Dynamic Nuclear Polarization of Silicon-Based Nanoparticle Magnetic Resonance Imaging Agents

M. C. Cassidy[1], J. W. Aptekar[2], M. Lee[2], R. L. Walsworth[2,3], and C. M. Marcus[2]

[1]School of Engineering and Applied Sciences, Harvard University, Cambridge, MA, United States, [2]Department of Physics, Harvard University, Cambridge, MA, United States, [3]Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, United States

Introduction - Silicon-based nanoparticles offer promise as biologically targeted magnetic resonance imaging (MRI) agents based on their exceptional NMR properties [1], lack of background signal and diverse functionalization chemistry [2]. Specifically, the long room-temperature nuclear relaxation (T_1) times makes them suitable candidates as *ex-vivo* polarized imaging agents, as they can be transported and administered on practical time scales without significant loss of polarization. Low temperature Dynamic Nuclear Polarization (DNP) has been shown to be powerful technique for enhancing the nuclear spin polarization of silicon particles many orders of magnitude above the equilibrium value [3]. This technique employs microwave irradiation of paramagnetic defects that exist at the silicon-silicon dioxide interface, which in turn polarize nearby nuclear spins. Polarization of the crystalline core of the nanoparticle is then achieved via nuclear spin diffusion through dipole-dipole interactions from nuclei near the surface. In this study we present results from DNP experiments on silicon-based nanoparticles of a variety of sizes, morphologies and fabrication methods. We will also discuss requirements for transporting prepolarized particles and mechanisms for imaging the hyperpolarized nanoparticles in-vivo.

Methods - DNP experiments were performed at 4 K in a 2.9 T superconducting NMR magnet (f_{NMR} = 24.4 MHz, f_{ESR} = 81 GHz). A custom built cryostat and insert with a vertical saddle coil probe allows for rapid loading and unloading (< 5 s) of the hyperpolarized sample without disturbing the cryogenic setup. Microwave irradiation of the sample was provided by a waveguide-coupled 80mW Gunn diode source (Quinstar) held at room temperature. For each measurement, a train of 90° saturation pulses was used to null any existing polarization before the irradiation period began, and the NMR signal amplitude taken from the Lorentzian fit of the signal from a free induction decay after a 90° pulse.

Results – Figure 1 shows results from DNP studies on micron sized silicon particles at 4 K. The polarization increases with microwave irradiation time (Fig. 1a), however a significant enhancement above equilibrium polarization is seen even at short irradiation times of 400 s. A narrow (~ 500 Hz) feature in the NMR lineshape (Fig. 1a inset) is evident for irradiation times greater than 10 minutes, which is indicative of the transfer of polarization to the nuclei in the crystalline core of the sample. No polarization was seen without irradiation (Fig. 1a inset). Nuclear polarization was also found to be dependent on the microwave irradiation frequency (Fig. 1b), with a peak when the sample is irradiated just below the ESR frequency, characteristic of the thermal mixing DNP mechanism [4].

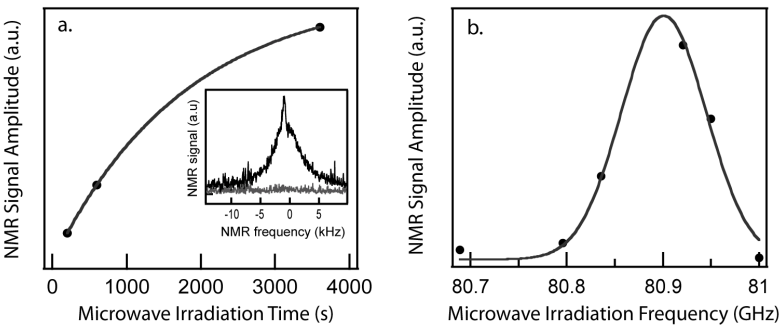

Figure 1 – Dynamic nuclear polarization of micron sized silicon particles at 4 K. a) Dependence of the NMR signal on microwave irradiation time at an irradiation frequency of 80.92 GHz. The solid line is to guide the eye. Inset: NMR signal lineshapes after microwave irradiation at 80.92 Ghz (black) for 1 hour and no irradiation (grey). b) NMR peak amplitude vs. microwave irradiation frequency for irradiation times of 400 s.

Discussion – Silicon-based nanoparticles studied here are shown to be extremely receptive to nuclear hyperpolarization via low temperature, microwave induced DNP. The degree of nuclear polarization is found to increase significantly with irradiation time, allowing for the long T_1 nuclei in the crystalline core of the particles to be polarized via spin diffusion. The setup developed allows for the unique ability to remove the hyperpolarized sample quickly for administration to a subject. Further investigation is being undertaken into the exact transportation and storage mechanisms required to maintain maximum polarization for in-vivo imaging applications.

Acknowledgements - This work was supported by the NIH under grant no. 1 R21 EB007486-01A1 and the Harvard NSEC.

References -

[1] Aptekar, J.W. *et al. Nature Nanotechnology* submitted (2008)
[2] Schwart, M.P. *et al. Phys. Status Solidi A-Appl. Mat.* 202, 1380-1384 (2005)
[3] Dementyev, A.E. *et al. Phys. Rev. Lett.* 100, 127601 (2008)
[4] Slichter, C.P. Principles of Magnetic Resonance *Springer*, Berlin (1996)