

## THE LITHIUM-SULFURYL CHLORIDE BATTERY: DISCHARGE BEHAVIOUR

G. RAZZINI and S. ROVELLINI

*Centro Studio Processi Elettrodici del C.N.R., Polytechnic of Milan (Italy)*

F. ALESSANDRINI, B. DI PIETRO and B. SCROSATI

*Istituto di Chimica Fisica, University of Rome (Italy)*

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### Summary

The properties of the lithium-sulfuryl chloride battery have been examined in terms of discharge performance and characteristics. The results indicate that the  $\text{Li}/\text{SO}_2\text{Cl}_2$  system is intrinsically capable of delivering large current outputs at high voltages. Upon storage and long term discharge, however, the cell is affected by the two major polarization phenomena typical of lithium-inorganic electrolyte batteries, *i.e.*, the passivation of the anode and the inactivation of the cathode.

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### Introduction

Lithium-inorganic electrolyte batteries are of great technological interest since they are characterized by high energy density values. The majority of the investigations in this field have been concentrated on the lithium-thionyl chloride system which has been extensively studied with respect to general discharge behaviour and performance [1 - 3], passivation of the anode [4, 5], storage [6] and safety [7].

No comparable attention has so far been given to the lithium-sulfuryl chloride system despite certain intrinsic advantages such as higher voltage and lower toxicity. In addition, the results reported on this system are often contradictory, especially in the definition of the discharge characteristics.

It therefore appeared to us to be of interest to reconsider the  $\text{Li}/\text{SO}_2\text{Cl}_2$  cell with a systematic investigation of its properties. In this paper we report results concerning its discharge behaviour.

### Experimental

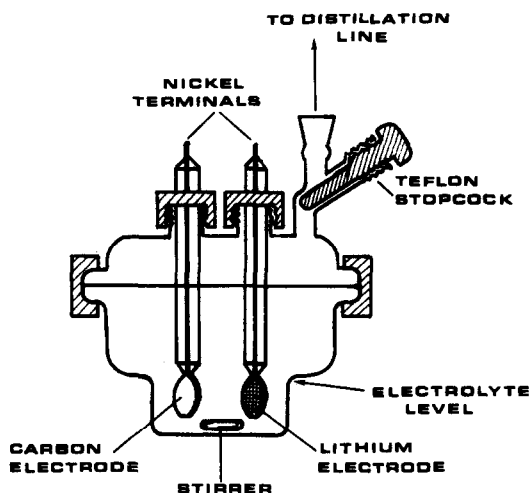
The electrolyte,  $\text{LiAlCl}_4$ , was prepared by direct reaction between  $\text{AlCl}_3$  and  $\text{LiCl}$ . Anhydrous aluminum chloride, a Fluka AG extra pure product,

was used as received. Lithium chloride, Merck reagent grade, was dried under vacuum at 150 °C for 48 h. The two components were intimately mixed in an argon glove-box and transferred to a glass tube which was then placed in a glass envelope. The  $\text{LiCl}-\text{AlCl}_3$  mixture was first heated at 100 °C under a chlorine stream for 6 - 8 h and then melted, still in the presence of the chlorine atmosphere. The product was cooled under a dry nitrogen stream. The final product had a pale yellow colour which turned white upon grinding. The X-ray powder analysis of the material so obtained showed all the major lines of  $\text{LiAlCl}_4$ , in accordance with the values reported in the literature [8].

Alternatively, electrolyte solutions were obtained by directly dissolving dry  $\text{LiCl}-\text{AlCl}_3$  mixtures in the purified solvent. The latter,  $\text{SO}_2\text{Cl}_2$ , is known to decompose easily into  $\text{SO}_2$  and  $\text{Cl}_2$ , thus assuming a yellow colour. Particular care was therefore devoted to the purification of the solvent and to the achievement of pure electrolyte solutions.

Sulfuryl chloride, a C. Erba reagent grade product, stored over molecular sieves, was degasified and then distilled under reduced pressure into a flask containing lithium chips. The colourless solvent so obtained was transferred into the electrochemical cell either by direct distillation or by a graduated syringe, according to the type of cell used.

Two types of cells, schematically represented in Figs. 1 and 2, were adopted for the electrochemical tests. The two-electrode glass cell was used for long term storage and discharge tests while the three-electrode Teflon cell was used mainly for the polarization studies.



glass cell

Fig. 1. Two-electrode glass cell.

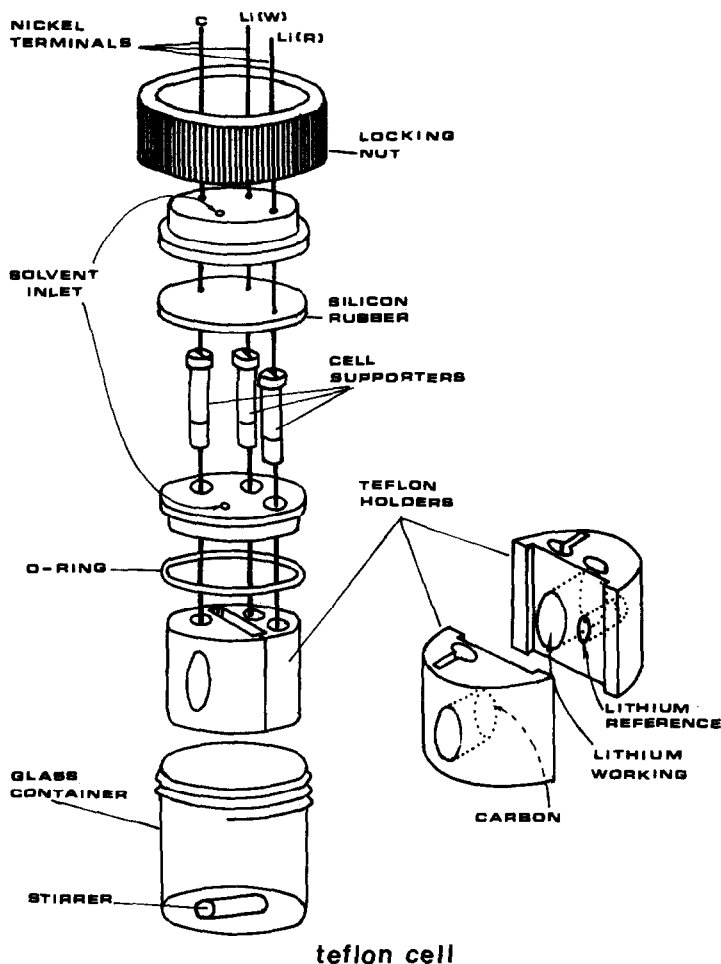


Fig. 2. Three-electrode Teflon cell.

The glass cell was assembled in the glove-box by loading the bottom part with known amounts of  $\text{LiAlCl}_4$  (or, alternatively, of the  $\text{LiCl}-\text{AlCl}_3$  mixture) and a magnetic stirrer. Following the procedure described by Behl *et al.* [1], the lithium electrode was formed by compressing two lithium disks (Foote Mineral Co.) onto a nickel screen to which was soldered a nickel wire terminal. The wire was inserted into a glass capillary tube up to the lithium pellet and sealed with epoxy resin. The carbon electrode was prepared by pressing a blend of carbon, a binder (Teflon dispersion) and water, maintained in a non-woven polypropylene envelope, onto the two sides of a nickel disk to which was soldered the nickel wire terminal. The electrode was dried in a vacuum oven at  $120^\circ\text{C}$  for 14 h, and the terminal was then inserted into a glass tube and sealed, as described for the lithium electrode.

The two electrodes were placed in the cell *via* the 'Sovirel' joints situated in the top part. The joints allow vertical movement of the glass

tubes and therefore of the two electrodes which were raised approximately up to the centre of the cell. The latter was transferred to the distillation line to receive, *via* the side tube, the purified solvent in quantity sufficient to obtain a 1.5M solution of  $\text{LiAlCl}_4$ . The complete dissolution of the salt was achieved with the help of the magnetic stirrer. The electrodes were then immersed in the solution and the cell located in a suitable desiccator (either containing  $\text{P}_2\text{O}_5$  or kept under vacuum) for the electrochemical tests.

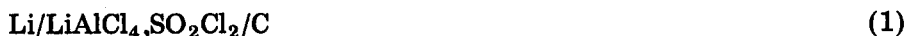
The Teflon cell (see Fig. 2) was also entirely assembled in the glove-box. In this case, however, the lithium reference and the lithium working electrodes, as well as the carbon electrode, were respectively pressed onto the nickel screen (provided with nickel terminal wires) directly into Teflon holders. In this way only the active materials face the electrolyte and the possibility of leaking to the nickel support is avoided. Furthermore, the surface of the electrodes remains well defined and the reference electrode is conveniently situated with respect to the other two.

To complete the cell, the two Teflon holders are brought into contact and placed in a glass container in which was placed a known amount of  $\text{LiAlCl}_4$  (or, alternatively, of the  $\text{LiCl}-\text{AlCl}_3$  mixture) and a magnetic stirrer. As depicted in Fig. 2, the top of the glass container was then sealed first by an O-ring, followed by a silicone rubber disk sandwiched between two Teflon covers, the latter having holes conveniently located to accommodate the nickel terminals (*via* cell supports) and to allow the introduction of the solvent. Finally, the sealing was assured by a threaded plastic locking nut.

A known amount of the solvent, again to form a 1.5M  $\text{LiAlCl}_4$  solution, was then syringed into the cell. After stirring to achieve complete dissolution, the cell was housed in the desiccator for the electrochemical tests.

## Results and discussion

### The cell



had a stable open circuit voltage (OCV) of 3.96 V at room temperature. In certain cases the OCV reached values around 4.0 V, and this is probably attributable to traces of chlorine in the solvent.

The overall polarization of the cell was tested by submitting it to progressively increasing current pulses (2.5 min) and recording the voltage attained under load as well as the time to recover the original OCV value after each pulse. The results, shown in Fig. 3, indicate that the polarization of the cell is mainly ohmic in nature over the range of current density examined. In fact the polarization curve is linear and the OCV value is rapidly attained after current interruption.

The above described behaviour, however, applies only to freshly made cells and has to be referred to their intrinsic, short term performances. Upon storage and long term discharge the  $\text{Li}/\text{SO}_2\text{Cl}_2$  cell, as with, generally, all the

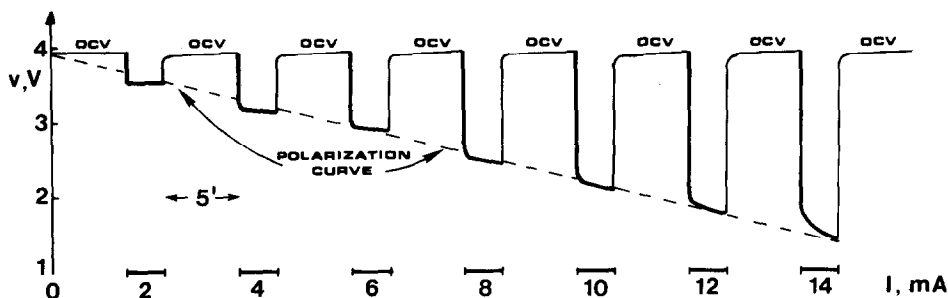


Fig. 3. Polarization test of a freshly made  $\text{Li/LiAlCl}_4, \text{SO}_2\text{Cl}_2/\text{C}$  cell at  $25^\circ\text{C}$ . Electrode surface:  $1.2\text{ cm}^2$ .

lithium-inorganic solvent batteries, is affected by two major polarization phenomena, *i.e.*, the passivation of the anode and the inactivation of the cathode.

As widely described in the case of the  $\text{Li/SOCl}_2$  cell [4], the lithium electrode is readily passivated upon contact with oxychloride electrolytes by the formation of a poorly conductive film on its surface. This film exerts a protective action which prevents further corrosion of the electrode. On the other hand, the film has to be dissolved or fractured to allow current flow and this causes a voltage delay at the initial stage of the discharge, which becomes particularly severe for cells stored for prolonged times and/or discharged at low temperature [9].

This effect is shown in the case of the  $\text{Li/SO}_2\text{Cl}_2$  system in Fig. 4 where the voltage response of type (1) cells submitted to short current pulses after progressive storage times, and to continuous discharge after 70 h of storage, is illustrated.

The initial voltage delay of the cell is entirely associated with the anode passivation with no contribution from the cathode, as demonstrated in Fig. 5, where single electrode polarizations, determined *vs.* a Li reference electrode, are reported for the discharge at  $5\text{ mA cm}^{-2}$  of a  $\text{Li/SO}_2\text{Cl}_2$  cell stored for 70 h.

The progressive anodic passivation of the  $\text{Li/SO}_2\text{Cl}_2$  cell upon storage is further shown in Fig. 6, where polarization curves of the lithium electrode, obtained after various periods of contact with the electrolyte, are compared. This figure also shows how current flow through the electrode results in the partial dissolution of the passivation film, thus improving its polarization behaviour.

In the case of the  $\text{Li/SOCl}_2$  system it has been found that the anode passivation film consists primarily of  $\text{LiCl}$  [2, 4]. However, in addition to  $\text{LiCl}$ , traces of S have also been detected in the film [10] and it has been suggested that sulphur, being a possible product of the cell reaction, could diffuse to the Li anode, thus contributing to its passivation [9].

A similar hypothesis can also apply to the  $\text{Li/SO}_2\text{Cl}_2$  case since we have detected by X-ray analysis both  $\text{LiCl}$  and S on the lithium electrode surface of cells stored after partial discharges.

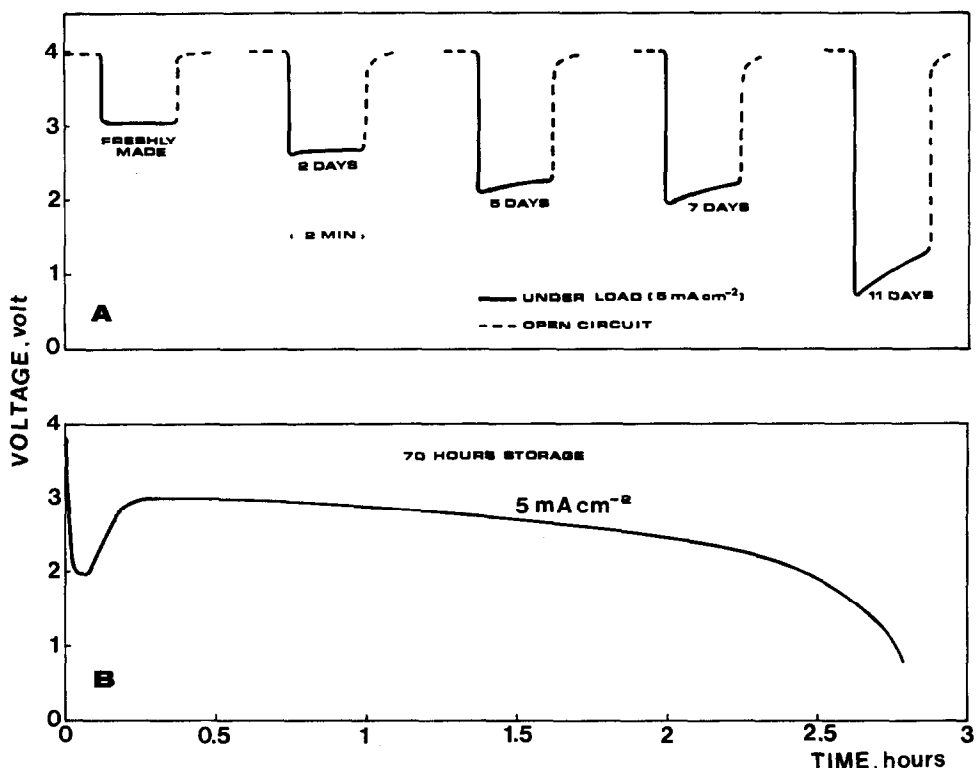


Fig. 4. Discharge behaviour of the Li/LiAlCl<sub>4</sub>·SO<sub>2</sub>Cl<sub>2</sub>/C cell under short current pulses after progressive storage time (curves A) and under continuous load after 70 h storage (curve B).

As shown in Fig. 5, the polarization of the Li/SO<sub>2</sub>Cl<sub>2</sub> cell at the end of the discharge is almost entirely due to the carbon electrode. The polarization of the carbon electrode is probably due to the deposition of solid discharge products which progressively reduce the activity of its surface. This effect becomes more severe as the rate of discharge increases.

The above considerations are supported by the results reported in Fig. 7. The voltage of a type (1) cell, discharged at 5 mA cm<sup>-2</sup>, decayed below 2 V after 3 h, giving only 3% of the theoretical capacity\*. However, after a short interval to recover the original OCV, the cell satisfactorily supported a further discharge at a lower rate, *i.e.*, 1 mA cm<sup>-2</sup>, delivering another 4% of the theoretical capacity. The cell was then submitted to a formal recharge by passing current (1 mA cm<sup>-2</sup>) in the opposite direction to that of discharge. During this process the cell voltage stabilized around 4.3 V, and the following discharge, still at 1 mA cm<sup>-2</sup>, was again satisfactory up to a length of time comparable with that of the 'recharge' (see Fig. 7(B)). This procedure was repeated several times and the cell always recovered its discharge capabilities

\*Calculated for the lithium electrode on the basis of process (5).

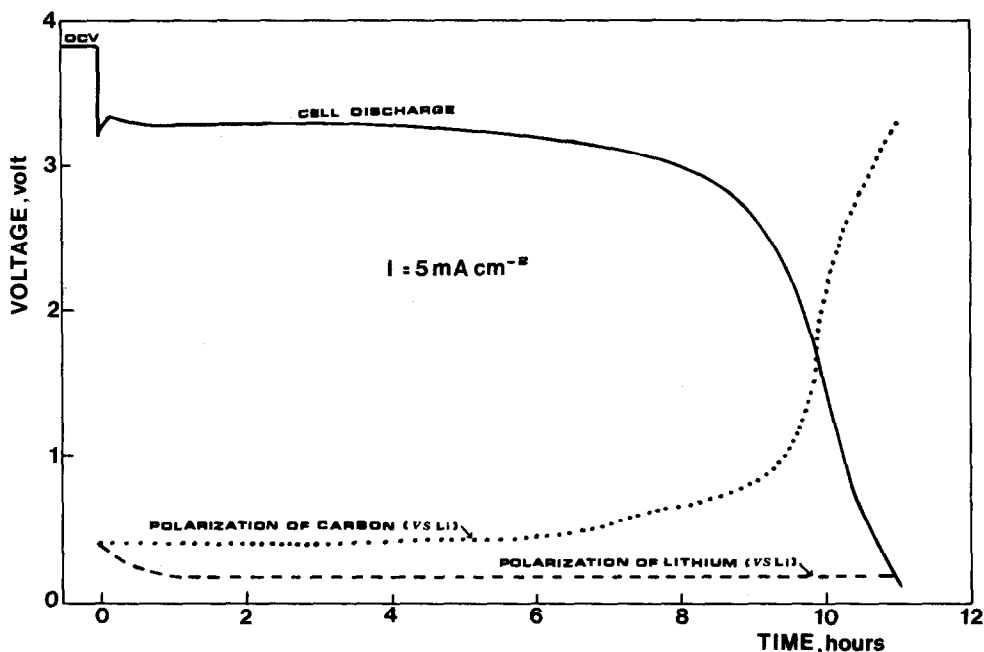


Fig. 5. Lithium and carbon electrode polarization (*vs.* Li) during the discharge of the Li/LiAlCl<sub>4</sub>, SO<sub>2</sub>Cl<sub>2</sub>/C cell.

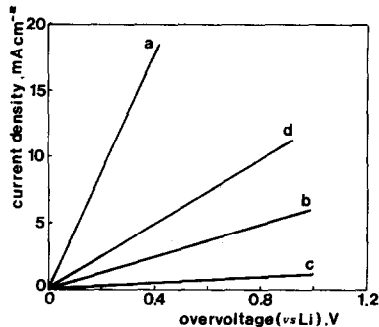


Fig. 6. Polarization of the lithium electrode in the Li/LiAlCl<sub>4</sub>, SO<sub>2</sub>Cl<sub>2</sub>/C cell at 25 °C. Curve a, freshly made cell; curve b, after 17 h of storage; curve c, after 65 h of storage; curve d, after 65 h of storage followed by one hour discharge under 1 kΩ load.

after each 'charging' cycle. The total capacity delivered after all the discharges, however, still remained a fraction of the theoretical value.

It is therefore probable that the effect of passing current through the cell is that of an electrochemical regeneration of the carbon electrode surface, possibly with the partial dissolution of products deposited during discharge. A similar effect has been noticed also in the case of the Li/SOCl<sub>2</sub> cell [11]. The 'charging' cycles may then be considered more realistically as 'regeneration' cycles.

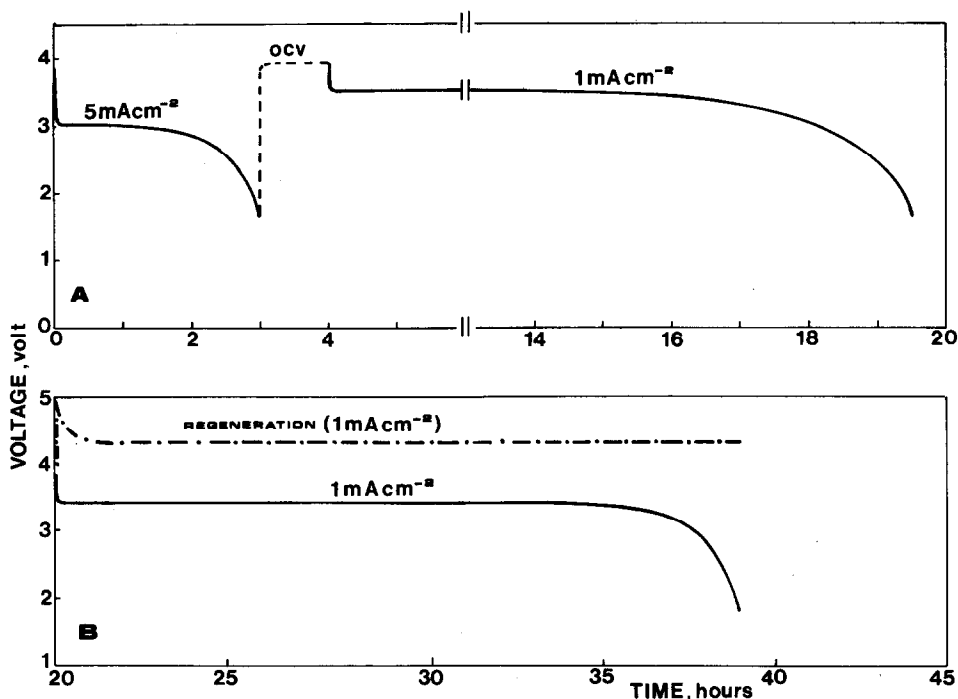


Fig. 7. Progressive discharge behaviour of the Li/LiAlCl<sub>4</sub>,SO<sub>2</sub>Cl<sub>2</sub>/C cell at 5 mA cm<sup>-2</sup> and at 1 mA cm<sup>-2</sup> (curves A) and after electrochemical regeneration (curve B).

The phenomenon is undoubtedly of interest and deserves further investigation. To carry out this investigation in a correct way, a precise knowledge of the nature of the discharge products is needed. Unfortunately, there is still some disagreement between the conclusions reached by the various authors who have investigated the discharge process of the Li/SO<sub>2</sub>Cl<sub>2</sub> cell.

Behl [12], as well as Gilman and Wade [13], have suggested the following reaction



on the basis of cyclic voltammetry of the carbon electrode and of the analysis of the solid cathodic products, respectively.

On the other hand, Salmon and Ramsay [14], again as a result of cyclic voltammetry and coulometric studies, proposed the following reaction sequence



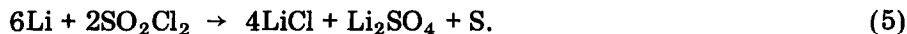
and, in total,





suggesting that reaction (3) is probably occurring at a high rate and reaction (4) at a slow rate.

Finally Auburn and Marincic [2] suggested the possible decomposition of  $\text{Li}_2\text{S}_2\text{O}_4$  into sulphur and lithium sulphate, according to the reaction



After the discharge of cells examined in our laboratories we have observed the presence of yellow crystals, possibly identified as sulphur, on the carbon electrode pellet and this might support a process of type (5). However, the complex nature of the  $\text{Li}/\text{SO}_2\text{Cl}_2$  system, in particular in relation to the instability and reactivity of the solvent, tends to suggest that a general, exact definition of the discharge process is not easily achievable. In fact, it is quite possible that the nature of the discharge products is dependent on critical experimental factors, such as the type of components of the cathodic mixture and their relative composition as well as on the morphology of the final cathodic pellet.

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