NMR STUDIES ON SOLID STATE POLYMER ELECTROLYTES

Ramesh Kumar Mani

December 1, 2008

Contents

MEMORIAL UNIVERSITY
Newfoundland & Labrador, Canada

Nuclear Magnetic Resonance

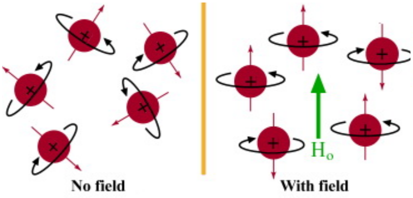
- NMR exploits the magnetic properties of certain nuclei.
- Subatomic particles can be imagined as spinning on their axes.
- If the number of neutrons and the number of protons are both even, then the nucleus has NO spin.
- The overall spin of the nucleus is determined by the spin quantum number I.
- For Non-zero spin; Magnetic Moment;

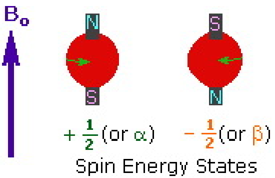
$$\mu = \gamma \cdot I$$

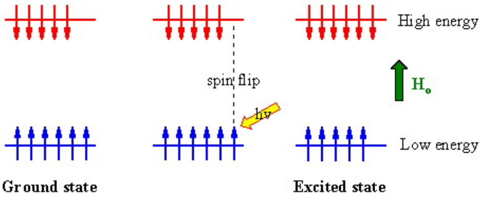
Dr. Joseph Hornak,, *The Basics of NMR.,* A non-technical overview of NMR theory

MEMORIAL UNIVERSITY
Newfoundland & Labrador, Canada

NMR
Spin Energy States







Dr. Joseph Hornak„ *The Basics of NMR.*, A non-technical overview of NMR theory

Resonance Energy

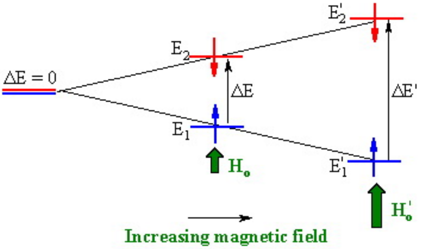


Figure: Difference in Energy

Dr. Joseph Hornak„ *The Basics of NMR.,* A non-technical overview of NMR theory

Caclulating Transition Energy

- The nucleus has a positive charge and is spinning. Magnetic moment, μ, which is proportional to its spin, *I*.

$$\mu = \frac{\gamma \cdot I \cdot h}{2\pi} \quad (1)$$

γ - magnetogyric ratio, h - Planks Constant

- The energy of a particular energy level is given by;

$$E = -\frac{\gamma \cdot H}{2\pi} mB \quad (2)$$

B - Strength of magnetic field

- The difference in energy between levels;

$$\Delta E = -\frac{\gamma \cdot H \cdot B}{2\pi} \quad (3)$$

NMR Spectrometer

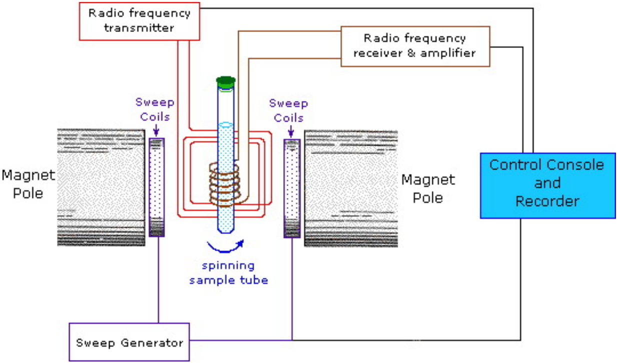
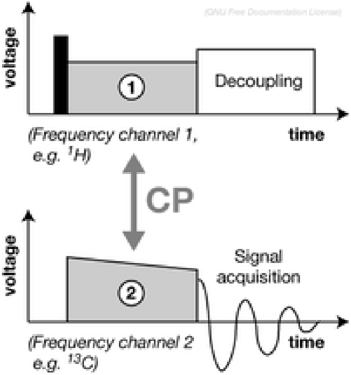


Figure: NMR Spectrometer

http://www.cem.msu.edu/ reusch/VirtualText/Spectrpy/nmr/nmr1.htm

solid-state NMR spectroscopy



- In media with no or little mobility anisotropic interactions have a substantial influence on the behaviour of a system of nuclear spins.
- High-resolution conditions in solids can be established using magic angle spinning (MAS) or macroscopic sample orientation.
- A fundamental RF pulse sequence in most solid-state NMR experiments is cross-polarization (CP).
- CP is a basic building block of most pulse sequences in solid-state NMR spectroscopy.

Schaefer, J., *Journal of the American Chemical Society .,* **98** (1976) 1031

Basics of ^{2}H and ^{7}Li NMR

- In solid-state ^{2}H NMR, the first order quadrupolar interaction,

$$\omega_Q(\theta, \phi) = \pm \frac{\delta}{2} \left(3 \cdot cos^2\theta - 1 - \eta \cdot sin^2\theta \cdot cos2\phi\right) \tag{4}$$

  $\pm$ sign corresponds to the two allowed transitions between the Zeeman levels; θ, ϕ - orientation of the EFG tensor with respect to B_0.

- In solid-state ^{7}Li NMR ($I = 3/2$), first order quadrupolar interaction affects the frequencies of the two satellite transitions $|\pm 3/2\rangle \longleftrightarrow |\pm 1/2\rangle$, but not that of the central transition $|-1/2\rangle \longleftrightarrow |+1/2\rangle$.
- Therefore, the ^{7}Li NMR spectra of powder samples are comprised of a narrow line and a broad line corresponding to the central and satellite transitions, respectively.

M. Vogel., *J. Phys. Chem. B.*, **112** (2008) 11217–11226

MEMORIAL UNIVERSITY
Newfoundland & Labrador, Canada

Solid Polymer Electrolytes

- Great amount of work in the field of polymer research has focused on poly(ethylene oxide) (PEO).
- Dynamic and structural properties of melt-crystallized PEO depends on various factors; M_w and end groups.
- PEO consists four different regions;
- Ionic conductivity of PEO is due to polymer segmental motion in amorphous region.
- PEO has the ability to dissolve metal salts and got low T_g.
- Nuclear magnetic resonance (NMR) spectroscopy provides access to the dynamics of both crystalline and amorphous PEO.

M. Vogel., *J. Phys. Chem. B.*, **112** (2008) 11217–11226

MEMORIAL UNIVERSITY
Newfoundland & Labrador, Canada

Ionic Conductivity

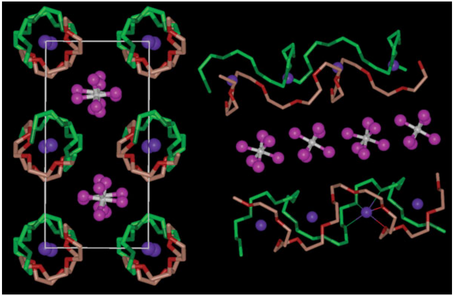


Figure: The structure of the polymer electrolyte $PEO_6:LiSbF_6$

- Sample: crystalline and amorphous forms of $PEO_6:LiSbF_6$
- By combining $LiSbF_6$ with methoxy end-capped PEO of low weight-averaged molecular mass (Mw = 1,000) a crystalline 6:1 phase was obtained.

MEMORIAL UNIVERSITY
Newfoundland & Labrador, Canada

Zlatka., *Letters to Nature.*, **412** (2001) 520

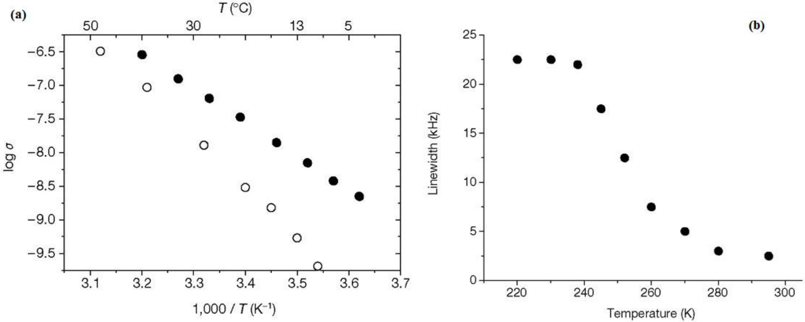


Figure: (a) Ionic conductivity σ (S cm^{-1}) of amorphous (open circles) and crystalline (filled circles) PEO_6:$LiSbF_6$ as a function of temperature. (b) ^{1}H NMR linewidth as a function of temperature for amorphous PEO_6:$LiSbF_6$.

Zlatka., *Letters to Nature.*, **412** (2001) 520

Crystalline Polymer Electrolytes
Ionic Conductivity

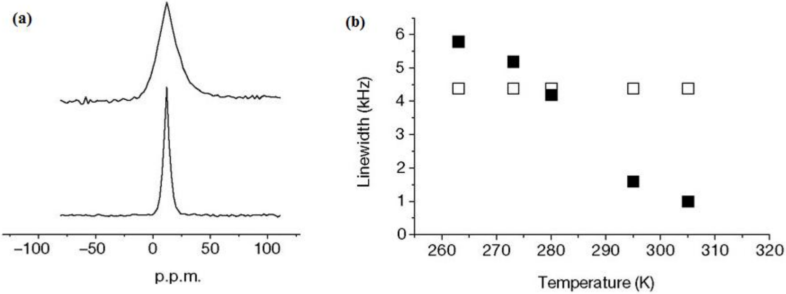


Figure: (a) PEO_6:$LiXF_6$ for X = Sb,P. a, Proton-decoupled static ^{7}Li spectra for amorphous (upper line) and crystalline (lower line) PEO_6:$LiSbF_6$. (b), Linewidth variations for the crystalline complex PEO_6:$LiPF_6$ as a function of temperature: ^{31}P (open squares) and ^{7}Li (filled squares).

Zlatka., *Letters to Nature.*, **412** (2001) 520

Reasons

- Ion transport in solids $\rightarrow$ Hopping of ions
- Polymer electrolytes $\rightarrow$ Ions move in dynamic environment accelerated by polymer chain motion.
- Achievable ionic conductivity in amorphous polymers $\rightarrow 10^{-4}$ S cm^{-1}.
- Conductivity can be enhanced by organizing the stucture.

MEMORIAL UNIVERSITY
Newfoundland & Labrador, Canada

LiI-PEO based Solid Electrolytes

- Composite polymer electolytes consisting of poly ethylene oxide, a lithium salt and an inorganic oxide have received considerable attention.
- Presence of inorganic oxide can improve;
  - Electrical Conductivity
  - Stability of Li/Polymer electrolyte interfacial resistance.
  - Interfacial ion transport through grain boundaries.
- NMR methods are well suited for studying;
  - Ionic environments and mobility in disordered and hetrogeneous polymer electrolytes.
  - Coexistence of mobile and immobile Li^+ phases.

Y.Dai., *Solid State Ionics.*, **106** (1998) 25-32

MEMORIAL UNIVERSITY
Newfoundland & Labrador, Canada

LiI-PEO based Solid Electrolytes

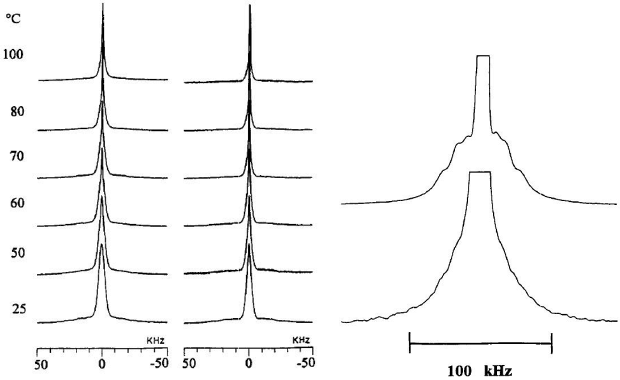
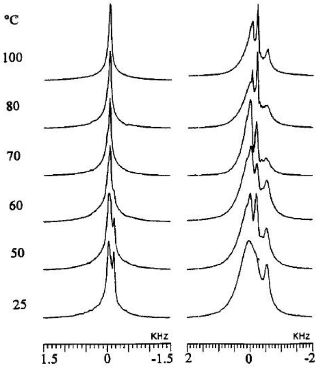


Figure: 1. Line variable ^{7}Li NMR Spectra of $P(EO)_{1.5}LiI$ with 6 Vol% Al_2O_3 (Left), Without Al_2O_3. 2. With Al_2O_3 (Bottom) without Al_2O_3 (Top).

Y.Dai., *Solid State Ionics.*, **106** (1998) 25-32

LiI-PEO based Solid Electrolytes



- The right side peak is associated with Li^{+} ions in close proximity to the protons from PEO.
- Left side peak represents Li in more purely ionic configuration.
- In the sample without Al_2O_3, the third peak represents crystalline LiI regions and it remains even at higher temperature.
- Surface interaction between LiI and Al_2O_3 can create high defect density and thus suppresseing the formation of crystalline LiI.

Figure: 1. ^{7}Li NMR Spectra of $P(EO)_{1.5}$LiI with 6 Vol% Al_2O_3 (Left), Without Al_2O_3(Right).

MEMORIAL UNIVERSITY
Newfoundland & Labrador, Canada

Y.Dai., *Solid State Ionics.*, **106** (1998) 25-32

Conclusions

- Solid state NMR Spectroscopy can be used for a media with no or little mobility anisotropic interactions.
- ^{1}H NMR linewidth as a function of temperature was used to find the T_g for amorphous PEO_6:$LiSbF_6$.
- ^{7}Li spectra was used to distinguish between amorphous and crystalline $P(EO)_6$:$LiSbF_6$.
- ^{7}Li and ^{31}P spectra were used to find the relative contributions of cation and anion transport to conduction in the 6:1 crystalline polymer electrolytes.
- ^{7}Li spectra was used to find the Coexistence of mobile and immobile Li^+ phases and the conductivity of $P(EO)_{1.5}$LiI with 6 Vol% Al_2O_3 and without Al_2O_3 samples.

Zlatka., *Letters to Nature.*, **412** (2001) 520

Y.Dai., *Solid State Ionics.*, **106** (1998) 25-32