Complementary Techniques
NMR, ESR and μSR

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Caveat

All depends on the actual chemical system under investigation
Starting point

- Muon is an extrinsic probe implanted into a material
- Magnetic properties like $^1\text{H}$ and $e^{-1}$, all $S=1/2$

- Muon implants as a diamagnetic muon think NMR
- Muon implants as muonium, or reacts to give a muoniated radical think ESR (spin label)
Diamagnetic muons and NMR Structure

Unlike NMR, muons are NOT a structural tool

- Cannot guide where the muon implants
- Difficulty assigning the implantation site without assuming a structure
- Short lifetime precludes any “chemical shift” information
- Exception, the Knight shift in a metal, information on the electronic structure
Diamagnetic muons and NMR Dynamics

- Both NMR and muons can be used to study dynamic processes
- Timescales for both depend on parameter being observed
  - NMR: Population, chemical shift, $J$, $T_1$ and $T_2$
  - $\mu$SR: $T_1$ and $T_2$
- Averaging of dipolar interactions by the motion of the spin
  - Nuclear-nuclear dipole for NMR
  - Muon-nuclear dipole for $\mu$SR
- Similar range of rates accessible ($\gamma_\mu \sim 3.184\gamma_H$)
Short muon lifetime 2.2 µs

Slow chemical reactions

Conformational exchange

Spin-lattice relaxation

Lineshape perturbations

Molecular tumbling and Diffusion

Population exchange

Averaging of NMR parameters by vibrations and rotations

Time window

(Magnitude of dependent interaction)^{-1}
Case study
Li$^+$ diffusion in Li-ion battery anodes

Use the muon response as an indirect measurement of Li$^+$ diffusion

<table>
<thead>
<tr>
<th>Method</th>
<th>$D_{Li}$ (cm$^2$ s$^{-1}$)</th>
<th>$D_{Li}$ (cm$^2$ s$^{-1}$)</th>
<th>$E_a$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu^+SR$ (at 310 K)</td>
<td>$7.6(3) \times 10^{-11}$</td>
<td>—</td>
<td>270(5)</td>
</tr>
<tr>
<td>Li-NMR$^{11}$ (at 314 K)</td>
<td>$3.8 \times 10^{-11}$</td>
<td>—</td>
<td>550</td>
</tr>
<tr>
<td>Li-NMR$^{44}$ (at 373 K)</td>
<td>$10^{-8}$</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Electrochemical impedance$^{38}$ (at 298 K)</td>
<td>$10^{-9}$ - $10^{-7}$</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>First principles calculations$^{42}$ (at 300 K)</td>
<td>$0.9 \times 10^{-11}$</td>
<td>—</td>
<td>283</td>
</tr>
<tr>
<td>First principles calculations$^{45}$ (at 300 K)</td>
<td>—</td>
<td>$1-10 \times 10^{-11}$</td>
<td>510</td>
</tr>
</tbody>
</table>

Case study
Li$^+$ diffusion in Li-ion battery anodes
Motional narrowing from $^7$Li NMR spectrum

NB Instrument used not optimal, too long pulse lengths 6-9 µs for $\pi/2$

$^7$Li NMR relaxation times $T_1$, $T_{1p}$ and $T_2$

J Langer et al
PHYSICAL REVIEW B 88, 094304 (2013)
Diamagnetic muons and NMR Reactions

- NMR extremely versatile
- $\mu$SR very limited
  - Movement from one trapped site to another is diffusion
  - Delayed formation of muonium
- Show as an “excess” relaxation rate
Muoniated radicals and ESR Structure

- Muoniated radicals are formed when muonium adds to a double bond
- ESR a probe for the local environment - spin labels
  - Solvation in membranes
  - Distance probes - separation between two labels
- (ESR can be used to study structure with unpaired electrons in general)
- $\mu$SR only used as a probe for the local environment
- Hyperfine couplings constants depend on the polarity of the medium
Muons or ESR spin labels

**Muons**
- Target molecule itself might be muoniated
- Insensitive
- Simple system (or complex without other muon targets)

**ESR**
- Structure compromised by having spin label added
- Sensitive
- Complex systems
Resonant fields reflect differences in the hyperfine coupling constants $A_H$

Typically $> 100$ MHz

E. Roduner et al
Hyperfine coupling between the electron and $^{14}$N nuclear spin

$\sim 1540$ MHz

Smaller than $\mu$SR
$1 \text{mT} = 10 \text{ G}$

Strength of reaction field from the solvent

D. Marsh, C. Toniolo
Muoniated radicals and ESR Dynamics

- Both ESR and $\mu$SR can be used to study dynamics
- ESR requires a spin label - nitrooxide ions
- Both rely on averaging of hyperfine coupling constants
- Similar time window
Complex analysis of conformers for a 72R2 mutant of T4L with torsional oscillations and conformational jumps

Alberta Ferrarini et al

2-phenyl ethanol in 35% wt $C_{12}E_4$

Probe is the molecule partitioning
General comparison

NMR
- **Target**
  - Intrinsic NMR active nucleus e.g. $^{13}$C
- **Detection**
  - Induced voltage in a coil
- **Phase**
  - Solid, liquid, rarely gas
- **Sensitivity**
  - Depends on nucleus but < 10 mg

µSR
- **Target**
  - Implanted muon, muonium or muoniated radical,
- **Detection**
  - Positron decay product, scintillator/PMT
- **Phase**
  - Solid, liquid, gas
- **Sensitivity**
  - Typically 1-2 g