

## The SWING system, a nonaqueous rechargeable carbon/metal oxide cell

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### Abstract

The SWING system contains an anode consisting of a carbonaceous material and a cathode made from lithium-containing transition metal oxides, which are either manganese-, nickel-, or cobalt-based. The cell operates with a liquid organic electrolyte and is cycled between 2.7 and 4.3 V, respectively, with an average charge/discharge voltage of about 3.5 V. Instead of metallic lithium, the cell is using the available lithium ions from the cathode for cycling. A high faradaic cycling efficiency of  $>0.998$  of the well-balanced cell is observed and allows for more than 600 cycles (100% DOD). Using lithiated manganese spinels at the cathode instead of cobalt or nickel compounds would be desirable in maintaining an environmentally-compatible cell. Advances in increasing the stability of such manganese compounds have been achieved by doping with cobalt, for instance. Main development work in the future has to be focused on the stability of the electrode materials upon storage of the charged SWING cell at high temperatures.

### Introduction

The interest in high energy density batteries has motivated the investigations of rechargeable lithium systems in the past [1]. Through much effort, the development of cells using metallic Li or Li alloys as anode materials was advanced based on attractive theoretical performance data like 3185 W h/l and 1027 W h/kg for a Li/MnO<sub>2</sub> system, for instance. Unfortunately, disadvantages like the poor cycleability of metallic Li and the problems of dendritic growth have not been solved up to now.

Metallic anodes have been replaced by selected carbon materials to overcome some of these disadvantages[2]. In conjunction with a cathode made from a lithiated transition metal oxide like LiCoO<sub>2</sub>, for instance, rechargeable Li cells have been built where Li ions swing between both intercalating electrodes upon cycling [3]. This mechanism allows for high cycle life with some reduction of energy density. It offers an attractive compromise in overall cell performance and safety. The SWING process is schematically depicted in Fig. 1. The following paragraphs will describe investigations regarding electrode materials for SWING cells and give preliminary data on cell performance.

### Experimental

All experiments were carried out in an argon glove box. If not stated otherwise, potentials refer to the Li/Li<sup>+</sup> electrode. Solvents and salts used for the electrolytes

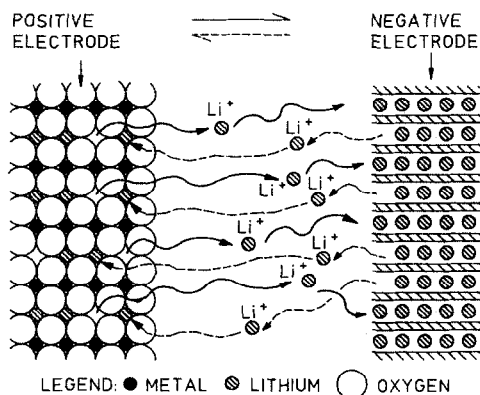


Fig. 1. Schematic description of the SWING system.

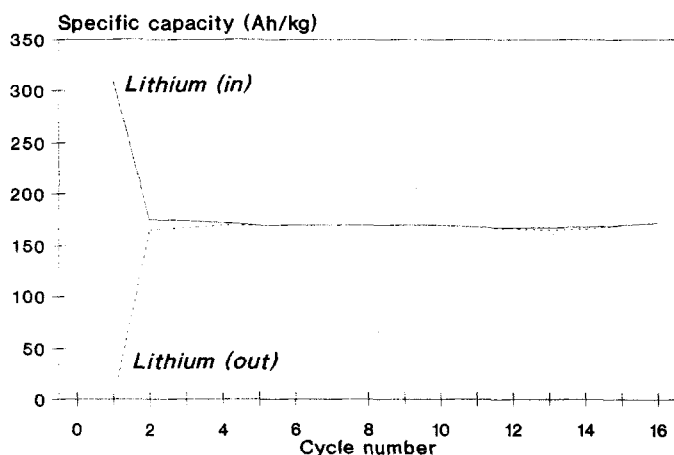


Fig. 2. Cycling behavior of a C/Li coin-type cell; charge/discharge current:  $0.5 \text{ mA/cm}^2$ , cell voltage range : 0 to 1 V.

were dried, prior to use, by conventional means and kept under argon. Lithiated transition metal oxides were prepared according to methods given in refs. 4–6. The carbonaceous material was a specially-prepared compound with a turbostratic structure. Specific capacities were determined mainly in coin-type cells of size 2025 with a 1 M  $\text{LiClO}_4$ /propylene carbonate (PC) electrolyte, if not stated otherwise, by using an in-house built computer-controlled current supply and data logger.

## Results and discussion

Representative cycling results of the negative electrode versus Li are shown in Fig. 2. It is striking that upon the first lithiation step the carbon anode intercalates 309 mA h/g (active material). However, during the following Li extraction process only 179 A h/kg (active material) of the initially reacted h Li is available. Even an

increase of the electrode potential up to 4 V versus Li/Li<sup>+</sup> cannot recover all the Li: there is still a remaining loss of 23%. This irreversible loss is attributed to two mechanisms: the formation of a protective solid electrolyte interface [7-9] and a residue compound within the carbon electrode [10].

Figure 3 shows the charge/discharge curve of a carbon electrode against Li. After the above-mentioned conditioning the carbon anode shows an attractively high faradaic efficiency of >0.998 when cycled between 0 and 1 V versus Li. This voltage range has been chosen to simulate the expected conditions in SWING cells on the anode. The ohmic polarization during charge and discharge with a current density of 1 mA/cm<sup>2</sup> accounts for approximately 60 mV.

The high faradaic efficiency reflects itself in the comparison of the secondary capacities  $K_s$  of metallic Li and a carbon anode. The secondary capacity depends upon the primary capacity  $K_p$ , the demanded cycle number  $Z$ , and the cycling efficiency  $\beta$ , the relationship is:

$$K_s = \frac{K_p}{1 + Z - Z\beta} \quad (1)$$

where  $K_s$  denotes for secondary capacity,  $K_p$  for primary capacity,  $Z$  for demanded cycle number, and  $\beta$  for cycling efficiency.

In Fig. 4 the secondary capacity values are given as a function of cycling efficiency stating that 500 full cycles should be reached. It is obvious the  $K_s$  value for Li with  $\beta=0.97$  gives 241 A h/kg instead of  $K_p=3860$  A h/kg, thus demanding a sixteen-fold surplus of metallic Li in the rechargeable cell. By comparison, a carbon anode with  $\beta=0.998$  gives a  $K_s$  value of 170 A h/kg instead of  $K_p=364$  A h/kg. Therefore, only a twofold surplus is necessary.

The above description highlights one of the major advantages of using a carbon anode: a SWING cell will only use a small amount of active Li and will simultaneously offer a high cycle life.

In order to meet the goal of achieving an average cell voltage of 3.5 V in the SWING system, the charge/discharge behavior of the carbon anode (Fig. 3) demands a cathode material with a working potential of about 4 V versus Li/Li<sup>+</sup>. In Fig. 5

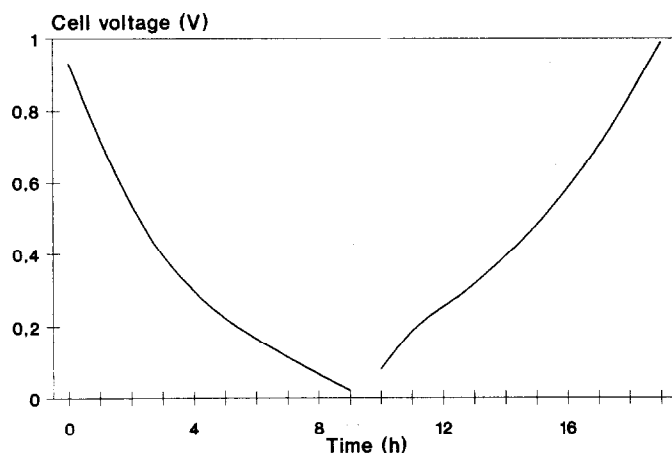


Fig. 3. Voltage behavior of a C/Li coin-type cell; charge/discharge current: 0.5 mA/cm<sup>2</sup>.

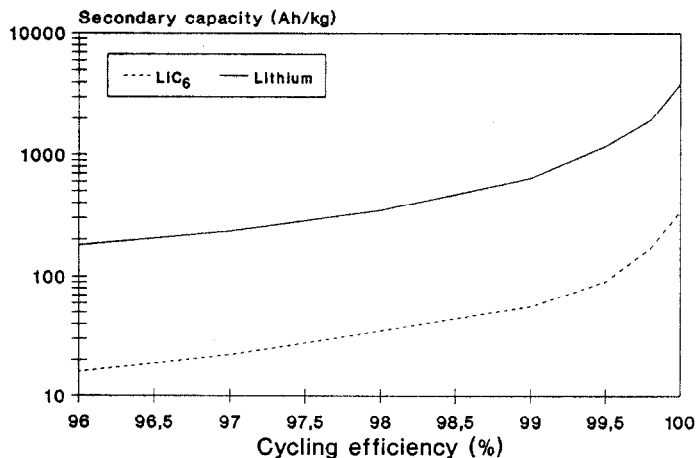


Fig. 4. Secondary capacity  $K_s$  as function of cycling efficiency given for 500 full cycles.

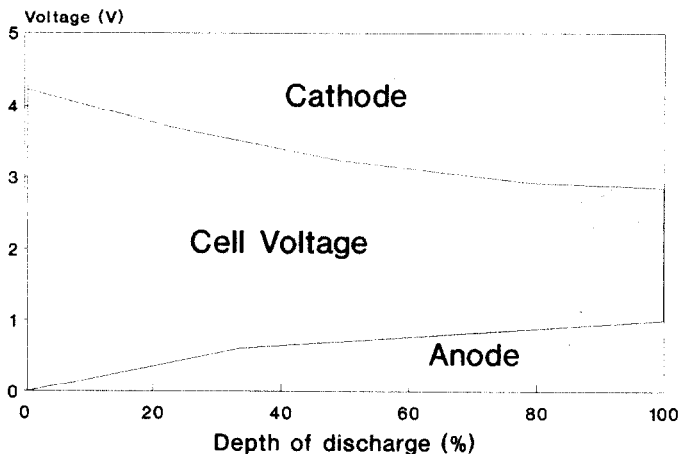


Fig. 5. Schematic behavior of electrode potentials and cell voltage for the SWING system.

this concept is depicted schematically. The resulting cell voltage will accordingly sweep between about 4 V in the charged and about 3 V in the discharged state. The additional requirement regarding the cathode is that the available amount of Li in the cell should be initially stored within the cathode material, thus allowing the cell to be assembled in air.

In Fig. 6 the working principle of a SWING cell is schematically described. Starting with Li-free carbon anode and a lithiated cathode, the cell is conditioned during the first charge by reacting all the available Li in a specified potential range with the negative electrode. In the following discharge step, some Li remains irreversibly lost resulting in a reduced cycleable Li amount, *i.e.*, cell capacity. However, as stated above this amount of Li is very efficiently cycled over the next intercalation/extraction processes with a loss of <0.2% of Li per cycle.

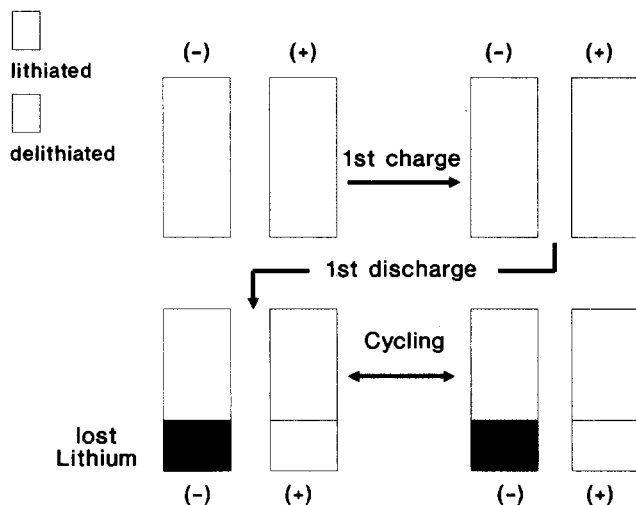


Fig. 6. Schematic description of the lithium distribution in the SWING system electrodes during cycling.

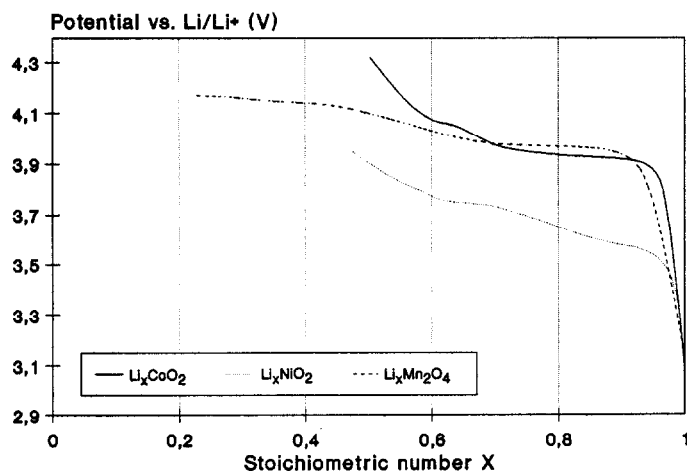


Fig. 7. Open-cell voltages of cathode materials suitable for the SWING system.

There are only a few known inorganic compounds which fulfill the above mentioned constraints: Li-containing oxides based on nickel, cobalt or manganese. In Fig. 7, the measured open-cell voltage (OCV) curves for the three pure oxides  $\text{LiNiO}_2$ ,  $\text{LiCoO}_2$ , and  $\text{LiMn}_2\text{O}_4$  are given. All of them offer most of the cycleable Li in the potential range between 3 and 4.2 V.

For environmental reasons manganese compounds are desirable although the accessible amount Li on the 4 V plateau is in the range of 100 A h/kg, i.e., lower by 20 to 40% compared with the nickel and cobalt compounds. Another important drawback has been observed upon cycling the  $\text{LiMn}_2\text{O}_4$  spinel versus Li in the cell voltage range from 3.3 to 4.2 V. This concerns the structural stability of the material

which has been found to be poor over prolonged cycling. We observed a slow dissolution of the manganese compound which results in a continuous loss in capacity (see Fig. 8).

To overcome this problem, the effect of doping the spinel structure with foreign metal atoms like cobalt has been investigated. Cobalt has been chosen because, among other reasons, an increase of the manganese(IV):manganese(III) ratio, within the otherwise undisturbed spinel structure, was expected. This would result in a stabilization of the host structure which might be pronounced especially at high degree of delithiation.

In Fig. 9 the observed lattice constant of the different cobalt-doped manganese spinel compounds and the cycleable capacity in the 10th cycle versus a metallic Li anode are given. As can be seen, a compound with a composition of  $\text{Li}_{0.954}\text{Co}_{0.151}\text{Mn}_{1.84}\text{O}_4$

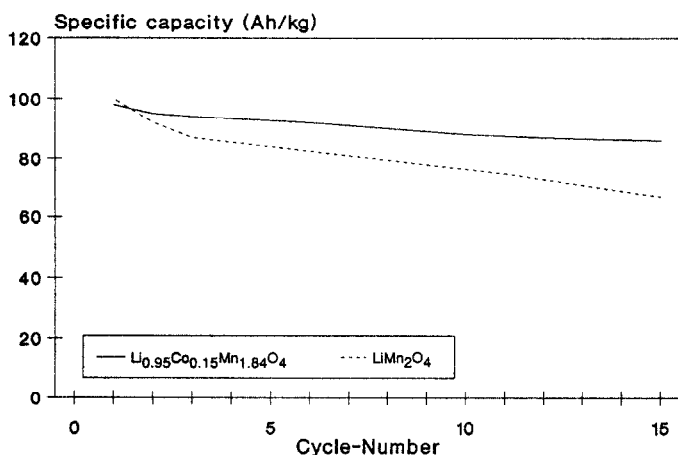


Fig. 8. Cycle life of a  $\text{Li}/\text{LiMn}_2\text{O}_4$  and a  $\text{Li}/\text{Li}_{0.954}\text{Co}_{0.151}\text{Mn}_{1.84}\text{O}_4$  cell; charge/discharge current:  $0.5 \text{ mA}/\text{cm}^2$ , cell voltage range: 3.3 to 4.3 V.

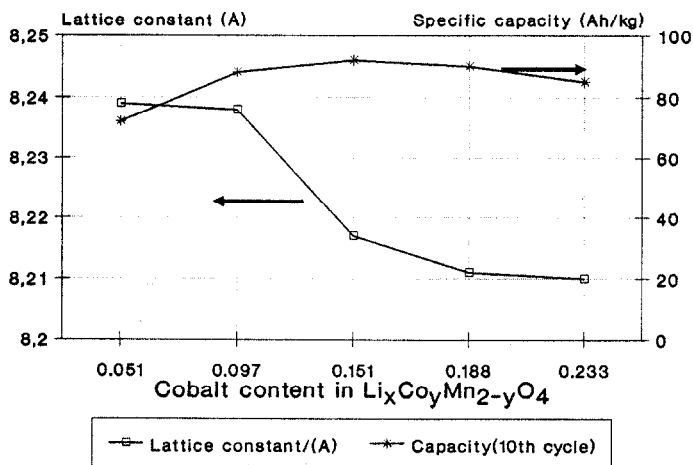


Fig. 9. Capacities and lattice constants for cobalt-doped manganese spinel compounds ( $\text{Li}_x\text{Co}_y\text{Mn}_{2-y}\text{O}_4$ ).

with a cubic lattice constant of  $8.217 \text{ \AA}$  shows most promising results. Figure 8 depicts the first characteristic cycles achieved in a coin-type cell with a metallic Li anode of a pure  $\text{LiMn}_2\text{O}_4$  spinel and the above described cobalt-doped compound. The data confirm that doping with cobalt increases the cycling stability, offering a cycleable capacity of about  $90 \text{ mA h/g}$ .

By combining a carbon anode and the cobalt-doped manganese spinel in a coin-type cell to prepare the SWING system, we achieved the cycling results depicted in Fig. 10.

The  $\text{LiCoO}_2$  compound is another attractive cathode material. From the OCV curve (Fig. 7) a higher capacity is expected and we found a cycleable Li amount of  $120 \text{ mA h/g}$  in the cell voltage range of 3.3 and 4.1 V versus a Li anode. One main issue regarding the stability of electrode materials is depicted in Fig. 11. As is found

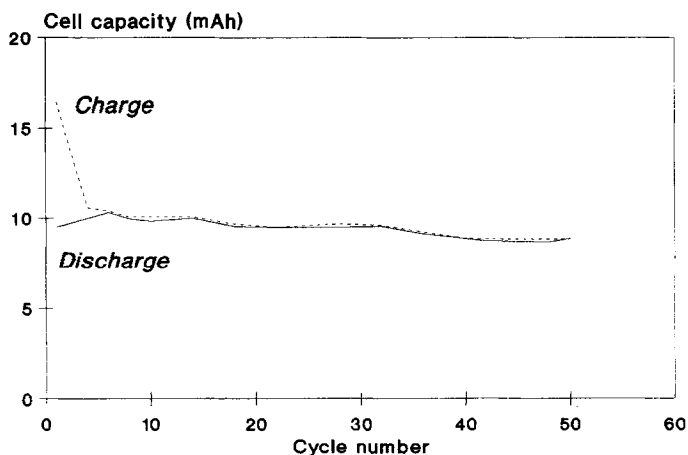


Fig. 10. Cycling behavior of  $\text{C/Li}_{0.954}\text{Co}_{0.151}\text{Mn}_{1.84}\text{O}_4$  SWING cell; charge/discharge current:  $0.5 \text{ mA/cm}^2$ , cell voltage range: 2.0 to 4.2 V.

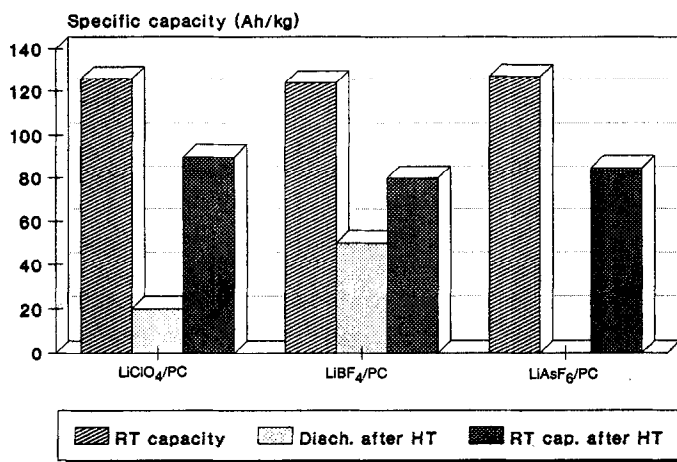


Fig. 11. Irreversible loss of capacity of a  $\text{Li/LiCoO}_2$  cell upon storage at  $60 \text{ }^\circ\text{C}$  for 10 days.

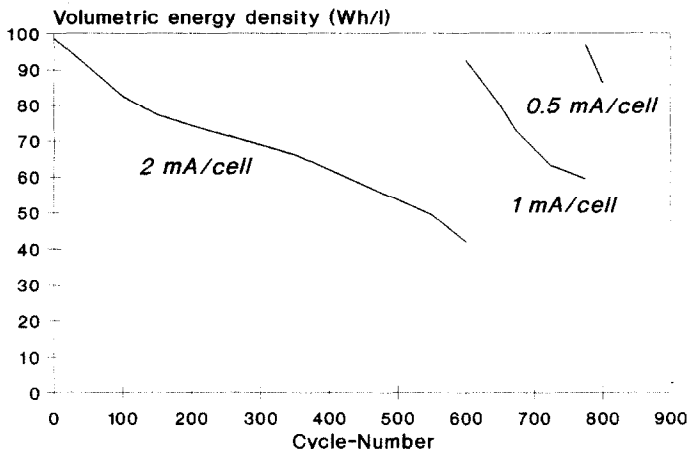


Fig. 12. Cycle life of a C/LiCoO<sub>2</sub> SWING cell for different charge/discharge currents and a voltage range between 2.7 and 4.3 V.

TABLE 1

Features of the SWING cell (Li-C/LiCoO<sub>2</sub>, 1.0 M LiClO<sub>4</sub>/PC)

|  |  |
|--|--|
| Average discharge voltage              | 3.5 V  |
| Capacity                               | 20 mA h (at 1 mA/cm <sup>2</sup> )<br>15 mA h (at 2 mA/cm <sup>2</sup> )     |
| Energy density                         | 140 W h/l (at 1 mA/cm <sup>2</sup> )<br>105 W h/l (at 2 mA/cm <sup>2</sup> ) |
| Self-discharge (25 °C)                 | 10% per month  |
| Cycle life (100% DOD)                  | 600 (50% capacity remaining)   |
| Short circuit                          | maximum current is 154 mA,<br>no capacity degradation                        |
| Safety                                 | no reaction (hot plate test 200 °C)  |
| 50% overcharge (1 mA/cm <sup>2</sup> ) | 10% loss of cycleable capacity   |
| Storage at 60 °C for 10 days           | 15% loss of cycleable capacity   |

already for the carbon anode [10] the LiCoO<sub>2</sub> cathode material also reveals stability problems upon storage of the delithiated, i.e. charged, electrode at 60 °C. In Fig. 11 the observed irreversible loss of cycleable capacity is shown for different electrolytes used. Because the same observations have also been made for other cathode materials stored in the delithiated state further development work will be focused to solve this high temperature storage problem.

In Fig. 12 the cycling behavior of a 2016-coin-type cell with a carbon anode and a LiCoO<sub>2</sub> cathode is given. The cell shows a reasonable capacity even after 600 full cycles at room temperature with a charge/discharge current density of 1 mA/cm<sup>2</sup>. The initial cell capacity can be recovered by reducing the charge/discharge rates as indicated



in Fig. 12. Therefore, we attribute the observed decline in capacity to a deterioration of the electric contacts within the pressed electrodes of the coin-type cell. The main features of the above described cell are given in Table 1.

## Conclusion

By replacing a metallic Li anode with a selected carbon compound, the faradaic efficiency of the negative electrode in a rechargeable Li battery can be increased to  $> 0.998$ . Thus, a reduction of the Li content in the cell is achieved and the expected cycle life increased. By combining the carbon anode with a Li-containing transition metal oxide compound like  $\text{Li}_{0.951}\text{Co}_{0.151}\text{Mn}_{1.84}\text{O}_4$  or  $\text{LiCoO}_2$ , a cell is constructed in which the Li ions swing between the intercalating electrode materials. The data of such a SWING cell indicate an attractive compromise in cell performance regarding cycle life, operating voltage, energy density and charge/discharge rates. First investigations concerning safety indicate that SWING cells are superior to conventional Li cells. Future development work will be focused on improving the stability of the electrode materials in order to overcome the observed losses of capacity upon storage of the charged electrodes and SWING cells at elevated temperatures.

## Acknowledgement

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