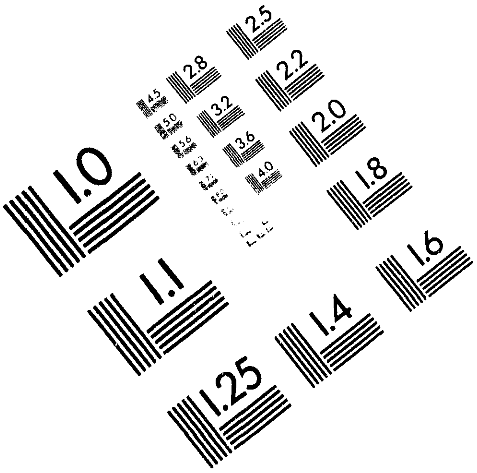
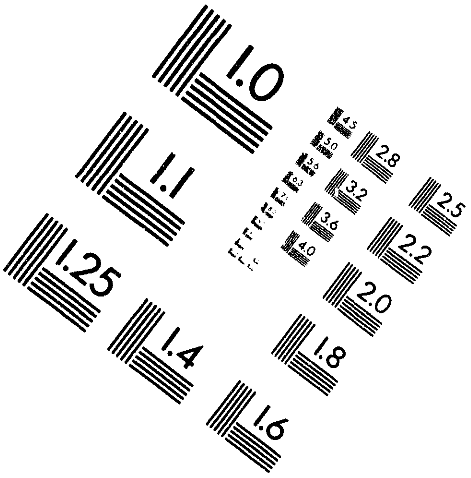


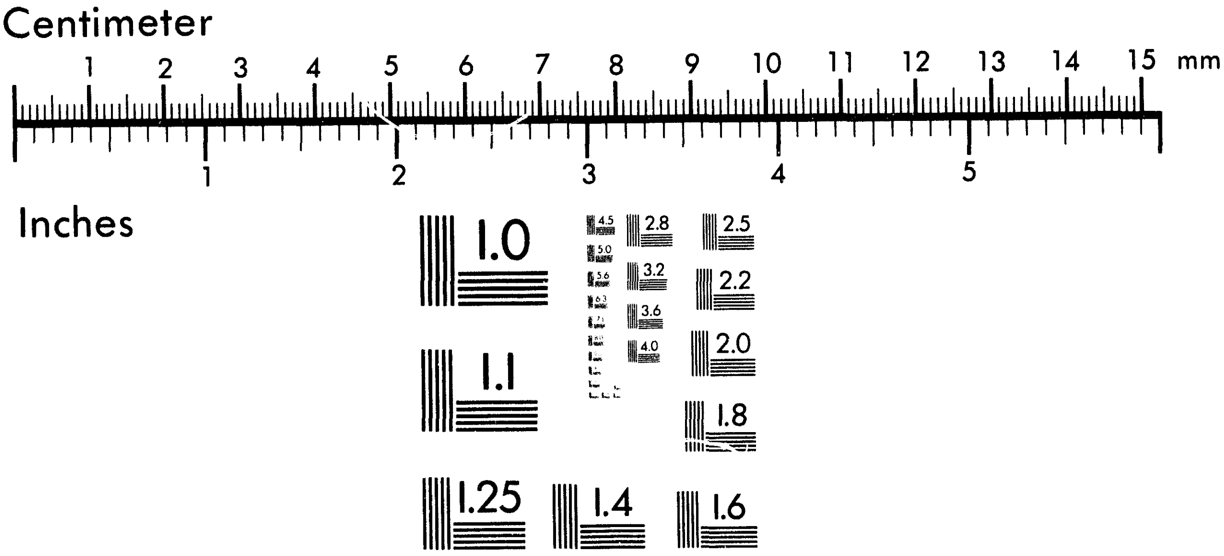
AIIM

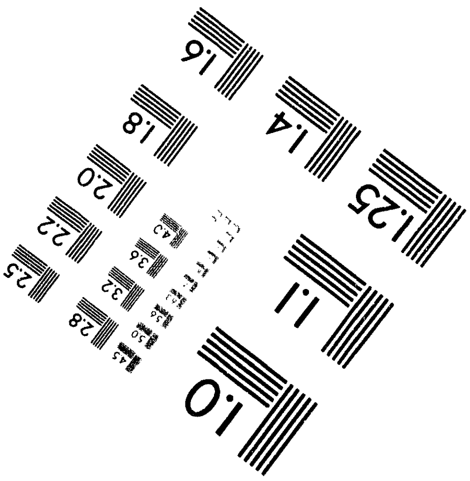
Association for Information and Image Management

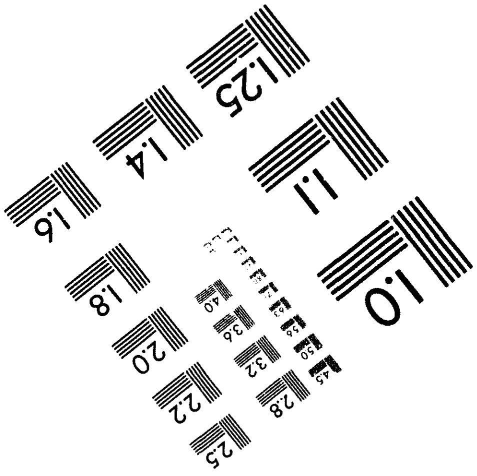
1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910

301/587-8202









MANUFACTURED TO AIIM STANDARDS
BY APPLIED IMAGE, INC.

1 of 1

'2

Will be published as Proc. 4th Intern. Symp.
on Polymer Electrolytes, Newport, RI, June 20-24, 1994.

Conf-940690--1

✓BNL-60409

A New Family of Anion Receptors and Their Effect on Ion Pair Dissociation and Conductivity of Lithium Salts in Non-aqueous Solutions

H. S. Lee, X. Q. Yang, and J. McBreen

Brookhaven National Laboratory, Upton, NY 11973. U.S.A.

Y. Okamoto

Polytechnic University, Brooklyn, New York 11201

Abstract

A new family of anion receptors based on aza-ether compounds have been synthesized. Since the anion complexation of these compounds is not based on either positively charged sites or hydrogen bonding, they have a potential to be used in lithium batteries as electrolyte additives. When these compounds are added into non-aqueous electrolytes using lithium salts, such as LiCl/THF or LiBr/THF, the ionic conductivity can be dramatically increased. Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy studies show that Cl^- anions are complexed with the nitrogen groups in these compounds. The increase in ionic conductivity and the degree of complexation, are both related to the number of $R=CF_3SO_2$ groups that are used to substitute the amine hydrogen atoms in these aza- ether compounds.

Introduction

Ion pairing is an important problem in ionic conductivity studies, since it is directly related to the charge carrier number, which is the other governing factor in the conductivity beside the charge carrier mobility. One way for increasing the free ion concentration is to add a neutral ligand

MASTER

gtb

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED ✓

to coordinate the cation or the anion. Coordination is expected to increase the cation-anion distance of closest approach and thus decrease ion pair formation. Although studies about using crown ether, such as 18-crown-6, and 12-crown-4, for cation coordination had been reported by Saloman[1] and Matsuda[2] respectively, there is little work on anion coordination due to the lack of suitable anion receptors. However, anion coordination is much more important than cation coordination in lithium battery electrolytes since our goal is to increase the concentration of free lithium cations. The achievement of anion coordination would open a new approach for lithium battery electrolyte development. The design and synthesis of receptor molecules for the selective complexation of ions has been an active area for past two decades. Although various compounds which are cation receptors have been synthesized and widely studied, the number of host molecules for anions is very low. To accomplish anion binding, most of the reported host molecules contain positively charged sites or Lewis acid metal centers. In last two years, there were a few reports about using neutral compounds to complex anions[3,4]. However, the complexation was formed through hydrogen bonding which restricts their application in lithium batteries. We have synthesized a family of aza-ether based compounds as anion receptor molecules which are not based on either positively charged sites or hydrogen bonding. A electron-withdrawing group, labeled as $R=CF_3SO_2$ was used to substitute amine hydrogen atoms in linear aza- ethers, multi-branched aza- ethers, and cyclic aza-crown ethers. The molecular structures of these compounds are shown in figure 1. The linear compounds were named as L4R, L5R, L6R, and L8R according to the number of R groups. The multi-branched compound and the cyclic compound was named as M6R and C4R respectively. The unsubstituted starting compound for L6R was named as L6H. This nomenclature is summarized in Table I. In the unsubstituted aza crown ether, the local charge around nitrogen atoms is negative, therefore, it can complex positively charged cations, such as Li^+, Na^+. When the amine hydrogen atoms are substituted by the electron withdrawing groups, $R=CF_3SO_2$, the local charge around nitrogen atoms become positive. Therefore, the R substituted aza- crown ether, C4R, can complex small anions, for example, Cl^-. In order to complex larger anions, say Br^-, R substituted aza- linear compounds, such as L6R, L8R, were used. The ion complexation of these new anion receptors was studied by ionic conductivity and x-ray absorption spectroscopy of lithium salts in non-aqueous electrolyte using the R substituted and unsubstituted aza- compounds as additives. In this paper, we will report our preliminary data for linear aza- ether compounds as additives in LiCl/THF solution. The studies on multi-branched and cyclic aza- ether compounds and the effects of these compounds in other salt/solvents electrolytes is under way.

Experimental

The synthesis procedure and characterization will be reported separately later. LiCl salt and THF solvent were both purchased from Aldrich, and used without further purification.

Conductivity measurements were made at 25 ° C using a Hewlett-Packard 4129A Impedance Analyzer in the frequency range from 5Hz to 10 MHz. The conductivity cells were home built and had Pt electrodes. The cell constants were calibrated using a 0.05N KCl standard aqueous solution. The ionic conductivity of solutions formed by adding various aza- ether compounds to the 0.2M LiCl/THF solutions was compared with the conductivity of LiCl/THF solution without additives.

NEXAFS measurements were made at Beam Line X19A of the National Synchrotron Light Source. The data were collected as fluorescence excitation spectra using a large solid angle ionization chamber as the fluorescence detector. The solutions after being used in conductivity measurements were poured into cells with Kapton windows for NEXAFS studies. Each of these solutions were then dropped on Kapton tapes to evaporate the THF solvent for studying complexation in solid state.

Results and Discussion

The Ionic conductivity data of 0.2M LiCl salt in pure THF solution, as well as the data for same solutions with various additions of aza- ether compounds are listed in Table II. The ionic conductivity of LiCl in THF is very low, in the range of $1.6\text{x}10^{-6}$ S/cm at room temperature. When the unsubstituted aza- ether compound L6H was added into LiCl/THF solution, the conductivity increased to $4.2\text{x}10^{-6}$ S/cm range. The increase is not significant. Since the unsubstituted aza-compounds complex cations, the increase of conductivity can be attributed to the increased free anion concentration. When the corresponding substituted compound L6R was added, the ionic conductivity increased to $7.6\text{x}10^{-4}$ S/cm, which is two orders of magnitude higher than either the pure LiCl solution or the solution using unsubstituted L6H as additive. The ionic conductivity also depends on the number of R groups in the additives. The ionic conductivity increases from $8.4\text{x}10^{-5}$ S/cm for L4R to $1.4\text{x}10^{-3}$ S/cm for L8R, when the number of R groups increased form 4 to 8. Since the R group is a strong electron withdrawing group, it creates a positively charged environment surrounding the nitrogen atoms. Therefore, we believe that the anions, not the cations, are complexed with the nitrogen atoms in the R-substituted compounds. This type of complexation would move the equilibrium point of ionization of LiCl in THF and create more free Li^+ ions, which in turn , increases the conductivity.

In order to confirm that the anions are complexed with the nitrogen atoms in the R-substituted aza- ether compounds and to find out the detail structure of the complexes, x-ray diffraction studies on single crystals of the complex is needed. However, the complexation may take place only in solution not in the solid state. Even if it does occur in the solid state, it might be very difficult to grow single crystals for x-ray diffraction studies. Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy provides us an useful tool to study the coordination symmetry of the Cl^- ions both in solution and in solid state. In the NEXAFS experiment, as the incident x-ray energy was scanned through the potassium *K*-edge, the ejected photoelectrons sequentially probe empty electronic levels of the sample being studied, resulting in fine structure in the near edge absorption spectrum. The relaxations of these excited states take place by either the emission of Auger electrons or fluorescence photons. The spectrum depends on bonding, valence, and coordination symmetry of the potassium atoms in the sample.

Figure 2 shows x-ray absorption curves, at the chlorine *K* edge, for (a) LiCl salt, (b) 0.2M LiCl/THF solution, (c) 0.2M LiCl + 0.2M L6H in THF solution, and (d) 0.2M LiCl + 0.2M L6R in THF solution. The "white line" peak above the edge is due to dipole-allowed transitions to final states of *p* symmetry[5,6]. The structure of the "white line" is very sensitive to the coordination of the absorbing atom, it has been used to study the coordination of K in KI/PEO complex[7] and ion pairing of potassium salt in plasticizers[8]. For most of the chloride salt in solid state, the white line is split into several peaks as a result of the removal of the degeneracy of the final *p* states due to the electric field surrounding the Cl^- ions caused by the paired cations. However, the white line in curve (a) for LiCl in the solid state is a featureless broad peak, similar structures were found for Cl^- in free ion state, such as KCl in dilute aqueous solution. We are not sure why the Cl edge structure of LiCl salt is different than other chloride salts now, but the featureless broad peak of white line for LiCl salt would tell us any white line splitting of the Cl edge resulted in adding aza-ether compounds is not attributed to the Li^+-Cl^- pairing. In curve (b), the "white line" did not change significantly when the LiCl salt was dissolved in THF indicating that the interaction between solvent and Cl^- is not strong enough to cause a splitting. In curve (c), when unsubstituted aza- ether L6H was added into the solution, the white line structure is about the same as in curve (a) and (b), implying no complexation between this compound and the Cl^- anion. In curve (d), a clear split was observed when R-substituted aza- ether compound L6R was added into the solution. This is a strong evidence that Cl^- is complexed with nitrogen atoms of the R-substituted aza- ether compounds.

In order to find out whether the complexation between the Cl^- and the R-substituted aza ether compounds is stable or not in solid state, the NEXAFS spectra at the chlorine *K* edge, for the solid samples after evaporating the THF solvent were also taken. The results are plotted in figure 3. The solutions used were: (a) 0.2M LiCl + 0.2M L4R, (b) 0.2M LiCl + 0.2M L5R, (c) 0.2M LiCl + 0.2M L6R, and (d) 0.2M LiCl + 0.2M L8R. These spectra are basically the same as the solution samples. The white line splitting depends on the number of R groups in the R-substituted aza- ether compounds complexed with Cl^-. It is interesting to note that the intensity of a sharp feature labeled (A) correlates with number of R groups in the aza- ether compounds. When the additive is L4R, having four R groups, feature (A) is only a shoulder in curve (a). In the spectrum for sample using L5R with five R groups as additive, the intensity of feature (A) grows and becomes a clear peak. In curve (c) and (d), the intensity of feature (A) grows stronger and stronger when the number of R groups in the additives increases to six and eight in L6R and L8R. The similar correlation exists between the ionic conductivity and the number of R groups as shown in Table II. When L4R was used as additive, the ionic conductivity is 8.4×10^{-5} S/cm. When the number of R groups in the additives increased to 5, 6, and 8, the corresponding ionic conductivities increased to 1.4×10^{-4} S/cm, 7.2×10^{-4} S/cm, and 1.4×10^{-3} S/cm. Since all of these spectra are for samples in the solid state rather than in solution, we conclude that the stable complexes were formed in both solution and in solid state.

Conclusion

Ionic conductivity and NEXAFS studies show that the newly developed R-substituted aza ether compounds form stable complex with Cl^- anions, increase the ionic conductivity by increasing the concentration of free Li^+ cations, when used as additives in LiCl/THF electrolyte. The degree of complexation and conductivity also depends on the number of R groups in the linear aza compounds.

Acknowledgement

This work was supported by the U. S. Department of Energy Division of Materials Science of the Office of Basic Energy Sciences, Under Contract No. DE-AC02-76CH00016.

References

1. M. Salomon, *J. Solution Chem., 19, 1225 (1990)*
2. Y. Matsuda, H. Hayashida and M. Morita, *J. Electrochem. Soc., 134, 2107 (1987)*
3. W. B. Farnham, D. C. Roe, D. A. Dixon, J. C. Calabrese, and R. L. Harlow, *J. Am. Chem. Soc. 112, 7707 (1990).*
4. S. Valiyaveettil, J. F. J. Engbersen, W. Verboom, and D. N. Reinhoudt, *Angew. Chem. Ed. Engl., 32, 900 (1993)*
5. M. Brown, R. E. Peierls, and E. A. Stern, *Phys. Rev. B15, 738 (1977).*
6. C. L. Spiro, J. Wong, F. W. Lytle, R. B. Greegor, D. H. Maylotte and S. H. Lamson, *Fuel, 65, 327 (1986).*

7. X. Q. Yang, J. M. Chen, and T. A. Skotheim, Y. Okamoto, J. Kirkland, and M. L. denBoer, *Phys. Rev. B40, 7948, (1989).*

8. X. Q. Yang, H. S. Lee, J. McBreen, Z. S. Xu, T. A. Skotheim, Y. Okamoto, and F. Lu, *J. Chem. Phys. 101 (4), 7416 (1994),*

√

Table I

Nomenclature of aza- ether compounds used in this paper

Structure	Nomenclature
$H(NHCH_2CH_2)_3NH_2$	L6H
$R(NRCH_2CH_2)NR_2$	L4R
$R(NRCH_2CH_2)_2NR_2$	L5R
$R(NRCH_2CH_2)_3NR_2$	L6R
$R(NRCH_2CH_2)_5NR_2$	L8R
$N(CH_2CH_2NR_2)_3$	M6R
Cyclic $(CH_2RNCH_2CH_2CH_2RNCH_2)_2$	C4R

$R = CF_3SO_2$

Table II

Ionic conductivities of LiCl/THF based electrolytes with various aza- ether compound additives.

Composition	Conductivity ($S.cm^{-1}$)
0.2M LiCl/THF	$1.6x10^{-6}$
(0.2M LiCl + 0.2M L6H) /THF	$4.2x10^{-6}$
(0.2M LiCl + 0.2M L4R) /THF	$8.4x10^{-5}$
(0.2M LiCl + 0.2M L5R) /THF	$1.4x10^{-4}$
(0.2M LiCl + 0.2M L6R) /THF	$7.2x10^{-4}$
(0.2M LiCl + 0.2M L8R) /THF	$1.4x10^{-3}$
(0.2M LiCl + 0.2M M6R) /THF	$1.7x10^{-3}$
(0.2M LiCl + 0.2M C4R) /THF	$2.3x10^{-4}$

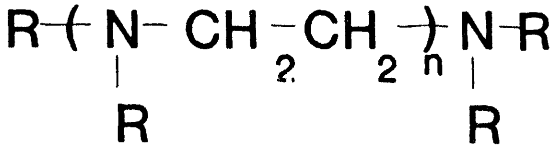
Figure Captions

Figure 1. Ion complexation of unsubstituted and R-substituted aza- ether compounds.

Figure 2. Near-edge x-ray absorption spectra at the *K* edge of chlorine, for (a) LiCl salt, (b) 0.2M LiCl/THF solution, (c) 0.2M LiCl + 0.2M L6H in THF solution, and (d) 0.2M LiCl and 0.2M L6R in THF solution.

Figure 3. Near-edge x-ray absorption spectra at the *K* edge of chlorine, of solid state samples, for: (a) 0.2M LiCl + 0.2M L4R, (b) 0.2M LiCl + 0.2M L5R, (c) 0.2M LiCl and 0.2M L6R, and (d) 0.2M LiCl + 0.2M L8R.

Fig. 1 Lee et al

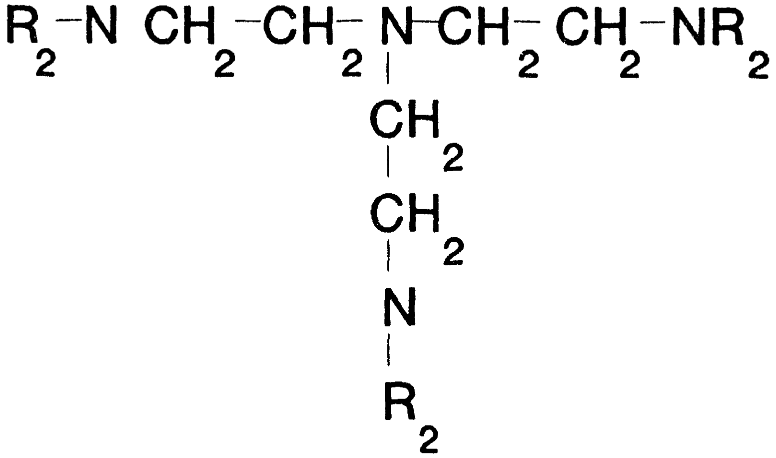


$R-(\underset{|\atop R}{N}-CH_2-CH_2)_n-\underset{|\atop R}{N}-R$

n=1, 2, 3, 4, 5

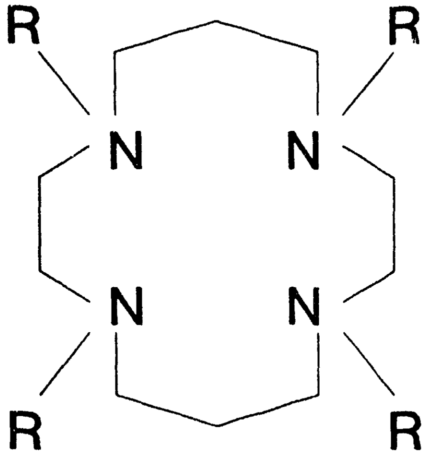
$R=CF_3SO_2$

R substituted linear aza ether compounds



$R_2-N\,CH_2-CH_2-\underset{|\atop CH_2-CH_2-N-R_2}{N}-CH_2-CH_2-NR_2$

R substituted branched aza ether compound



R substituted cyclic aza ether crown

Fig 2 Lee et al

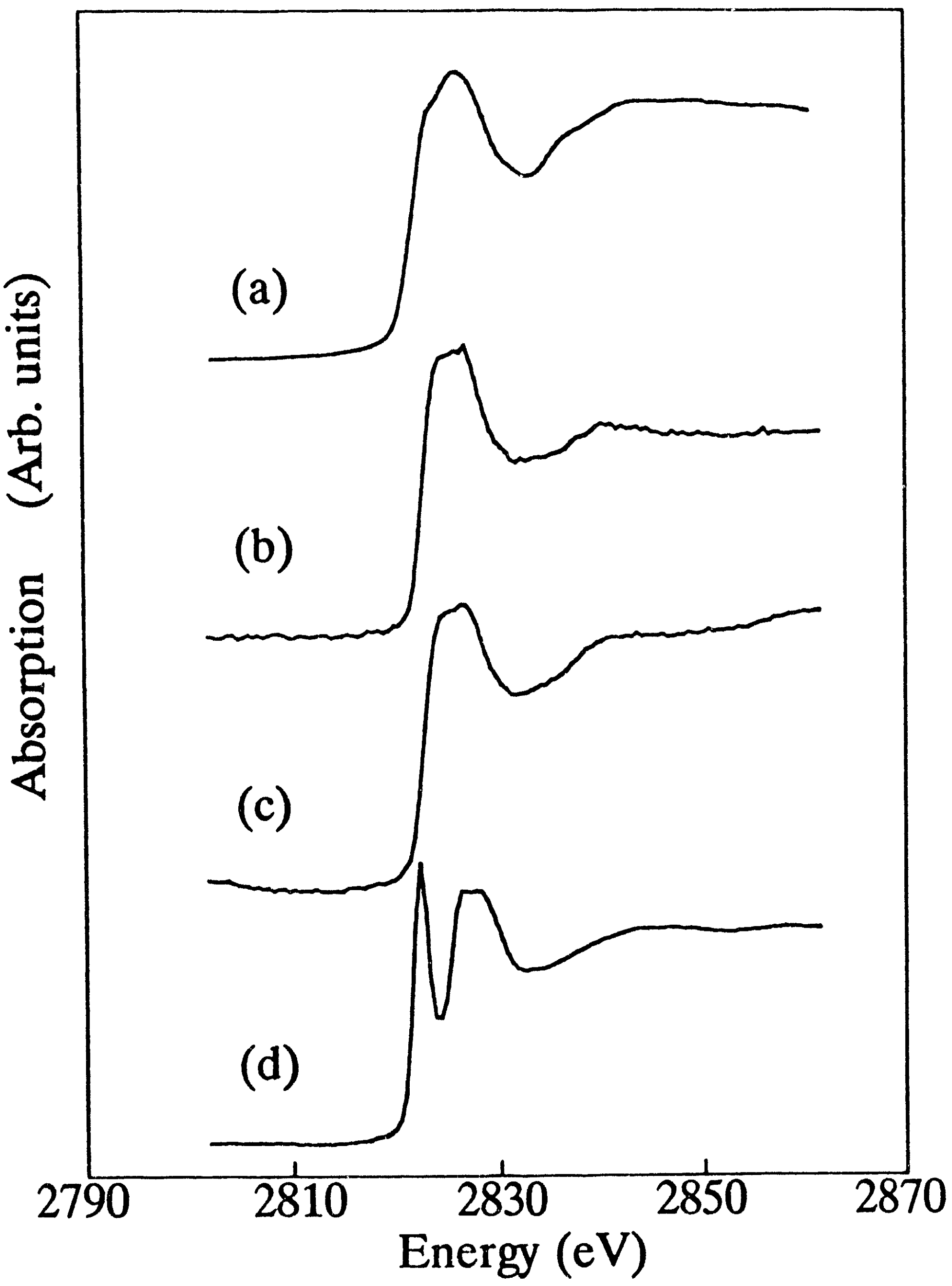
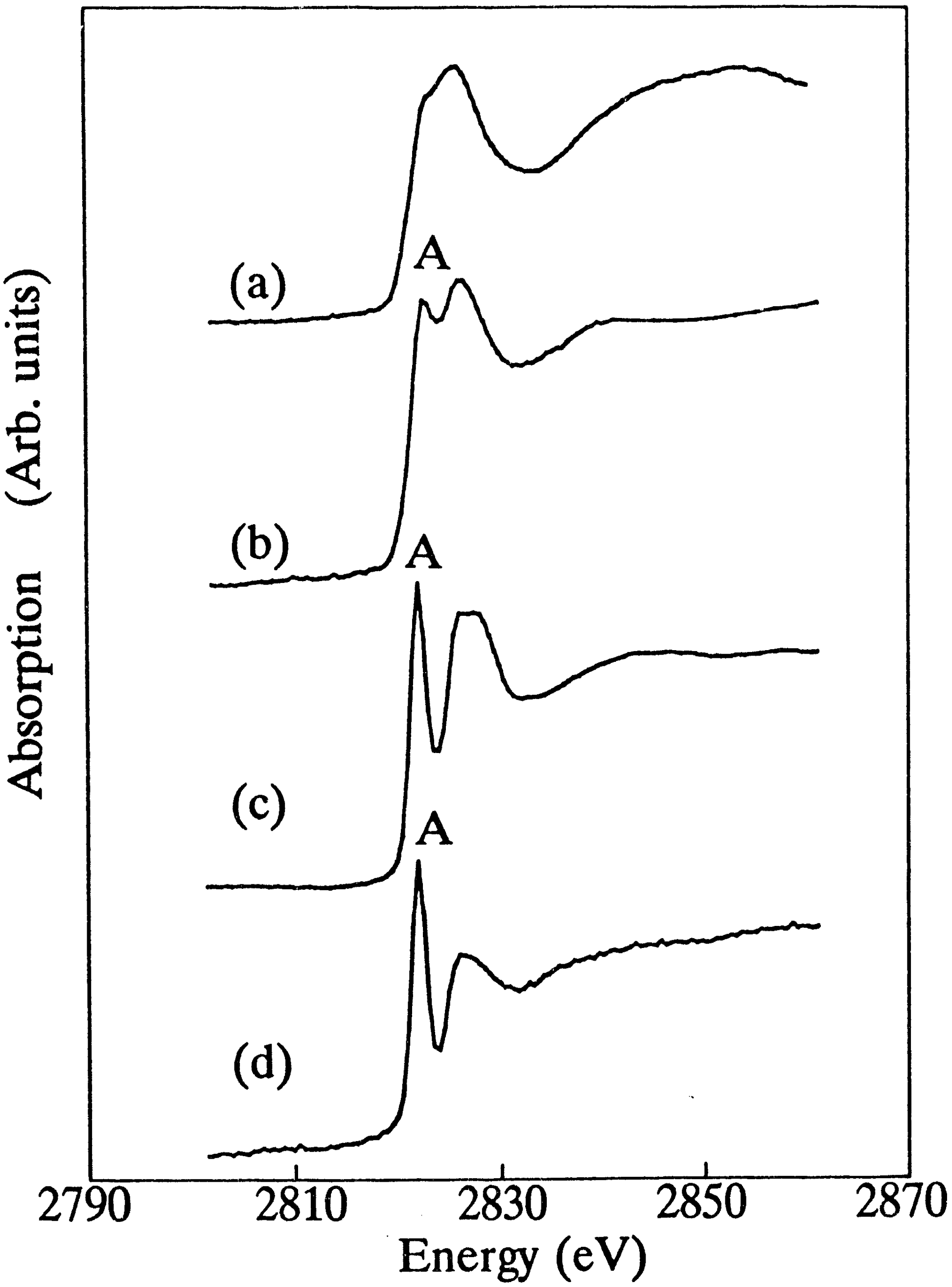


Fig 3 Lee. et al



DATE
FILMED
9 /26/ 94

END