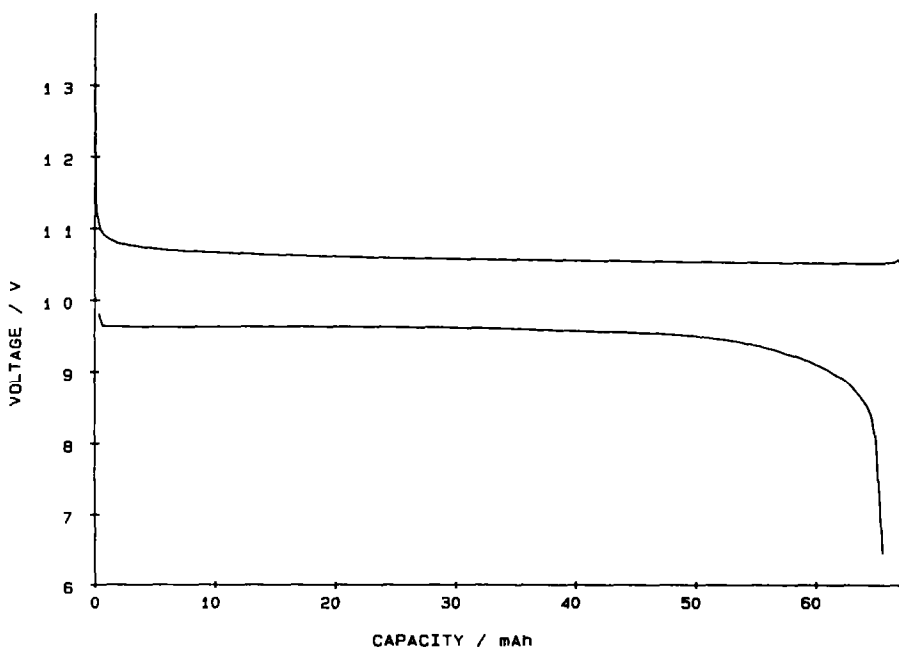

Fig 3 Charge (upper) and discharge (lower) curves obtained during continuous cycling of a type (a) $NiCl_2/Ni$ electrode against an aluminium counter electrode at $C/5$ (20 6 mA) Electrode contained 0 281 g Ni, 0 224 g NaCl, 0 013 g S, giving a nominal capacity for $NiCl_2/Ni$ of 103 mA h

Figure shows a 60% initial utilization of NaCl A utilization of > 80% was achieved when the initial charge was performed at a slower rate (FeCl₂/Fe electrodes tested in this cell also exhibited excellent dynamic behaviour, having small polarization losses and flat charge/discharge curves) Upon continuous cycling of the cell at the same constant current, a steady decline in capacity, corresponding to about 3% per cycle, was noted This suggests that this configuration would be unsuitable for extended testing, but can be used to evaluate electrode performance over a limited number of cycles

The nickel electrode used above contained an amount of sulfur corresponding to about 2 5% of the electrode weight Sulfur was added in an attempt to prevent nickel grain growth during cycling which leads to a decrease in capacity [7] There is no evidence of any redox activity of the sulfur in the charge/discharge curves of Fig 3 However, when a larger quantity of sulfur was added to the electrolyte (1% of electrolyte weight), additional plateaus developed on both charge (~ 1 20 V) and discharge (a short plateau at 1 09 V and a longer one at 0 74 V) This is shown in Fig 4 Sulfur clearly contributes significantly to the electrochemistry under these conditions, a fact which did not emerge from earlier studies of sulfur-doped Na–NiCl₂ cells [7] Much further work will be needed to establish the detailed role of S in these cells
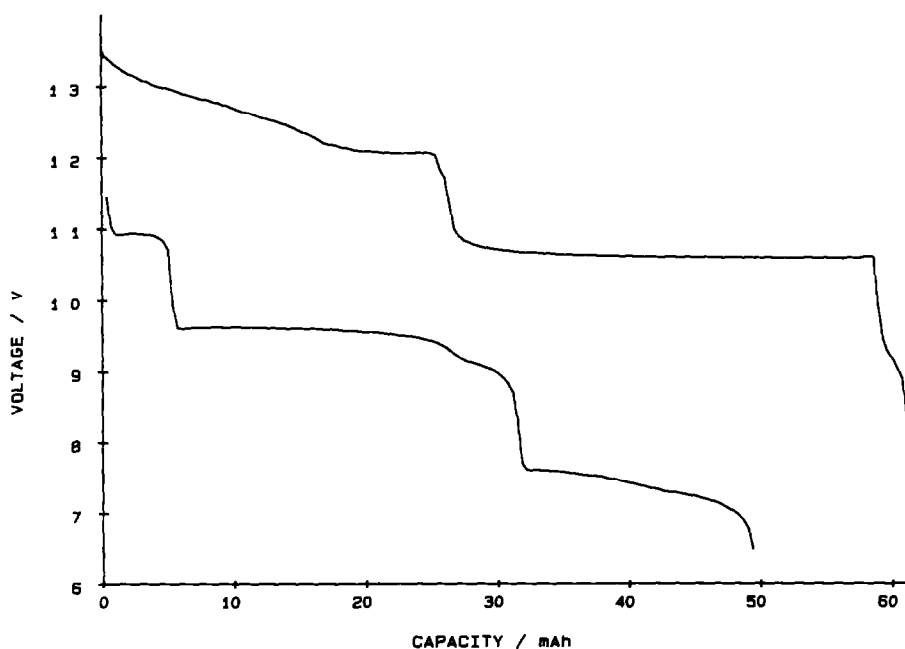

Fig 4 Charge (upper) and discharge (lower) curves obtained during continuous cycling of the same electrode as in Fig 3 against an aluminium counter electrode at C/5 The electrolyte contained 1 wt % sulfur in this case The curves shown here are 7 cycles on from those in Fig 3 and show a loss of electrode capacity

We have also studied the charge/discharge behaviour of type (b) planar electrodes incorporating either Fe or Ni as the transition metal In these electrodes the current flow lines are parallel to each other and perpendicular to the electrode–electrolyte interface, as in the flat-plate cell design which has been proposed recently to achieve improved performance in sodium–metal chloride cells [15] Thus the study of our type (b) electrodes is directly relevant to expected developments in the design of full-sized operational cells and batteries The performance of a type (b) $NiCl_2/Ni$ electrode is shown in Fig 5 Again, polarization losses are small and the charge/discharge curves are flat over most of the charge and discharge The electrode was cycled at $C/9$, a slower rate than previously, which allowed for a more efficient initial utilization of NaCl ($> 90\%$ for the initial charge in this case)

As with the type (a) electrodes, the type (b) electrode of Fig 5 showed a slow decline in capacity over about 20 cycles It is clearly important to determine the cause of the capacity losses in order to devise a strategy to counter the problem The most obvious possible cause is the dissolution of either solid $NiCl_2$ or NaCl from the electrode into the melt, and its transport into the bulk electrolyte Transition metal dichlorides (e g , $NiCl_2$, $FeCl_2$ and $CoCl_2$) are known to have very low solubility in neutral or slightly basic chloroaluminate melts [16–18], however, over many charge/discharge cycles
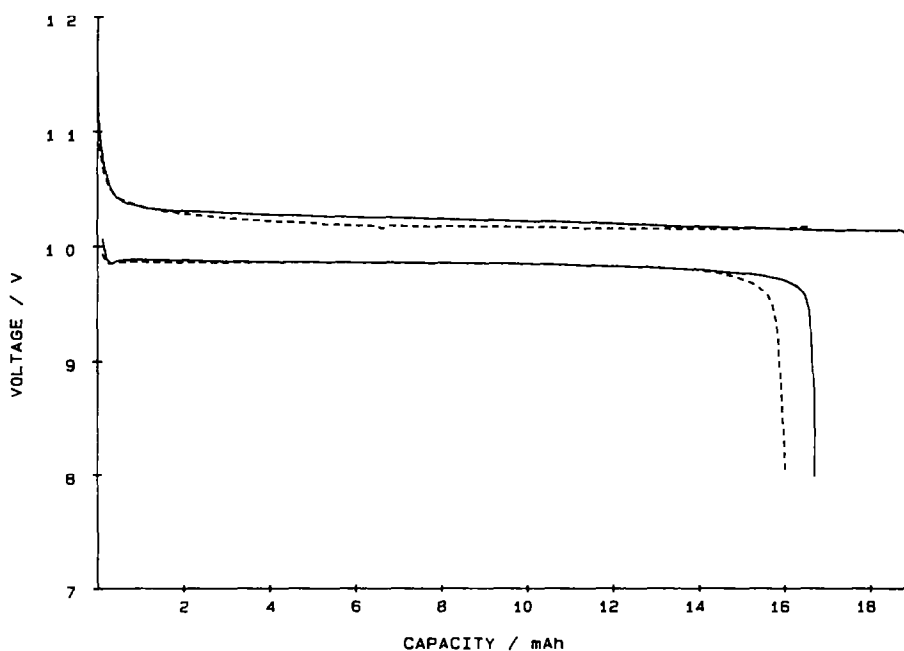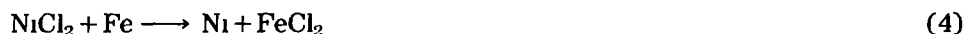

Fig 5 Charge (upper) and discharge (lower) curves for the first two cycles of a type (b) $NiCl_2/Ni$ electrode against an aluminium counter electrode at $C/9$ (2 2 mA) Nominal capacity = 19 5 mA h, electrode thickness 5 mm (solid lines, first cycle, dashed lines, second cycle)

the cumulative effect of dissolution of NiCl$_2$ could be appreciable While some of the capacity loss noted in our experiments may be due to such solubility effects, there is evidence that other causes are also important For example, the electrode of Fig 5 showed a discharge capacity of 47% at the nominal 5-h rate, after a period of continuous cycling When the rate was reduced to a 9-h rate, a capacity of 79% was observed This large discrepancy between the capacities is suggestive of a kinetic limitation on the electrode performance Further studies are presently in progress, with a view to identifying more closely the causes of capacity losses in these electrodes, and possibly remedying the problem.

Another example of the utility of the present type of cell is illustrated by the open circuit voltages plotted in Fig 6 In this case two MCl$_2$ electrodes were used, where M = Fe and Ni. After fabrication of these type (a) electrodes in the usual way, the Ni electrode was anodically converted to NiCl$_2$, using an Al counter electrode, before the Fe electrode was introduced to the cell The cell was then discharged in stages, with the voltage being measured after 30 min at open circuit following each discharging stage The overall discharge reaction in this cell is

$$NiCl_2 + Fe \longrightarrow Ni + FeCl_2 \tag{4}$$

The measured open circuit voltage shows two clear discharge plateaus, separated by about 13 mV A similar 12 mV step has been reported in the
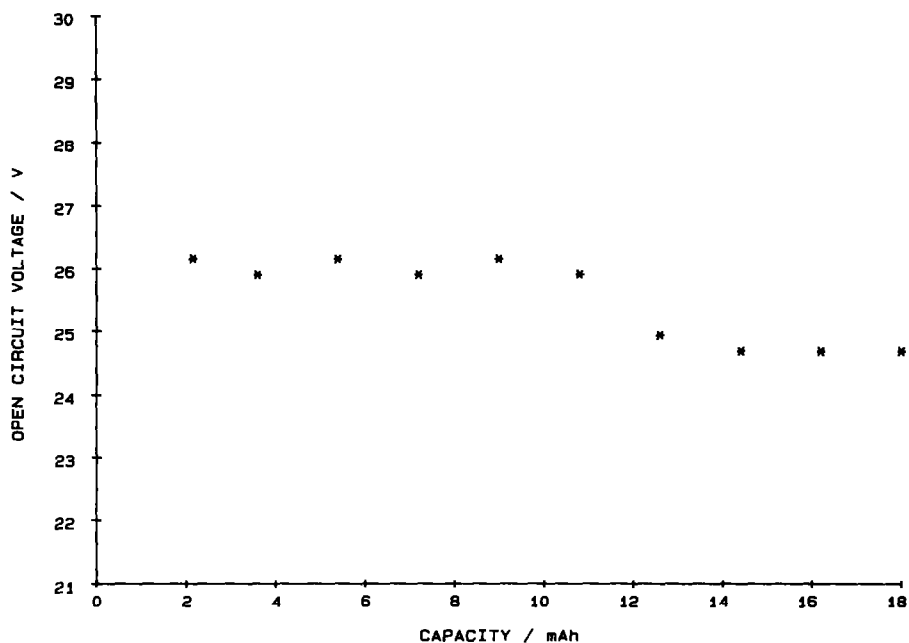

Fig 6 Open circuit voltages for an iron–nickel cell consisting of type (a) electrodes, discharged stepwise at 10 mA Voltages were measured after 30 min at open circuit
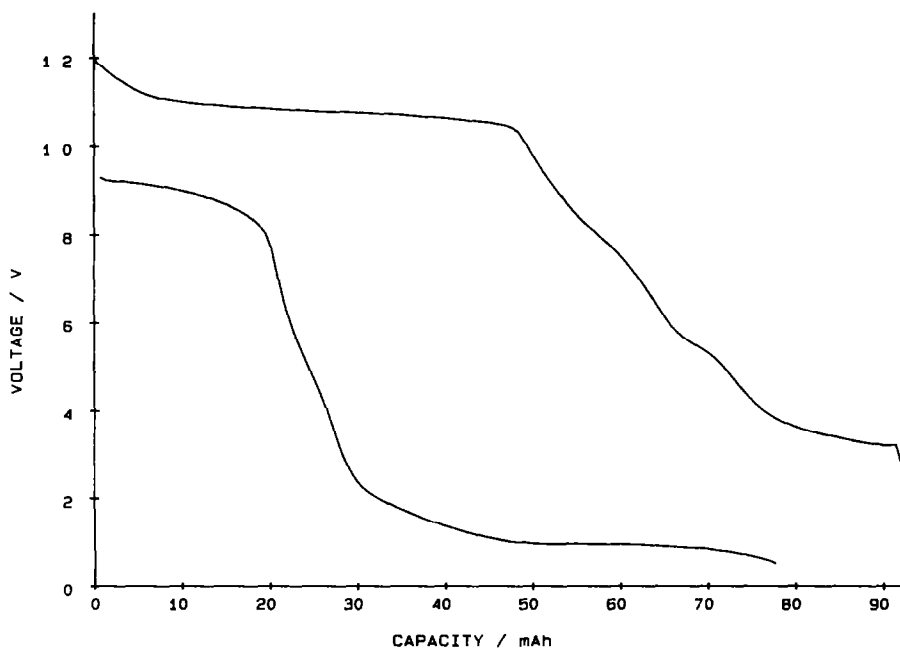
Fig 7 Charge (upper) and discharge (lower) curves for a type (a) VCl₂/V electrode against an aluminium counter electrode at C/5 7 (20 mA) Electrode contained 0 108 g V 0 373 g NaCl and 0 187 g Ni, giving a nominal capacity of 114 mA h

oxidizes unreacted V to VCl_2 The direct anodic conversion of V to VCl_2 is clearly very inefficient, though whether the problem is one of electrode design or is due to inherent kinetic limitations of this couple, is not clear from the present experiments The difficulty of the direct anodic oxidation of V to VCl_2 obviously has unfavourable implications for the operation of a cell such as that represented by reaction (8) Reactions (7) and (8) also suffer from low cell e m f values and relatively expensive reagents, and are unlikely to be of any practical value

Conclusions

The undivided cell described above can be of value for short term electrochemical studies of MCl_2/M electrodes Before it can be used for extended cycling tests, the problem of progressive capacity losses will have to be overcome Tests are currently underway using a cell design where the cathode is separated from the bulk melt by either a porous glass diaphragm or by β''-alumina The results of these studies should be useful in establishing whether or not solubility of cathode reagents is a major cause of capacity loss Post mortem studies on cycled cathodes should also be of value in this respect

Of the MCl_2/M electrodes we have studied, Ni and Fe demonstrate superior reversibility to Mn and V

Acknowledgements

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