Field Probes with In-Situ Controllable Thermal Relaxation Times

David O. Brunner[1], Simon Gross[1], Jennifer Nussbaum[1], Benjamin E. Dietrich[1], Christoph Barmet[1,2], and Klaas P. Pruessmann[1]
[1]Institute for Biomedical Engineering, University and ETH Zurich, Zurich, Switzerland, [2]Skope Magnetic Resonance Technologies LLC, Zurich, Switzerland

Introduction: NMR based magnetic field sensors have been demonstrated to measure the dynamic magnetic field evolution inside an MRI scanner with extreme accuracy[1]. Based on these measurements system imperfections as well as externally induced field perturbations can be assessed and then corrected for in post-processing[2] or by real-time field feed-back[3]. However, once the FID of the probe relaxed or got dephased, the field and the k-space trajectory cannot be tracked anymore. The probe can only be re-excited after the coherences have thermally relaxed. Otherwise occurring spurious echoes would impinge the field measurement which is based on the signal evolution of an FID in the magnetic field. When manufacturing the probes, the relaxation times of the NMR active sample are therefore adjusted by relaxation agents to the targeted repetition time in the application. Alternatively, several fast relaxing probe sets are employed in interleaved fashion which allows acquiring the magnetic field evolution continuously[4], but inflicting a suboptimal random-walk error propagation when tracking k-space trajectories. In this work we present an approach to adapt the thermal relaxation times (T_1, T_2) of NMR based field probes in-situ by use of reversible electrochemical reactions inside the probe.

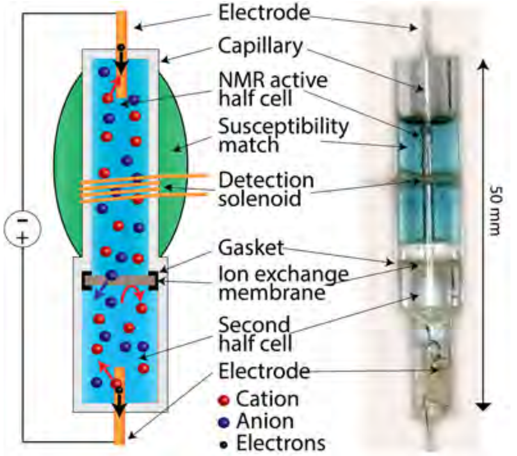

Figure 1: Scheme and prototype of the probe with tunable relaxation time.

Methods: The thermal relaxation in the field probe is adjusted by paramagnetic metal ions (dopant) that offer very low T_1/T_2 ratio maximizing the signal yield. Thereby the relaxation time is dependent on the concentration $c(X)$ and the ambient conditions of the dopant X influencing its specific relaxivity $(r^X_{1,2})$ with respect to T_1 and T_2:

$$R_{1,2} = {}^{1}\!/_{T_{1,2}} \propto r^0_{1,2} + r^X_{1,2} \cdot c(X)$$

The resulting relaxation time can hence be controlled by the concentration of the paramagnetic ions in the NMR active region. Secondary cells as employed in rechargeable batteries perform reactions in which the concentration of metal ions in the electrolyte or close to the electrode is dependent on the charging state. Similarly, a probe with controllable relaxation time was based on a microfluidic copper sulphate secondary concentration cell. The electrolyte in both half cells is aqueous copper sulphate $(Cu_2(SO_4)_2)$ where the Cu^{2+} ion acts as relaxation agent. The half cells are separated by an anion exchange membrane which lets the sulphate ions pass while hindering the copper ions from entering the other half cell. Thereby a concentration gradient between the two half-cells can be maintained. Applying a voltage to the copper electrodes oxidizes the copper at the anode increasing the concentration of Cu^{2+} in the corresponding half-cell. In turn $Cu^{2+}$is reduced at the cathode and plated onto the electrode decreasing the concentration in that half-cell. Charge is equilibrated by the exchange of sulphate ions through the membrane. By exciting and picking up the NMR signal in only one half-cell the NMR relaxation time of the probe is altering when charging/discharging the concentration cell.

The probe consists of a capillary (0.8 *mm* ID) initially filled with $14\ g/L\ Cu_2(SO_4)_2$ solution with sodium sulphate of equal molarity as passive electrolyte. The membrane was fitted into a PMMA housing that forms the second half-cell. Experiments were performed at 3T using the probe's tuned solenoid coil. The T_1 relaxation time was measured by a saturation recovery experiment using a two pulse sequence with variable delay between the pulses. T_2^* was assessed by the exponential decay of the FID. The electrochemical potential was applied by a lab voltage supply and the corresponding ion current was measured by a Picoammeter (Keythley, Cleveland, Oh.).

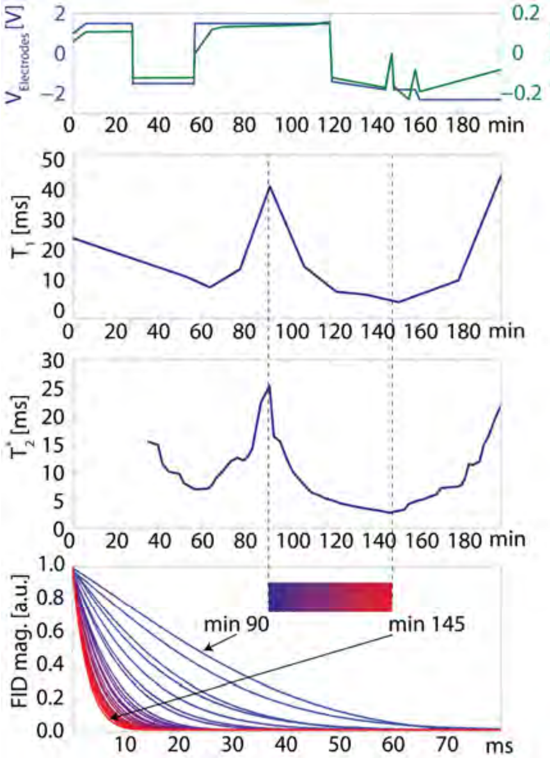

Figure 2: Top to bottom; Bias voltage and current, resulting T_1/T_2 relaxation times; FIDs obtained color coded by the time of acquiring indicated by the color bar.

Results: Fig.2 shows the obtained results. The top row plots the applied voltage across the electrodes and the resulting ion current in the 100 μA range. Two cycles of enriching copper ions and depleting the half-cell were run over 180 *min* in total. The corresponding behaviour of the relaxation times are plotted below showing that they could be controlled within a range of 4-45 *ms* T_1 and 4-25 *ms* in T_2^* as limited by the static shim. The plot at the bottom shows FIDs acquired coloured from blue to red dependent on the time of their acquisition.

Discussion: Electrochemical processes known from battery and electroplating applications offer MR compatible means to control relaxation times of fluids employed in NMR based field probes. By adapting the relaxation time of the probe, the field measurement can be optimized for the targeted application enabling a single probe to cover most of the applied sequences ranging from fast gradient echoes to single-shot read-outs with the same acquisition and signal processing chain. The proposed copper sulphate electrolysis is thereby only one potential candidate reaction. An alternative was also found based on manganese salts that can be electrolyzed into manganese and its oxide omitting the necessity of an ion selective membrane, however at the cost of enhanced susceptibility matching problems due to the strong paramagnetism of these substances. Also many similar photochemical reactions are potential candidates, some of them involving more complex chemical compounds in the system.

The reaction speed of the current approach is mainly limited by the speed of ion migration in the capillary. The speed of relaxation change can therefore be optimized by reducing the distance between the electrodes and the NMR active region or by enhancing the diffusive ion transport by convection or mixing as it could be induced by localized heating, stirring, rotation, vibrations or ultrasound induced pressure gradients

Rather than tuning the relaxation times other material parameters can be controlled by similar reactions e.g. the bulk susceptibility. Closely controlling relaxation time and/or susceptibility could also be applied for calibration, validation and reference phantom setups in which they could not only alter a property but also induce stationary spatial gradients of that property.

In common with many other secondary cells the studied field probe exhibits limits regarding cycle lifetime caused by electrode abrasion, dendrite formation or gassing. Many of the known counter-measures however, such as optimizing charging currents and local potentials or chemical adjuvants are compatible with the proposed NMR field probe.

References: 1) DeZanche et al. MRM 2008 2011, 2) Barmet et al. MRM 2008, 3) Duerst et al. MRM 2014 4) Dietrich et al. Proc. ISMRM