The working principle of the ZEBRA battery
During discharge, sodium ions are transported from the anode across the ceramic separator into the cathode. Nickel chloride is converted to metallic nickel, and sodium chloride precipitates. The nickel backbone of the cathode forms the electronically conductive pathway, while ionic conductivity is ensured by the molten salt electrolyte.

Cell reactions
Pos. electrode \( \text{NiCl}_2 + 2\text{Na}^+ + 2\text{e}^- \rightarrow \text{Ni} + \text{NaCl} \)
Neg. electrode \( 2\text{Na} \rightarrow 2\text{Na}^+ + 2\text{e}^- \)
Net cell reaction \( \text{NiCl}_2 + 2\text{Na} \rightarrow \text{Ni} + \text{NaCl} \)

Model validation
The process is modelled as a coupled physical / electrochemical model. Dissolution / precipitation of both NaCl and NiCl\(_2\) is considered in the mechanism. The disappearance of respective precipitate at full charge and discharge affect the concentration of reacting species in the electrolyte and are important features in the model. The chemical reaction rates of the two salts are interrelated through the concentration of their common ion. The current is described with a kinetic expression containing the nickel ion concentration and mass transport limitations between nickel and bulk electrolyte (eq. 1). The nickel and chloride ion concentrations are modelled with time dependent mass balance expressions including both the chemical and electrochemical reaction rates and mass transport of nickel ions to the nickel chloride surface. The secondary electrode reaction is not modelled here, and measurements are done above the equilibrium potential of the iron reaction.

The main elements of the model are:
- Dissolution kinetics of NaCl(s)
- Dissolution kinetics of NiCl\(_2\)(s)
- Diffusion of Ni(II) specie between Ni(s) and NiCl\(_2\)(s)
- Kinetics of electrochemical reaction of Ni(II) to Ni(s)

Validation and simulation
The model is validated with data from single cell GITT (Galvanostatic intermittent titration technique) at low rate charge and discharge (figs. 2-3). The variation in nickel and chloride ion concentration calculated in the simulation of the first discharge-relaxation sequence in fig. 2 can be seen in fig. 4. The nickel ion concentration can be seen to influence the polarization of the positive electrode, and after current is turned off, the relaxation of the nickel ion concentration occurs on the same time scale as that of the chloride ion concentration. The voltage relaxation, assumed to depend on the dissolution / precipitation reactions in the cell, can be used to deduce the precipitation rate constants of sodium chloride and nickel chloride. At low discharge rates the model can describe the cell voltage, however, as the current is increased, effects of uneven current distribution in the porous electrode not taken into account in the model worsen the model prediction of cell behaviour (fig. 5).

Conclusions
- A local kinetics model was validated with low current GITT charge and discharge experiments and used to describe cell behaviour at low rate charge and discharge.
- Nickel ion concentration at the electrode surface is a major rate limitation factor during operation.
- The relaxation time scale of the battery at current cut-off is dependent on the dissolution / precipitation of NaCl.

Fig. 1 Schematic image of cross-section of the inner structure of a battery cell. The positive electrode is enclosed by the β-alumina separator. The negative electrode fills the space between the separator and the cell casing. Left, charged. Right, discharged.

Fig. 2 Measured and simulated voltage during GITT discharge, I=2A, T = 300°C, SOC 84-36

Fig. 3 Measured and simulated voltage during GITT charge, I=2A, T = 300°C, SOC 32-72

Fig. 4 Simulated concentrations at discharge and relaxation, SOC 84

Fig. 5 Measured and simulated voltage during discharge, I=2A-6A, T = 300°C