

Iranian Dual-Use Lithium Related Research

Open Source Annotated Reference Guide

Compiled by Mark Gorwitz

2020

Updated March 2021

Table of Contents

Section I: Schooling the Scientists

Section II: Lithium Deposits in Iran

Section III: Lithium Separation Techniques

Section IV: Lithium Chemical Isotope Exchange Research

Section V: Lithium Ceramics Properties for Tritium Breeders

Section VI: Tokamak Lithium Ceramic Breeder Studies

Section VII: Indirect Drive Laser Fusion

Section VIII: Tehran Research Reactor Tritium Production Experiments

Section IX: Neutron Generator Research

Section X: End Notes

Construction of the National Research Center for Stable Isotopes Separation-Applications Development

August 24, 2019

Dr. A.Salehi, President's deputy and AEOI head on Aug/13, in a ceremony held in Fordow site, with the presence of top organization authorities, inaugurated the initial construction step for the stable isotopes separation-applications development. In the follow up presentation he made the following points.

Stable isotopes have numerous beneficial applications and diverse procedures. Putting aside the centrifuge method, there are other procedures such as, chemical exchange, refrigerating and membrane distillation, as well as heat penetration which we plan to deploy in such facilities.

The complex has gone through various lab stages, and must now be further developed. The entire project premises is 5000 square meters including 8 workshops and 8 lab facilities, which is unique in Western Asia.

The Fordow site is one of the most valuable facilities among the AEOI complexes. During the last 4 years, considering the 5000 area of this center, around 16000 square meters has been added to this site's buildings of which national center of material should be mentioned. This center which was established 2 years ago, offers services not limited to the nuclear area, but helps the country's general industry network.

Besides the National Material Center, the National Vacuum Center must be mentioned that was inaugurated in early April which still awaits completion. A comparison of Fordo conditions 3 to 4 years ago and now shows how far the site has advanced. The number of the scientific expert personnel of the site have also been increased noticeably.

We have 1044 centrifuges machine which are in the vacuum position. Two cascades of this number are in rotation, without enrichment processing, but it could easily be operational.

We have cooperation with other countries such as E-U members and Russia, within the JCPOA framework, with respect to Fordo activities which is going well.

At present, the outstanding AEOI projects are the two Bushehr power plants, no 1 and 2, which based on agreement with Russia, the concrete casting will probably be performed in October. The nuclear industry with 15000 personnel has a healthy growth and has not been stopped at any juncture. The pace of trend all depends on the orders issued by relevant senior authorities which will be accordingly implemented.

<https://www.iranwatch.org/library/governments/iran/atomic-energy-organization-iran-aeoi/construction-national-research-center-stable-isotopes-separation-applications>

Section I: Schooling the Scientists

Thesis:

Fereidoun Abbasi-Davani, 2000, Nuclear physics, PhD, listed as obtaining degree from AmirKabir University?, Shahid Beheshsti University? Ferdowsi University

Afarideh Hossein, 1988, A Study of Fission in ^{238}U Induced by Monoenergetic Neutrons and Heavy Ions and of Light Particle Emission in ^{252}Cf Spontaneous Fission, PhD., University of Birmingham

S.M. Kabir, 1971, Measurements of Calculations of Spatial Distribution of Fast Neutron Spectra in Iron and Iron-Uranium Assemblies from a 14-MeV Source, PhD., Department of Physics, Aston University

Abouzar Kiyani, 1993, Designing and Construction of a Quadruple Pauli Ion Trap for use in Mass Spectrometry, M.Sc., Department of Nuclear Physics, Imam Hossein University

Rahim Koohi-Fayegh, 1977, Implementation of the Unfolding Code FERDOR, M.Sc. Project Report, Department of Physics, University of Birmingham

Rahim Koohi-Fayegh, September 1980, Neutron Spectrum Measurement in a Beryllium-Lithium Fluoride Assembly using an NL 213, Scintillator, PhD, Department of Physics, University of Birmingham

Mashallah Pourmansoori, 1975, The Study of Gamma-Rays Associated with Fast Neutron Interactions in Extended Assemblies, PhD., Aston University

Maijeh Rahbar, 1978, Testing of Inelastic Scattering Data by Integral Measurements in ^{238}U Spherical Shells, PhD, University of London Reactor Centre, Department of Mechanical Engineering, Imperial College of Science and Technology

Javad Rahighi, 1985, High Resolution Neutron Spectrometer Development and 14 MeV Neutron Scattering by Bi, PhD., Department of Physics, University of Edinburgh

Conference Presentations:

Experimental techniques for 14 MeV neutron benchmark studies

Abstract:

The use of proton-recoil proportional and scintillation counters for measurements with 14 MeV neutrons is discussed. Details are given of investigations into their performance and that of the unfolding codes used and examples of their application in LiF and LiF-Be integral assemblies are presented.

Authors: Scott, M.C., Koohi-Fayegh R. and Evans, N.

Publication date: October 27-29, 1980

Specialist Meeting on nuclear data and benchmarks for reactor shielding, Paris, France

Experimental and computational analysis of neutron flux transmitted from spherical Beryllium shells; Andazehgiri va mohasebe-ye shar norton-e taragosilid-e az pust-e'ha-ye koravi-ye Berilium

Abstract

Beryllium is known to have a very low threshold for the (n, 2n) reaction and as a result can be and has been used as a neutron multiplier in the military and the industry, for example, for the enhancement of fast neutron flux in reactor. Flux measurements have been performed for a number of Beryllium assemblies and calculations have been made using the well-known and complicated MCNP code. It has been shown that, in general, some discrepancies between the experiment and the theory exist which could be caused by the uncertainties in the ${}^9\text{Be}$ cross-sections.

Authors: Koochi-Fayegh, R; Miri, H; Hadizadeh, M H

Publication Date: Jul 01, 1998

Iranian annual physics conference, Chekid-e-ye konferans-e fizik-e Iran, Guilan (Iran, Islamic Republic of), 23-25 Aug 1997; Other Information: PBD: 1998

Journal Articles:

Neutron spectrum measurements from 1-16 MeV in beryllium assemblies with a central D-T neutron source

Abstract

Beryllium has been proposed as both a neutron multiplier and as a plasma facing material for fusion reactors, and its neutron cross section up to 15 MeV or so is consequently of considerable importance, particularly for the (n, 2n) reaction. This paper reports on the results of a series of 14 MeV neutron transmission measurements using an NE213 scintillation spectrometer with three different thicknesses of beryllium shells. The experimental results are then compared with MCNP Monte Carlo calculations using the ENDF/B-VI data set. For all three shells the experimental results lie above those calculated for neutron energies between 8 and 11 MeV, whilst between 1 and 4 MeV they lie below. It is concluded that there are continuing uncertainties in the data.

Authors: Koochi-Fayegh, R; Abad, Miri Hakim; Green, S; Scott, M C

Publication Date: Jul 01, 2000

DOI: 10.1016/S0306-4549(99)00106-1

Annals of Nuclear Energy (Oxford); Journal Volume: 27; Journal Issue: 11

(Koochi-Fayegh acknowledges the University of Birmingham for assistance towards work undertaken in subsequent sabbatical leave periods. It should be noted that this research became the subject of a December 10, 2004 newspaper article entitled "High-energy neutron experiments in Iran raise suspicions: diplomats, AFP)

The calculated neutron energy spectrum of alpha-neutron sources using the Monte Carlo method, M. Khalaj, R. Koochi-Fayegh and M.H. Hadizadeh Yandi, Iranian Journal of Physics Research, 1999, Volume 2(1), pp39-44, In Farsi

Neutron spectrum measurement in D + Be reaction; Andazehgriye teif-e energiye notron'ha-ye sarie dar vakonesh-e D+Be

Abstract

In this project the neutron spectra from the reaction of deuteron on beryllium nuclei is measured. The energies of deuterons were 7, 10, 13 and 15 MeV, and these measurements are performed at 10, 30 and 50 degrees relative to the beam of deuterons. The detector used is 76 by 76 mm right circular cylinder of NE-213 liquid scintillator. The zero crossing technique is used for gamma discrimination. For the elimination of the background radiation, a Polyethylene block, 40 cm in thickness, with inserted cadmium sheets, and a lead block, 5 cm in thickness, were used. In order to obtain the background radiation spectrum, the latter blocks were placed between the target and the detector to eliminate neutron and gamma radiations reaching the detector directly. ¹⁹⁹ORIST code is used to unfold the neutron spectra from the measured pulse height spectra and ^{5S} and ^{RES} codes are used to obtain the detector response matrix.

Authors: Abbasi Davani, F; Etaati, G R; Afarideh, H; Koochi Fayegh, R; Aslani, G R

Publication Date: Jun 30, 2002

Iranian Journal of Physics Research; Journal Volume: 3; Journal Issue: 2

Measurement and calculation of high energy neutron flux in aluminum, graphite, water and paraffin assembly, R. Izadi-Najafabadi, R. Koochi-Fayegh and H. Afarideh, Iranian Journal of Physics Research, 2003, Volume 4(1), pp13-21, In Farsi

Abstract:

In the experimental section of this project, the energy spectrum of fast neutrons is measured, after being passed through large blocks, approximately 1m³ each, of graphite, aluminum, water and paraffin. Neutrons were produced via ⁷Li(p,n)⁷Be reaction by bombarding a lithium target with 25 or 30 MeV protons of the cyclotron of the Nuclear Research Centre for Agriculture and Medicine in Karaj.

Section II: Lithium Deposits in Iran

Conference Papers:

Activity Coefficient of Major Ions in the Urmia Brine at Different Temperatures

N. Banafshe, Department of Marine Chemistry, Mazadaran University

17th Iranian Physical Chemistry Conference, October 21-23, 2014

RECOVERY OF LITHIUM FROM URMIA LAKE BY ADSORPTION ONTO ALUMINIUM HYDROXIDE

N Heidari - Department of Chemistry, Urmia University, Urmia, Iran

P Momeni - Department of Chemistry, Urmia University, Urmia, Iran

18th Iranian Seminar on Physical and Theoretical Chemistry, March 5-8, 2016

Abstract:

Of the several hypersaline water bodies present on the surface of the earth, the Urmia Lake is the one that has attracted and attracts the most attention. The Urmia Lake located at the NorthWest of Iran. The recovery of lithium as lithium aluminate from Urmia Lake was studied. Aco-precipitation method was utilized using aluminum salt as $(AlCl_3, 6H_2O)$ Lithium ion is adsorbed onto aluminum hydroxide, Results obtained show that high Li^+ adsorption was carried out at pH ~ 7 for Urmia lake Also, Lithium ions uptake decreased with increasing temperature from $30^\circ C$ to $40^\circ C$. The maximum adsorption amount of 3 $Al(OH)_3$ is at $30^\circ C, pH = 7$ and density 1.31. The obtained results from adsorption Li^+ of Urmia Lake was compared with two isotherm models, Langmuir and freundlich isotherm.

Journal Articles:

Hydrogeochemistry of seasonal variation of Urmia Salt Lake, Iran

Samad Alipour, University of Urmia

Saline Solutions, 2006, Vol. 2(9)

Section III: Lithium Ion Separation and Purification Techniques

Thesis:

Process Design for Extraction of Lithium from Brines

Mohammad R. Barzegari, 2012, Amirkabir University of Technology

Characterization of Lithium Presence in Brine and Extraction of Lithium from Brine Resources of Iran

Moazeni Afarani, Maryam / 2013

1. Type of Document: M.Sc. Thesis
2. Language: Farsi
3. Document No: 44864 (07)
4. University: Sharif University of Technology
5. Department: Materials Science and Engineering
6. Advisor(s): Askari, Masoud; Nusheh, Mohammad
7. Abstract:
8. One of the basic resources for lithium extraction is brine which is very abundance in Iran. It is important to characterize these brines and their compositions to select a suitable method for lithium recovery from them. By investigation of the local brines and determining lithium and other alkali metals composition in them, the ion exchange

process using titanium dioxide ion-sieve with nanotube morphology is suggested as highly effective method for lithium extraction from Iranian brines. Due to high advantages of hydrothermal process, TiO₂ nanotubes were produced by this method and the optimum parameters of hydrothermal reactions were reported. In this way, hydrogen titanate nanotubes with 70 nm diameter and 2410 nm length were synthesized at 150°C for 48 hr. Li₄Ti₅O₁₂ spinel phase was prepared by means of second hydrothermal of hydrogen titanate nanotubes in 0.2 M LiOH solution at 120°C for 24 hr and then heat treated at 350°C for 2 hr. Finally, TiO₂ ion sieve was prepared by acid treatment of lithium titanate spinel with 0.5 M HCl solution. Microstructural characterization of synthesized nanostructure materials were carried out by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infra-red (FT-IR) and ultra violet visible (UV-Vis) spectrums. Lithium adsorption capacity of this ion sieve from synthetic solutions was evaluated in different lithium concentrations. The results showed that the adsorption capacity increased by increasing lithium concentration and the final value reached to 39.43 mg/g

Selective Adsorption of Li⁺ Ion on Lithium Adsorbents

Hajipour, Hengameh / 2013

1. Type of Document: M.Sc. Thesis
2. Language: Farsi
3. Document No: 44756 (07)
4. University: Sharif University of Technology
5. Department: Materials Science and Engineering
6. Advisor(s): Askari, Masoud
7. Abstract:
8. Interest in lithium sources has been increasing because of wide applications of the metal in high-energy storage lithium batteries and its compounds in other fields. Lithium appears in lake, brines and several minerals such as spodumene, petallite, and lepidolite. Several methods such as ion exchange (adsorption), solvent extraction, and coprecipitation have been investigated for the extraction of lithium from seawater, brine, and geothermal water. The adsorption method is suitable for recovery of lithium from seawater because certain inorganic ion-exchange materials show extremely high selectivity for lithium ions only. The objective of this study is to evaluate the applicability of nano-structured lithium adsorbent for the recovery of lithium from seawater. The investigations on structure and chemical composition, morphology and Li⁺ adsorption properties of the adsorbents were carried out by X-ray diffractometer (XRD), field emission gun scanning electron microscopy (FESEM) and atomic absorption spectrophotometer (AAS). It was found that lithium ion sieves had potential application for lithium recovery from aqueous phases and under optimized conditions the maximum lithium uptake has been obtained 17 mg/g in LiCl solution. Kinetic experiments suggested that the adsorption process followed the Freundlich model.

<http://repository.sharif.edu/resource/390631/-/preview/37708/>

Lithium Recovery from Brine Sources of Iran by Precipitation Method

Jandaghi, Mohammad Reaz / 2014

1. Type of Document: M.Sc. Thesis
2. Language: Farsi
3. Document No: 46456 (07)
4. University: Sharif University of Technology
5. Department: Materials Science and Engineering
6. Advisor(s): Askari, Masoud

Abstract:

Lithium is one of the most commonly used metals in industry with a wide variety of applications including batteries, lubricating grease and pharmaceutical products. Demand for lithium is expected to rise with the increasing adoption of electric vehicles. Market reports have predicted that world lithium demand will increase by 2.5 times from 2010 to 2020. Therefore, there is a pressing need to develop new sources of lithium to support this anticipated increase in demand. Lithium can be extracted from salt brine and lithium containing minerals as lithium compounds.

Salt brines are the most abundant lithium sources available in the world, comprising about 60% of all known lithium deposits. Producing lithium by evaporating salt brine is also less costly than directly extracting it from lithium minerals. This makes salt brines as an important sources of lithium to meet future market demand in the world. Chemical composition of brine determines sufficient method for extraction of lithium from it.

A major limitation of lithium extraction from salt brine is the difficulty in processing brine with a high magnesium to lithium (Mg/Li) ratio. It is important for the extracted lithium compounds to have low magnesium content to avoid magnesium contamination in the downstream products. This makes lithium extraction from salt lakes with a high Mg/Li ratio a difficult task, as additional steps and costs are incurred to reduce the magnesium content of the brine solution to an acceptable level. The additional cost varies directly with the Mg/Li ratio.

This research was done on KHOR-BIYABANAK as very high Mg/Li salt brines in the world with proportion of magnesium to lithium about 300 and the main lithium source of Iran. In this regard caustic soda, ammonia, dolomite, calcium carbonate and lithium hydroxide were utilized as magnesium and boron removing agent and Sulfuric acid used for calcium exclusion from brine. Also Disodium phosphate and disodium carbonate were employed as precipitant for lithium phosphate and lithium carbonate production respectively. Furthermore effect of parameters like reaction time and temperature, solution rest time and amount of precipitants and how are added to brine on lithium recovery and final product purity were investigated. Results indicated that production of high purity lithium phosphate (99/9%) from KHOR-BIYABANAK's brine is achievable. But production of lithium carbonate is faces more problem compared with lithium phosphate because of higher solubility of lithium carbonate comparison to lithium phosphate and higher limit of lithium concentration in solution for lithium carbonate

precipitation. So optimized condition for lithium carbonate precipitation reaction leads to production of 97% purity lithium carbonate.

Lithium Adsorption on TiO₂ Ion-sieve from Magnesium Treated Brine Sources

Nagi Toosi, Alireza / 2015

1. Type of Document: M.Sc. Thesis
2. Language: Farsi
3. Document No: 48053 (07)
4. University: Sharif University of Technology
5. Department: Materials Science and Engineering
6. Advisor(s): Asgari, Masoud

Abstract:

Brines are one of the main resources for lithium extraction and Iran has got many high magnesium and low lithium brine resources. In order to extract lithium, it is required to carefully identify these resources and their associated compounds and then an appropriate method can be adopted to extract lithium. Among the Previous researches, Bahadori, Jandaghi and Moazeni developed methods for removal of undesirable brines elements, Deposition of lithium from refined brine and lithium adsorption anatase ion-sieves membrane respectively; in this study it has been tried to investigate the optimization of the adsorption process, onto the TiO₂-B ion sieve with nanotube morphology. TiO₂-B nanotubes were synthesized using hydrothermal method in NaOH solution. Nano titanate spinals were synthesized utilizing a second hydrothermal process in LiOH solution. Finally acid washing was carried out for lithium desorption from the resulting structure of the previous stage in order to obtain lithium. Nano ion-sieves derived from the abovementioned method were exposed to a synthetic medium containing specified amount of lithium ions to achieve an optimal condition of adsorption by adjusting the solution pH, adsorption time, acid washing concentration and acid washing time. Then, The optimal condition obtained then was used for the real brine which was initially refined from Calcium, Bore and Magnesium by using dilute H₂SO₄, contacting with Prolite 108 ion-exchange resin and adding a combination of NaOH and LiOH respectively. Characterization of the nanotubes was carried out using X-ray diffraction (XRD), scanning electron microscopy (SEM), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM) and Brunauer–Emmett–Teller (BET). The optimized condition was adopted at the solution pH of 12, adsorption time of 48 hours, acid washing concentration of 0.1M and acid washing time of 28 hours which resulted in maximum lithium adsorption percentage of 96.2% for the synthetic medium and 80% for the brine contacting average amount of 80 and 50 ppm lithium ions in solution respectively. Adsorption measurements were carried out by atomic adsorption spectroscopy (AAS). Maximum capacity obtained from the experiments was about 18 mgs per gram of Nano absorbent. The result were appropriately fitted to the freundlich. Adsorption model and kinetic investigation revealed pseudo-second order kinetics shoving chemisorption adsorption.

Lithium Extraction from Urmia Lake Brines

Soleimani Khalaji, Milad / 2016

1. Type of Document: M.Sc. Thesis
2. Language: Farsi
3. Document No: 49005 (07)
4. University: Sharif University of Technology
5. Department: Materials Science and Engineering
6. Advisor(s): Askari, Masoud; Alamolhoda, Ali Asghar

Abstract:

Using a Lithium Selective Ion Sieve is one of the most advanced processes for Extraction of lithium from Brines. The ability to Extract Lithium selectively from brines make the ion sieve suitable for brines with low concentrations of lithium. In this study brines samples from Urmia Lake with lithium concentration of 30 ppm was used. The main objective of this study was to find the best condition for lithium adsorption and desorption using the synthesized titanium dioxide ion sieve. In this study lithium selective ion sieve with nanotube morphology and Diameter of 81 nm was synthesized. Study on pH of synthesized solution containing lithium ions was carried out and pH=12 was concluded the optimum amount for adsorption process. Study on adsorption time showed that experimental data had a very good accordance with pseudo-second order kinetic model and after 48 hours, adsorption equilibrium was maintained. Effect of equilibrium lithium concentration in synthesized solution on adsorption capacity was studied and it showed that experimental data had a good accordance with Freundlich isotherm model. Study on desorption of lithium from ion sieve was also carried out and amounts of 8 hours and 0.1 molar for desorption time and HCl concentration was concluded. Finally the Adsorption process on Urmia Lake showed that 58 percent of lithium in the brine sample was adsorb by ion sieve.

Lithium Extraction with TiO₂ Nanotube Synthesized by Anodizing Method

Taghvaei, Nastaran / 2017

1. Type of Document: M.Sc. Thesis
2. Language: Farsi
3. Document No: 50635 (07)
4. University: Sharif University of Technology
5. Department: Materials Science and Engineering
6. Advisor(s): Askari, Masoud

Abstract:

Due to the technology advancement and the large-scale application of lithium-ion batteries in recent years, the market demand for lithium is growing rapidly and the availability of land lithium resources is decreasing significantly. As such, the focus of lithium extraction technologies has shifted to water lithium resources involving salt-lake brines and sea water. The ion exchange process is a promising method for lithium extraction from brine and seawater having low concentrations of this element. Among various aqueous recovery technologies, the

lithium ion-sieve (LIS) technology is considered the most promising one. This is because LISs are excellent adsorbents with high lithium uptake capacity, superior lithium selectivity and good cycle performance. These attributes have enabled LISs to separate lithium effectively from aqueous solutions containing different ions. In this study, titanium dioxide and then lithium titanate spinel with nanotube morphology was synthesized via anodizing method followed by chemical lithiation in LiOH solution. The produced $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spinel ternary oxide nanotube with about 100 nm diameter was then treated with dilute acidic solution in order to prepare an adsorbent suitable for lithium adsorption from local brine. Morphological and phase analysis of the obtained nanostructured samples were done by using Field Emission Scanning Electron Microscopy along with X-ray diffraction. The results showed titanium dioxide adsorbent could recover 37.5 mg/g of the lithium present in 112 mg/L of lithium solution.

Capability of $\text{TiO}_2(\text{B})$ -based Nanotubes to Adsorb Lithium Ion from Aqueous Solution

Shoghi, Ali / 2019

1. Type of Document: M.Sc. Thesis
2. Language: Farsi
3. Document No: 52051 (07)
4. University: Sharif University of Technology
5. Department: Materials Science and Engineering
6. Advisor(s): Askari, Masoud; Alamolhoda, Ali Asghar
- 7.
8. Abstract:
9. Due to the technology advancement and the large-scale application of lithium-ion batteries in recent years, the market demand for lithium is growing rapidly and the availability of land lithium resources is decreasing significantly. As such, the focus of lithium extraction technologies has shifted to water lithium resources. Among various aqueous recovery technologies, the lithium ion-sieve (LIS) technology is considered the most promising one. This is because LISs are excellent adsorbents with high lithium uptake capacity, superior lithium selectivity, and good cycle performance. TiO_2 -based nanotubes are an appropriate option for adsorbing lithium from solution due to their high specific surface area and environmentally friendly process. Among titanium dioxide phases, $\text{TiO}_2\text{-B}$ is a suitable host for small ions such as lithium due to its low density. In this thesis, $\text{TiO}_2\text{-B}$ nanotubes were successfully synthesized via hydrothermal method. By using $\text{TiO}_2\text{-B}$ nanotubes, lithium titanate nanotubes with the desirable phase of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ were fabricated by hydrothermal method with 0.8 M LiOH aqueous solution. Then, lithium ion-sieve was prepared by acid pickling with 0.01 M HCl for 24 h. Phase and morphology characterization were determined using XRD and FESEM analyses. Adsorption experiments at different times and various lithium concentrations showed that equilibrium obtained after 24 h. Lithium Adsorption tests from solutions containing various concentrations showed that by increasing lithium concentration from 200 to 2000 mg/L, the adsorption capacity ranges from 34.3 to the significant amount of 160.6 mg/g. Lithium quantity in the solutions was measured by ICP test. Using the pseudo-first-order and pseudo-second-order kinetic models, it was found that the experimental results followed the pseudo-second-order kinetic model. Comparison of experimental results and

Langmuir and Freundlich isotherm models indicated that experimental data are in good agreement with Freundlich adsorption isotherm. The study of Dubinin Radushkevich isotherm showed the lithium has been physically adsorbed onto ion-sieve. Furthermore, the BET surface area of ion-sieve was 115 m²/g

Books:

Recent Researches In Metallurgical Engineering Hardcover – January 1, 2014

by NUSHEH M (Author)

Product details

- **Hardcover**
- **Publisher:** INTECH (2014)
- **Language:** English
- **ISBN-10:** 9535103563
- **ISBN-13:** 978-9535103561

Conference Papers:

Lithium ore processing: an overview of the current and new processes

N.J. Welham, A. Nosrati and N. Setoudeh

Metallurgical Plant Design and Operating Strategies – World's Best Practice, September 11-12, 2017, Perth, WA., p185-194

Journal Articles:

Chemical separation of Li from Na⁺ and K⁺ ions using ion exchange resin (AG 50W-X8)

Analytical Chemistry: An Indian Journal, 2009

ISSN (PRINT): 0974-7419

Author(s): H.Karami, M.Sadeghi, S.Nemati, B.Zeinali

Abstract:

An ion-exchange method has been developed for separation of Li from alkali elements (Na and K). A column of AG 50W-X8 cation-exchange resin was found appropriate to separate lithium from the solution. In 0.1 M HCl solution sodium and potassium ions were completely stripped and lithium ions were passed from the column without any adsorption. All determinations of ions were performed by Atomic Absorption Spectroscopy. Separation and recovery efficiency was found was 99.24%.

Evaluation of lithium separation by dispersive liquid–liquid microextraction using benzo-15-crown-5

Journal of Radioanalytical and Nuclear Chemistry, 2012, Volume 293: Issue 1, Page Count: 247–254

Authors: Mohammad Mallah¹ and Mehrdad Davoudi²

- ¹ Nuclear Fuel Cycle Research School, Nuclear Science & Technology Research Institute, End of North Karegar Ave, Tehran, Iran

- ²Department of Chemistry, Islamic Azad University, Central Tehran Branch, Tehran, Iran

Abstract

In this article a dispersive liquid–liquid microextraction method was applied for evaluation of lithium separation from aqueous solution. Benzo-15-crown-5 (B15C5) was used as a chelating agent prior to extraction. An appropriate mixture of disperser solvent and extraction solvent were added rapidly into the aqueous sample containing lithium ion; as a result, a cloudy solution was formed which consisted of fine droplets of extraction solvent dispersed entirely into aqueous phase. The mixture was centrifuged and the lithium complex with B15C5 was sedimented at the bottom of the conical sample holder. Then, 2.0 mL of enriched phase containing lithium complex was used for determination of lithium ion by flame atomic absorption spectrometry. The conditions for the microextraction performance were investigated. Under the best optimized conditions, the accepted recovery factors for the lithium obtained, ranged from 37.24 to 99.63 %. Furthermore, high preconcentration factors (7.46–19.93) were also achieved. The relative standard deviation for three replicate measurements of 0.127 mg L⁻¹ of lithium was 2.83 %.

Adsorption behavior of Li⁺ from aqueous medium using zirconium oxide nano-ion sieve
Nanomaterials and Energy, Volume 3 Issue 3, May 2014, pp. 87-92

Authors:

Hengameh Hajipour, MSc
, , Maryam Moazeni, MSc
, , Masoud Askari, PhD
, , and Mohammad Nusheh, PhD*

Author Affiliations

Department of Materials Science and Engineering, Sharif University of Technology, Tehran, Iran
Department of Materials Science and Engineering, Sharif University of Technology, Tehran, Iran
Department of Materials Science and Engineering, Sharif University of Technology, Tehran, Iran
Department of Engineering, Zanjan Branch, Islamic Azad University, Zanjan, Iran

Abstract

Interest in lithium sources has been increasing because of wide applications of the metal in high-energy storage lithium batteries and its compounds in other fields. Lithium is found in sea and geothermal waters, lakes, brines and several minerals. Among several methods that have been suggested for the extraction of lithium from these resources such as adsorption (ion exchange), solvent extraction and co-precipitation, the adsorption method is more suitable for recovery of lithium from seawater because certain inorganic ion-exchange materials show extremely high selectivity only for lithium ions. The objective of this study is to evaluate the applicability of nano-structured zirconium oxide adsorbent for the recovery of lithium from the brine. The investigations on structure and chemical composition, morphology and Li⁺ adsorption properties of the adsorbents were carried out by X-ray diffractometer, field emission gun scanning electron microscope and atomic absorption spectrophotometer, lithium ion adsorptive isotherm and kinetic measurement. It was found that zirconium ion sieves had potential application for lithium recovery from aqueous phases, and under optimized conditions the maximum lithium uptake has been obtained 17 mg/g in lithium chloride solution. Kinetic experiments suggested that the

adsorption process followed the Freundlich model.

SYNTHESIS OF LITHIUM ION SIEVE NANOPARTICLES AND OPTIMIZING UPTAKE CAPACITY BY TAGUCHI METHOD

IRANIAN JOURNAL OF CHEMISTRY AND CHEMICAL ENGINEERING (IJCE) 2014 , Volume 33 , Number 4; Page(s) 15 To 24.

Author(s): ZANDEVAKILI SAEED*, RANJBAR MOHAMMAD, EHTESHAMZADEH MARYAM

* DEPARTMENT OF MINING ENGINEERING, SHAHID BAHONAR UNIVERSITY OF KERMAN, KERMAN, I.R. IRAN

Abstract:

Spinel-type of MnO₂ nanoparticles which successfully synthesized by a hydrothermal process, have a required capacity for lithium uptake from liquid resources. The most lithium adsorption capacity of 6.6 mmol/g of up to now was found to be an important limiting parameter for industrial applications. Therefore, increasing uptake capacity of these ion sieves by studying the effect of six effective parameters, involving lithium compounds, manganese compounds, oxidizing reagents, calcination temperatures, heating times and Li/Mn mol ratios was investigated. To this end, Taguchi L₉ (3⁴) orthogonal array was employed as a predominate method to evaluate these parameters and the results optimized by using analysis of variance (ANOVA) and analysis of mean (ANOM) in two separate stages. Although, all mentioned parameters had significant effect on lithium uptake capacity, but oxidizing reagents were the most effective factors. Hence, a new ion sieve with more than 9 mmol/g lithium adsorption capacity was synthesized for the first time, by applying this method.

Synthesis of a nanostructure ion sieve with improved lithium adsorption capacity

Micro & Nano Letters, 2014, Volume 9, Issue 7, p. 455 – 459

Author(s): Saeed Zandevakili ¹ ; Mohammad Ranjbar ² ; Maryam Ehteshamzadeh ³

- o Affiliations: 1: Department of Mining Engineering, Shahid Bahonar University, Kerman, PO Box 76169-133, Iran;
- 2: Mineral Industries Research Centre, Shahid Bahonar University, Kerman, PO Box 76169-133, Iran;
- 3: Department of Material Engineering, Shahid Bahonar University, Kerman, PO Box 76169-133, Iran

Abstract:

The low lithium adsorption capacity of different ion sieves was found to be an important limiting parameter for their use in industrial extraction. The maximum exchange capacity of 6.6 mmol/g obtained till now is not high enough for their economical industrial application. Therefore, an increase in lithium adsorption capacity by studying the effects of three parameters, involving manganese salt compound, lithium salt compound and Li/Mn mole ratio on synthesised ion sieves was investigated. Moreover, the ion sieves capability on the lithium uptake from lithium-

enriched solution was examined by the Taguchi experimental design method by L9 orthogonal array. Continuously, optimum conditions were predicted and confirmed by the experimental results. Based on the results, all mentioned parameters have significant effect on lithium uptake capacity, but lithium salt compound is the most effective factor. Finally, an appropriate ion sieve with lithium adsorption capacity >8.5 mmol/g was synthesised by applying the optimised conditions.

Recovery of lithium from Urmia Lake by a nanostructure MnO₂ ion sieve

Hydrometallurgy, Volume 149, October 2014, Pages 148-152

S. Zandevakili^{ab}, M. Ranjbar^{ab} and M. Ehteshamzadeh^c

^aDepartment of Mining Engineering, Shahid Bahonar University, Kerman, P.O. Box 76169-133,

^bIranMineral Industries Research Centre, Shahid Bahonar University, Kerman, P.O. Box 76169-133, Iran

^cDepartment of Material Engineering, Shahid Bahonar University, Kerman, P.O. Box 76169-133, Iran

Abstract:

The ion exchange process was employed to recover lithium from brine collected from Urmia Lake Iran, which contains saturated levels of Na, Mg, K and low Li ($2.45 \text{ mmol}\cdot\text{L}^{-1}$ or $17 \text{ mg}\cdot\text{L}^{-1}$). The high levels of these impurities in Urmia Lake would create difficulties during lithium processing if conventional techniques were used. To this end, the spinel-type MnO₂ nanorod, with the size about 40–90 nm in diameter and 150–900 nm in length, was first synthesized as a lithium ion sieve via a hydrothermal method. The lithium uptake capacity of this synthesized ion sieve reached to $9 \text{ mmol}\cdot\text{g}^{-1}$, which is the maximum value among the adsorbents studied to date. The crystalline structure, property and size of all products involving oxidizer, precursor and ion sieve are examined via powder X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Also the lithium selective adsorption property was investigated by measuring the distribution coefficients (K_d) of a series of alkaline and alkaline-earth metal ions, which is significant for lithium extraction from aqueous solutions with very low lithium content. Furthermore, the results show that the synthesized MnO₂ nanorods could be utilized in lithium extraction from Urmia Lake brine and other environments including sea water and waste water.

Adsorption behavior of Li⁺ from aqueous medium using zirconium oxide nano-ion sieve

Nanomaterials and Energy, Volume 3 Issue 3, May 2014, pp. 87-92

Authors:

Hengameh Hajipour, MSc

, , Maryam Moazeni, MSc

, , Masoud Askari, PhD

, , and Mohammad Nusheh, PhD*

Abstract

Interest in lithium sources has been increasing because of wide applications of the metal in high-energy storage lithium batteries and its compounds in other fields. Lithium is found in sea and

geothermal waters, lakes, brines and several minerals. Among several methods that have been suggested for the extraction of lithium from these resources such as adsorption (ion exchange), solvent extraction and co-precipitation, the adsorption method is more suitable for recovery of lithium from seawater because certain inorganic ion-exchange materials show extremely high selectivity only for lithium ions. The objective of this study is to evaluate the applicability of nano-structured zirconium oxide adsorbent for the recovery of lithium from the brine. The investigations on structure and chemical composition, morphology and Li^+ adsorption properties of the adsorbents were carried out by X-ray diffractometer, field emission gun scanning electron microscope and atomic absorption spectrophotometer, lithium ion adsorptive isotherm and kinetic measurement. It was found that zirconium ion sieves had potential application for lithium recovery from aqueous phases, and under optimized conditions the maximum lithium uptake has been obtained.

Hydrothermal synthesis and characterization of titanium dioxide nanotubes as novel lithium adsorbents

Materials Research Bulletin, 2015, Vol. 61, p70-75

Authors:

Moazeni, Maryam; Hajipour, Hengameh; Askari, Masoud ^[1]; Nusheh, Mohammad, E-mail: nusheh@mehr.sharif.edu ^[2]

1. Department of Materials Science and Engineering, Sharif University of Technology, Tehran (Iran, Islamic Republic of)
2. Metallurgy Group, Engineering Department, Zanzan Branch, Islamic Azad University, Zanzan (Iran, Islamic Republic of)

Abstract

The ion exchange process is a promising method for lithium extraction from brine and seawater having low concentrations of this element. To achieve this goal, it is vital to use an effective adsorbent with maximum lithium adsorption potential together with a stable structure during extraction and insertion of the ions. In this study, titanium dioxide and then lithium titanate spinel with nanotube morphology was synthesized via a simple two-step hydrothermal process. The produced $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spinel ternary oxide nanotube with about 70 nm diameter was then treated with dilute acidic solution in order to prepare an adsorbent suitable for lithium adsorption from local brine. Morphological and phase analysis of the obtained nanostructured samples were done by using transmission and scanning electron microscopes along with X-ray diffraction. Lithium ion exchange capacity of this adsorbent was finally evaluated by means of adsorption isotherm. The results showed titanium dioxide adsorbent could recover 39.43 mg/g of the lithium present in 120 mg/L of lithium solution.

Improvement of lithium adsorption capacity by optimising the parameters affecting synthesised ion sieves

Micro & Nano Letters 2015, 10 (2), 58-63.

Author(s): Saeed Zandevakili ¹ ; Mohammad Ranjbar ² ; Maryam Ehteshamzadeh ³

Affiliations: 1: Department of Mining Engineering, Shahid Bahonar University, Kerman, P.O. Box 76169-133, Iran;

2: Mineral Industries Research Centre, Shahid Bahonar University, Kerman, P.O. Box 76169-133, Iran;

3: Department of Material Engineering, Shahid Bahonar University, Kerman, P.O. Box 76169-133, Iran

Abstract:

Recent study has shown that the spinel type of MnO_2 nanoparticles have a required capacity for lithium extraction from liquid resources. The low lithium adsorption capacity of synthesized ion sieves was found to be an important limiting parameter for their use in industrial applications. Therefore, increasing the uptake capacity of different ion sieves by studying the effect of six effective parameters, involving lithium salt compound, manganese salt compound, oxidising reagent, calcination temperature, heating time and Li/Mn mol ratio, on the synthesised ion sieves was investigated. Hence, in this reported work, a specific approach based on the $L_9(3^4)$ Taguchi orthogonal array was employed to evaluate these parameters and to optimise them in two separate stages. Also, the relative importance of each factor was determined using analysis of variance. Although, all mentioned parameters had a significant effect on lithium uptake capacity, the oxidising reagent and the lithium salt compound were the most effective factors. Also, an appropriate ion sieve with a lithium adsorption capacity of more than 9 mmol g^{-1} was synthesised for the first time.

Enhancing removal and recovery of magnesium from aqueous solutions by using modified zeolite and bentonite and process optimization

Mohammad Amin Alaei Shahmirzadi¹, Seyed Saeid Hosseini¹ & Nicolas Raymond Tan²
Korean Journal of Chemical Engineering volume 33, pages3529–3540(2016)

Abstract

Natural and modified zeolite and bentonite are investigated and characterized for extraction of magnesium from aqueous solutions. Magnesium removals as high as 85.21% and 81.73% were achieved by calcined bentonite and microwave radiated zeolite, respectively. The effects of various operational parameters were studied and optimized using selected isotherms. Maximum Mg (II) adsorption capacities of 26.24 and 35.67 $\text{mg} \cdot \text{g}^{-1}$ were obtained on pristine and calcined bentonites, respectively. Thermodynamic studies suggest that magnesium adsorption on natural bentonite is spontaneous and endothermic (9.13 $\text{kJ} \cdot \text{mol}^{-1}$). Also, desorption study of natural bentonite demonstrates that HNO_3 is more effective by offering 89.11% desorption than other desorptive counterparts.

Selective Extraction of lithium from low-grade Gypsiferous Clays by reduction of Calcium and Magnesium content in the pregnant leach solution (PLS)

International Academic Journal of Science and Engineering, 2017, Vol. 4(2), p160-169
Mohammad.R Barzegari, Gholamhossein Ghorbankarimi, Hasan Saadati and Habibollah Torshizian

Abstract:

Lithium extraction from all deposits is associated with magnesium and calcium ions as main impurities. In this study, an effective way provided to extract the maximum amount of lithium from clay deposits while minimizing extraction of magnesium and calcium ions. After pre-

feasibility studies on extraction methods, the limestone-gypsum roasting with water-leaching technique was selected for final studies. After identifying effective parameters including furnace temperature, roasting time, the ratio of calcium carbonate to feed and the ratio of calcium sulfate to feed, Taguchi experimental design was used to optimize experimental conditions and variables. For this purpose, DX7 software and L25 array were used. A furnace temperature of 800 ° C, roasting time of 2 h, a calcium carbonate to feed ratio of 1:5 and a calcium sulfate to feed ratio of 4:5 were obtained as the optimal technical and economic conditions with a lithium recovery of 68.7%. The highest lithium recovery of 75.65% was obtained at a furnace temperature of 1100 ° C, roasting time of 5 h, a calcium carbonate to feed ratio of 1:5 and a calcium sulfate to feed ratio of 1:5. In both cases, magnesium was completely removed and the maximum content of calcium (in optimal technical and economic conditions) in the leach solution was 0.1%

Selective adsorption of lithium ions from Urmia Lake onto aluminum hydroxide

N. Heidari & P. Momeni¹

Environmental Earth Sciences, 2017, volume 76, Article number: 551

Abstract:

In the present study, recovery of lithium as lithium aluminate from Urmia Lake was investigated. A coprecipitation method was utilized by using an aluminum salt ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$). Lithium ions are adsorbed on aluminum hydroxide, which is prepared by adding NaOH and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ to the brines at $\text{Al}^{3+}/\text{Al}^{3+} + \text{Li}^+ + \text{Li}^+ \approx 5$. The results showed that the maximum Li^+ ion adsorption was adsorbed at $\text{pH} \approx 7$. Also, by increasing the temperature from 30 °C to 40 °C, lithium ions adsorption was decreased. The maximum adsorption amount of $\text{Al}(\text{OH})_3$ was at 30 °C, $\text{pH} = 7$ and density 1.31. The obtained results from adsorption of Li^+ of Urmia Lake were compared with four isotherm models, Langmuir, Dubinin–Radushkevich, Freundlich and Temkin isotherms. In addition, sulfuric acid was used for Li^+ desorption from aluminum hydroxide.

Preparation and characterisation of lithium ion exchange composite for the recovery of lithium from brine

Mineral Processing and Extractive Metallurgy: Transactions of the Institutions of Mining and Metallurgy

Volume 127, 2018 - Issue 3, Pages 176-181

Saeid Zandvakili & Mohammad Ranjbar

Abstract:

This paper presents the characterization and application of a new ion exchange composite, manufactured by poly vinylidene fluoride (PVDF) for recovery of lithium from natural brine. Synthesized MnO_2 nano-particles (HMO, final MnO_2 ion-sieve) having high selectivity for lithium adsorption were used as inorganic ion-exchange adsorbent. Subsequently, the lithium ion exchange composite (CHMO, final MnO_2 ion exchange composite) was prepared by dissolving PVDF in *N*-methyl-2-pyrrolidone, and mixing with (HMO) in equal ratios. The produced

polymeric solution acts as a binder and support to closely bond HMO together into a homogeneous three-dimensionally interpenetrating network after drying at 220°C. This composite presents a mesoporous/macroporous structure which allows free channel of the solution. It exhibits considerable Li^+ adsorption capacities of 19.22 and 11.06 $\text{mg}(\text{Li}^+) \text{g}^{-1}$ (CHMO) in LiOH solution and lithium-enriched Lake Urmia, respectively. Efforts for improvement of the overall performances of CHMO are still in progress.

Enhancing lithium leaching by mechanical activation

Mongolian Journal of Chemistry 19(45):44-48 · December 2018

Nader Setoudeh, Ataollah Nosrati and N. J. Welham

Abstract:

The lithium (Li) bearing minerals lepidolite and spodumene were mixed with different mass ratios of Na_2SO_4 and mechanically activated by milling in a planetary ball mill for 5 h. The milled samples were studied using thermogravimetry under an air atmosphere up to 950 °C. Isothermal heating of the milled samples was undertaken in a furnace at temperatures of 700 °C and 800 °C for 1 h. Hot water leaching of the calcines indicated that increasing the calcination temperature had a significant effect on the dissolution of lithium. The leaching of lithium from lepidolite was notably higher than that from spodumene.

Simultaneous Optimization of Adsorption Capacity and Stability of Hydrothermally Synthesized Spinel Ion Sieve Composite Adsorbents for Selective Removal of Lithium from Aqueous Solutions

Ind. Eng. Chem. Res. 2019, 58, 27, 12207–12215

Majid Bazrgar Bajestani, Ahmad Moheb and Mohammadali Masigol

Abstract:

The main aim of this paper was synthesis of spinel type lithium manganese oxide adsorbent with high adsorption capacity and stability for selective removal of lithium ion. In contrast with the previous works reported by other researchers, simultaneous improvements of adsorbent stability and adsorption capacity were investigated by insertion of cobalt into the spinel structure of lithium manganese oxide and optimization of the adsorbent preparation conditions. To this aim, the effects of calcination temperature and molar ratios of Li/Mn and Co/Mn on adsorbent capacity and stability were investigated via hydrothermal method for adsorbent preparation. Experiments were designed by using Design Expert Software and response surface methodology considering three independent variables each at three levels. It was found that the adsorbent synthesized at optimum conditions has high adsorption capacity of 53.52 mg/g and with only 2.52% adsorption capacity loss for two consecutive adsorption cycles. This achievement was also confirmed by XRD analysis. The structural morphology of the optimized adsorbent was characterized by SEM analysis. The result of BET analysis showed that the specific surface area of the optimized adsorbent was 2.564 m^2/g . Finally, the results of selectivity adsorption experiment revealed that the optimized adsorbent can be considered as a promising tool for selective separation of lithium ions from sodium ions with molar selectivity of 90.32.

Optimization of lithium separation conditions from Caspian seawater using fuzzy logic combined with dispersive liquid–liquid extraction

Geosystem Engineering, Volume 22, 2019 - Issue 3, Pages 169-178

Romina Pourhassan Motlagh Sharemi, Abbas Rashidi, Mohammad Hassan Mallah & Jaber Safdari

Abstract:

For optimization of separation conditions of lithium from the Caspian seawater, a new combination technique of liquid–liquid extraction and fuzzy logic is being used. In this research, disperser and extraction solvents, and ligand of benzo15-crown-5, have been quickly injected. It went to cloudy form solution contain small extraction solvent drops. The impact of different parameters such as the kind and concentration of benzo15-crown-5, the volume of disperser and extraction solvents, pH and extraction time have been optimized on the extraction percentage and analyzed using fuzzy logic. The effect of other metal ion on extraction percentage was also investigated. Under the optimized conditions (volume of tetrachloroethylene: 1.5 mL, volume of acetone: 120 mL, volume of benzo15-crown-5: 0.1 mL, concentration of benzo15-crown-5: 0.001 mol/L, and pH: 1), the extraction has increased to 74% for the synthesis sample and 31% for the real sample from Caspian seawater.

Lithium removal from seawater *via* liquid membrane transport using 12-crown-4 as a carrier and study of the effect of carbon nanotubes as a membrane additive

Analytical Chemistry, 2019, Issue 20

Mehrdad Yazdanpanah,^a Mir Mahdi Zahedi ^{*a} and Morteza Ziyaadini ^a

* Corresponding authors

^a Department of Marine Chemistry, Faculty of Marine Sciences, Chabahar Maritime University, P.O. 99717-56499, Chabahar, Iran
E-mail: ids.m.zahedi@gmail.com

Abstract

In this work, transport of lithium (Li) ions from seawater into an aqueous phase was performed by using a liquid membrane (LM) and 12-crown-4 as a carrier. Influential parameters on the extraction efficiency of Li including the pH of the feed and receiving phases, type of membrane solvent, carrier concentration, type & concentration of the stripping reagent in the receiving phase and its pH, temperature and time of transport were investigated and optimized. The effect of carbon nanotubes (CNTs) as an additive on the transportation of Li ions was evaluated. The results show that single walled carbon nanotubes (SWCNTs) have a positive effect on the Li transportation. Under the optimized conditions, the maximum Li transportation from the feed into the receiving phase was 12.0%. The selectivity of the proposed method in the presence of interfering ions such as Na⁺, K⁺, Ca²⁺ and Mg²⁺ was more satisfactory than that of reported methods. The method was successfully applied for the separation of Li from seawater samples.

Lithium recovery from mechanically activated mixtures of lepidolite and sodium sulfate

Mineral Processing and Extractive Metallurgy: Transactions of the Institutions of Mining and Metallurgy

Nader Setoudeh, Ataollah Nosrati & Nicholas J. Welham

Received 22 May 2019, Accepted 24 Jul 2019, Published online: 09 Oct 2019

Abstract:

Mixtures of lepidolite ore and sodium sulfate (Na_2SO_4) at mass ratios of 1:0.5 and 1:1 were prepared and milled using zirconia media in a planetary ball mill for 5 h. The 5 h milled samples were heated in a furnace at temperatures of 700°C or 800°C for one h under an air atmosphere. XRD results showed the formation of new phases such as LiKSO_4 , LiNaSO_4 and $\text{Li}_2\text{NaK}(\text{SO}_4)_2$ in the calcine. Unmilled samples showed no such reactions. The presence of well crystalline $\text{Li}_2\text{NaK}(\text{SO}_4)_2$ phase in the calcine after heating at 700 indicated that chemical reactions between the lepidolite and Na_2SO_4 occur at lower temperatures after 5 h milling. Hot water leaching of the calcines showed that phases such as LiKSO_4 , LiNaSO_4 and $\text{Li}_2\text{NaK}(\text{SO}_4)_2$ were responsible for the increase in solubility of lithium. Increasing the calcination temperature had a more significant effect on the lithium dissolution than increasing the fraction of Na_2SO_4 .

Acknowledgment

This research work was undertaken at Edith Cowan University (ECU) as part of a larger research project entitled 'Lithium Ore Processing' during Dr. Setoudeh's sabbatical leave from Yasouj University. The authors thank Yasouj University for granting sabbatical leave to Dr. Setoudeh and the School of Engineering at Edith Cowan University for hosting Dr. Setoudeh. Financial support for the project was provided by the Deputy of Research and Technology of Yasouj University, Edith Cowan University (ECU) and Welham Metallurgical Services. The authors gratefully acknowledge Dr. Guanlian Zhou for his kindly cooperation at chemical laboratory of ECU. Also acknowledged are the providers of the lepidolite ore who wish to remain anonymous, without their generosity this project could not have taken place.

Lithium extraction from mechanically activated of petalite- Na_2SO_4 mixtures after isothermal heating

Minerals Engineering, Volume 151, 1 June 2020, 106294

Dedication: Dr. Ataollah Nosrati passed away from cancer before submission of this paper. His co-authors would like to dedicate this paper to his memory.

Nader Setoudeh^{ab}, Ataollah Nosrati^{b1} and Nicholas J. Welham^{bc}

Materials Engineering Department, Yasouj University, Yasouj 75918-74831, Iran

Edith Cowan University, School of Engineering, Chemical Engineering Department, Perth, Australia

Welham Metallurgical Services, South Lake, Australia

a

b

c

Abstract

Mixtures of a petalite flotation concentrate and sodium sulphate (Na_2SO_4) with mass ratios of 1:0.5 and 1:1 were prepared and milled for 5 h using zirconia media in a planetary ball mill. The milled mixtures were heated at 800–1000 °C for 1 h in air in a muffle furnace. The XRD patterns for the calcines indicated that reaction between petalite and sodium sulphate results in formation of LiNaSO_4 , albite and spodumene phases. The results indicated that increasing temperature and/or amount of sodium sulphate in the mixtures both play a significant role in decomposition of petalite concentrate and formation of LiNaSO_4 phase. Leaching the calcines in hot water (80 °C) selectively dissolved the LiNaSO_4 . Solution analyses indicated that >99% lithium dissolution can be achieved for mixtures with 1:1 mass ratio after heating at 1000 °C for 1 h. The presence of phases such as quartz (SiO_2) and albite in the leach residues showed that roasting petalite concentrate with sodium sulphate (Na_2SO_4) and followed by hot water leaching is a sufficient process for selective lithium dissolution from a petalite concentrate.

Phase changes in mechanically activated spodumene- Na_2SO_4 mixtures after isothermal heating

Minerals Engineering, Volume 155, 15 August 2020, 106455

Dr. Ataollah Nosrati passed away from cancer before submission of this paper. His co-authors would like to dedicate this paper to his memory.

Nader Setoudeh^{ab}, Ataollah Nosrati^{b1} and Nicholas J. Welham^{bc}

Materials Engineering Department, Yasouj University, Yasouj 75918-74831, Iran

Chemical Engineering Department, School of Engineering, Edith Cowan University, Perth, Australia

Welham Metallurgical Services, South Lake, Australia

Abstract

Mixtures of spodumene + Na_2SO_4 with a mass ratio of 1:0.5 were prepared and milled using either zirconia or metallic media in a planetary ball mill for 5 h. The milled samples were heated in a furnace at temperatures ranging from 800 °C to 1000 °C for one hour under an air atmosphere. X-ray diffraction (XRD) results showed the traces of new phases such as LiNaSO_4 and β -spodumene in the produced calcine after isothermal roasting. Increasing temperature resulted in increasing formation of LiNaSO_4 and the XRD results were consistent with a thermodynamic assessment of the spodumene- Na_2SO_4 mixture. The results showed that changing the milling media did not have a significant role in formation of phase(s) during isothermal heating regime. The XRD results revealed that LiNaSO_4 was the major phase after heating a 5 h milled mixture of spodumene- Na_2SO_4 in both metallic and zirconia media at 1000 °C. There were signs of β -spodumene observed in the sample heated at 800 °C however the peaks of this phase were overlapped with LiNaSO_4 phase. The dissolution of lithium during

leaching in water reached ~92% for the 5 h milled samples after heating at 1000 °C irrespective of milling media used.

Section IV: Lithium chemical isotope exchange related research

Thesis:

The separation of lithium isotopes: physical and chemical methods

Abouzar Kiyani, Malek Ashtar University, undated

Lithium Isotopes Separation by Amalgam Electrolysis Method

Aryanpur, Vahid / 2010

1. Type of Document: M.Sc. Thesis
2. Language: Farsi
3. Document No: 40554 (46)
4. University: Sharif University of Technology
5. Department: Energy Engineering
6. Advisor(s): Outokesh, Mohammad; Ahmadi, Javad
7. Abstract:
8. Lithium has two stable isotopes naturally including ${}^6\text{Li}$ at 7.5% and ${}^7\text{Li}$ at 92.5% relative abundance. In spite of the similarities of lithium isotopes in common chemical reactions, they have some completely distinctive behaviors in nuclear reactions. ${}^6\text{Li}$ has considerable neutron cross section capturing in thermal neutron range about 945 barns while this feature for ${}^7\text{Li}$ is insignificant about 0.037 barns. This difference makes them to play different roles in nuclear uses. ${}^7\text{LiOH}$ is applied for pH adjustment of coolant in light water reactors. ${}^6\text{Li}$ is not only used as a shielding material against thermal neutrons, but also is known as a source of tritium in the blanket of fusion reactors which in turn increase the importance of lithium isotopes separation. Electrolysis is one of the most known lithium isotopes separation methods, involving mercury cathode and a neutral anode like titanium or graphite. In this project mass transfer has been determined as the slowest step which controls the rate of amalgam formation reaction theoretically and practically and the effects of an extensive range of parameters, including types of lithium compounds, temperature of the solution, type of the anode and of course electrolysis of mixture salts as a new idea to reach higher current efficiency and higher separation factor. An acceptable separation has attained for ${}^7\text{Li}$ in twenty stages up to 5% and more than 1% for ${}^6\text{Li}$ in 5 stages, demonstrating a substantial separation factor between 1.04 to 1.06 for LiOH and LiCl respectively.

Lithium Isotopes Separation by Electrolysis Amalgam by a Continuous Method

Kowsari, Mohammad Reza / 2013

1. Type of Document: M.Sc. Thesis
2. Language: Farsi
3. Document No: 44570 (46)
4. University: Sharif University of Technology
5. Department: Energy Engineering
6. Advisor(s): Outokesh, Mohammad; Ahmadi, Javad
7. Abstract:
8. Lithium has 9 isotopes which two isotopes are stable and remaining isotopes are unstable and have half-life. Lithium stable isotopes include ${}^6\text{Li}$ and ${}^7\text{Li}$ that their abundance is 7.53% and 92.47% respectively. Importance of lighter lithium isotope appears for its small cross section against thermal neutron and producing fusion reactors fuel in nuclear industries. Thermal neutron absorption cross section for ${}^6\text{Li}$ and ${}^7\text{Li}$ are 950 barn and 37 mbarn respectively. Interesting of these isotopes in nuclear industry is due to the large difference in the absorption cross section. ${}^6\text{Li}$ compounds implied for tritium producing in coat of nuclear fusion reactor with DT fuel. Following tritium is used in diagnosis of diseases such as thalassemia. ${}^6\text{LiD}$ compound applied as fuel in fusion nuclear reactors which worked by laser inertial encapsulation method. ${}^7\text{Li}$ in form of ${}^7\text{LiOH}$ applied in adjusting cooled fluid pH in light water reactor and as anti-corrosion compound in fission reactor. ${}^7\text{Li}$ is used in generating reactor (Breeding Reactor). The main use of ${}^6\text{Li}$, however, is as the source of tritium producing and used in nuclear fusion reactor. In 1388s, first experiment on lithium isotope separation by electrolysis carried on laboratory scale and batch method in IRAN. In this project imply same separation method but distinction is the scale is pilot and continuous method is chosen and important parameters have been studied. In this method, is used from mercury cathode and lithium hydroxide as feed which flow counter current into electrolysis cell. Implied anodes materials are stainless steel and coated titanium with ruthenium oxide. Parameters in this experiment are feed and mercury flow rate, lithium hydroxide concentration, current, anode type and amount of implied anode surface. Effect of each parameter studies on separation factor, efficiency, amount of lithium lost in feed and amount of lithium gained in product. In this project, separation is done by separation factors in range of 1.02 to 1.122 in single stage and in each step enrichment level was 0.2% and even was reached to 0.5%

(See also: Mohammadreza Kosari, **Lithium Isotope Separation in a Castner-Kellner Cell by Electrolysis Amalgam System by a Continuous Method**, MSc)

Study on Momentary and Overall Separation Factors in Lithium Isotopes Separation by Batch Electrolysis

Azad, Mohsen / 2015

1. Type of Document: M.Sc. Thesis
2. Language: Farsi
3. Document No: 47883 (46)
4. University: Sharif University of Technology
5. Department: Energy Engineering
6. Advisor(s): Otukesh, Mohammad; Ahmadi, Javad; Kowsari, Mohammad Reza
- 7.
8. Abstract:

Lithium has two stable isotopes, ${}^6\text{Li}$ and ${}^7\text{Li}$. Abundance of these isotopes are 7.53% and 92.43% respectively. Each isotope has an important role in nuclear industry. For example, ${}^6\text{Li}$ compounds is used in production of tritium in nuclear fusion reactors coated with DT fuel and as fuel in nuclear fusion reactors that operate with laser inertial confinement method applied. ${}^7\text{LiOH}$ is used to adjust the pH of the fluid coolant in light water reactors and also in Breeding Reactors. Lithium isotope separation in different ways so far been brought into operation. The other aspect to this work, it can be both continuous and batch for action. Lithium isotopes for the first time by electrolysis using the amalgam and mercury as cathode and titanium as an anode and a lithium salt dissolved done. Modelling of separation factor of lithium isotopes in a batch electrolysis cell with mercury cathode was subject of the current study. Modelling of this system can help design of the employed system to use in the separation units. The study investigated effects of different operational parameters including current density, and LiOH concentration and then modelling of them to predict the both momentary and overall separation factors. Between the both examined parameters, effect of current density was found to be the more significant than the other. The maximum single stage separation factor achieved in the present work was 1.136, which was obtained by using the current density of "0.184 Amp/cm²". Theoretical elucidation of the observed phenomena was accomplished using migration-diffusion theory, and the Bell-Gurneys' mechanism with special attention onto role of the chemical exchange. Accepting this postulate that "when a rate determining step prevails over the kinetics, its corresponding separation factor will determine separation factor of the system" would greatly simplify the theoretical interpretation.

Conference Papers:

A. R. Fakhari and M. Shamsipur, **An NMR Study of the Stoichiometry and Stability of Lithium Ion Complexes with 12-crown-4, 15-Crown-5 and 18-Crown-6 in Binary Acetonitrile-Nitrobenzene Mixtures,**

Proceeding of 9th Iranian of Analytical Chemistry, University of Tabriz, June 8-10, 1999, p. 15.

E. Karkhaneei, M. H. Zebarjadian and M. Shamsipur,

Lithium-7 NMR Study of Several Li+-Crown Ether Complexes in Binary Acetone-Nitrobenzene Mixtures, *ibid*, p. 108.

N. Alizadeh, M. Shamsipur, M. K. Rofouei and K. Alizadeh, **Lithium-7 NMR and an initio Calculation Studies of Complexation of Li+ Ion with 12-crown-4, Benzo-12-crown-4, 15-crown-5 in Binary Nitromethane-Acetonitrile Mixtures**, *ibid*, p. 124.

M.R. Kosari, M. Outokesh, S.J. Ahmadi, J. Rafeei and A. Aminian, **Application of Lithium Isotopes and Their Separation Method**, 1st National Conference on Application of Stable Isotopes, Ferdowsi University, Science Department, Mashhad, Iran, 2013

M.R. Kosari, S.J. Ahmadi, M. Outokesh, A. Aminian and J. Rafeei, **Study on Efficiency of Electrolysis System for Lithium Isotope Separation**, 1st National Conference on Application of Stable Isotopes, Ferdowsi University, Science Department, Mashhad, Iran, 2013

M.R. Kosari, S.J. Ahmadi, M. Outokesh, E. Najjarzade and M.A. Kiani, **Lithium Isotopes Production Technology by Amalgam Electrolysis Method**, The Conference on Commercialization, National Development and Engineering Sciences, Mazandaran, Iran, 2013

M.R. Kosari, S.J. Ahmadi, M. Outokesh and J. Rafee, **Lithium Isotopes Enrichment in order to Production of ⁶Li as Elementary Material in Fusion**, 3rd National Conference on New Technology of Chemistry and Chemical Engineering, Islamic Azad University, Ghochan, Iran, 2014

Journal Articles:

SPECTROPHOTOMETRIC STUDY OF THE THERMODYNAMICS OF COMPLEXATION OF LITHIUM AND SODIUM IONS WITH DIBENZO-24-CROWN-8 IN BINARY DIMETHYLFORMAMIDE-ACETONITRILE MIXTURES USING MUREXIDE AS A METALLOCHROMIC INDICATOR

Journal of Coordination Chemistry, Volume 35, Issue 3-4, 1995, pages 289-297

Habibollah Khajesharifi^a & Mojtaba Shamsipur^a

Department of Chemistry, Razi University, Kermanshah, Iran

Abstract:

Complexation of Li⁺ and Na⁺ with dibenzo-24-crown-8 has been studied in dimethylformamide-acetonitrile mixtures by means of a competitive spectrophotometric technique using murexide as metal ion indicator. Stabilities of the resulting 1:1 complexes were investigated at various temperatures and enthalpies and entropies of complexation were determined from the temperature dependence of the formation constants. Sodium forms a more stable complex with the crown ether than lithium. There is an inverse linear relationship between log K_f and the mole fraction of DMF in the solvent mixtures. The ΔH°-TΔS° plot of all thermodynamic data, obtained for both crown complexes in different solvent mixtures, shows a fairly good linear correlation, indicating the existence of an enthalpy-entropy compensation effect in complexation.

NUCLEAR MAGNETIC RESONANCE STUDY OF LITHIUM ION COMPLEXES WITH SEVERAL CROWN ETHERS IN BINARY ACETONITRILE-NITROMETHANE MIXTURES,

Journal of Coordination Chemistry, Volume 39, Issue 1, 1996, pages 33-42
Ebrahim Karkhaneei^a, Abbas Afkhami^a & Mojtaba Shamsipur^b

Abstract:

Lithium-7 NMR measurements were used to determine the stoichiometry and stability of Li⁺ complexes with 12-crown-4 (12C4), 15-crown-5 (15C5), benzo-15-crown-5 (B15C5), 18-crown-6 (18C6), dicyclohexyl-18-crown-6 (DC18C6) and dibenzo-18-crown-6 (DB18C6) in various acetonitrile-nitromethane mixtures at 27°C. In all cases studied, the variation in the ⁷Li chemical shift with the crown/Li⁺ mol ratio indicated the formation of 1:1 complexes in solution. The formation constants of the resulting complexes were evaluated from computer fitting of the mol ratio data to an equation which relates the observed chemical shifts to the formation constant. It was found that, in all solvent mixtures used, the stabilities of the resulting complexes vary in the order 15C5 > B15C5 > DC18C6 > 12C4 > 18C6 > DB18C6. There is an inverse relationships between log K_f of the complexes and the mol fraction of acetonitrile in the solvent mixtures.

LITHIUM-7 AND SODIUM-23 NMR STUDIES OF COMPLEXATION OF LI⁺ AND NA⁺ IONS WITH 1,10-PHENANTHROLINE, 2,2''-BIPYRIDINE AND 8-HYDROXYQUINOLINE IN SOME NON-AQUEOUS SOLUTIONS,

POLYHEDRON 1996, Volume 15, Number 20; Page(s) 3647 To 3652.

Author(s): MADRAKIAN T., AFKHAMI A., GHASEMI J., SHAMSIPOUR M.

Abstract:

NMR spectra of lithium-7 and sodium-23 were used to study the interactions of Li⁺ and Na⁺ ions with 1,10-phenanthroline, 2,2''-bipyridine and 8-hydroxyquinoline in nitromethane, nitrobenzene, acetonitrile and acetone solutions. The stoichiometry and stability of the resulting complexes were evaluated from non-linear least-squares fitting of the chemical shift-mole ratio data to appropriate equations. There is an inverse relationship between the stability of the complexes and the solvating ability of the solvents, as expressed by Gutmann donor numbers. In all solvents studied, Li⁺ forms more stable complexes than Na⁺ and, for each cation, the stability order of the resulting complexes is 1,10-phenanthroline > 2,2''-bipyridine > 8-hydroxyquinoline.

LITHIUM-7 AND SODIUM-23 NMR STUDIES OF THE COMPLEXATION OF LI⁺ AND NA⁺ IONS WITH 1,13-DIBENZO-24-CROWN-8 IN BINARY NITROMETHANE-ACETONITRILE MIXTURES

Journal of Coordination Chemistry, Volume 46, Issue 1, 1998, pages 1-11
Ebrahim Karkhaneei^a, Javad Zolgharnein^b, Abbas Afkhami^a & Mojtaba Shamsipur^b

Abstract:

⁷Li, ²³Na and ¹³C NMR measurements were used to study the stoichiometry and stability of Li⁺

and Na⁺ complexes with dibenzo2–4–crown–8 in binary nitromethane-acetonitrile mixtures. The resulting chemical shift-mol ratio data clearly reveal the formation of both 1:1 and 2:1 (metal/ligand) complexes in solution. Formation of the two adducts in nitromethane and acetonitrile solutions was further supported by monitoring the molar conductance of Li⁺ and Na⁺ solutions as a function of macrocycle/metal ion mol ratio. Stepwise formation constants of the 1:1 and 2:1 complexes were evaluated from computer fitting of the NMR mol ratio data to equations which relate observed metal ion chemical shifts to formation constants. In all solvent systems, sodium forms more stable complexes with the crown ether than lithium. There is an inverse linear relationship between the logarithms of the stability constants and the mol fraction of acetonitrile in the solvent mixtures.

NMR STUDY OF EXCHANGE KINETICS OF THE LITHIUM ION WITH CRYPTAND C222 IN BINARY ACETONITRILE-NITROMETHANE MIXTURES

Journal of Coordination Chemistry, Volume 44, Issue 1-2, 1998, pages 23-32

Mojtaba Shamsipur^a, Ebrahim Karkhaneei^b & Abbas Afkhami^b

Abstract:

The exchange kinetics of the lithium ion with cryptand C222 was studied in acetonitrile-nitromethane mixtures by lithium-7 NMR line-shape analysis. In all solvent mixtures used, and over the entire temperature range studied, the chemical exchange of the Li⁺ ion between the solvated and complexed sites was found to occur *via* a bimolecular mechanism. The activation parameters E_a, δH^\ddagger , δS^\ddagger and δG^\ddagger for the exchange have been determined. The free energy barrier for the exchange process appears to be nearly independent of the binary mixture composition. The results confirm the preferential solvation of the lithium ion with acetonitrile in the binary mixed solvent systems used.

NMR STUDY OF EXCHANGE KINETICS OF THE LITHIUM ION WITH CRYPTAND C222 IN BINARY ACETONITRILE-NITROMETHANE MIXTURES

Journal of Coordination Chemistry, Volume 44, 1998 - Issue 1-2, p23-32

Mojtaba Shamsipur, Ebrahim Karkhaneei & Abbas Afkhami

Abstract

The exchange kinetics of the lithium ion with cryptand C222 were studied in acetonitrile-nitromethane mixtures by lithium-7 NMR line-shape analysis. In all solvent mixtures used, and over the entire temperature range studied, the chemical exchange of the Li⁺ ion between the solvated and complexed sites was found to occur *via* a bimolecular mechanism. The activation parameters E_a, δH^\ddagger , δS^\ddagger and δG^\ddagger for the exchange have been determined. The free energy barrier for the exchange process appears to be nearly independent of the binary mixture composition. The results confirm the preferential solvation of the lithium ion with acetonitrile in the binary mixed solvent systems used.

Lithium-7 NMR study of the exchange kinetics of the lithium ion with cryptand C221 in methanol solution. Temperature dependence of the exchange mechanism

Polyhedron, Volume 17, Issue 21, 14 October 1998, Pages 3809-3815

Mojtaba Shamsipur¹, Ebrahim Karkhaneei² and Abbas Afkhami²

Department of Chemistry, Razi University, Kermanshah, Iran

Department of Chemistry, Bouali Sina University, Hamadan, Iran

Abstract

The exchange kinetics of $\text{Li}^+\text{C221}$ cryptate in methanol solution was studied by lithium-7 NMR line-shape analysis at a wide range of temperature. Depending on the temperature, two different exchange mechanisms were found to coexist to different extents. A dissociative pathway dominates at high temperatures (from 5 to 25°), while a bimolecular mechanism prevails at lower temperatures (from -30 to -60°C). At the temperature range of -30 to 5°C, both the dissociative and bimolecular mechanisms contribute to the metal exchange. For the dissociative pathway, the activation parameters were calculated as: $E_a=22\pm 2 \text{ kJ mol}^{-1}$; $\Delta H^\ddagger = 20\pm 2 \text{ kJ mol}^{-1}$; $\Delta S^\ddagger = -144\pm 8 \text{ J mol}^{-1} \text{ K}^{-1}$. While for the bimolecular mechanism they are: $E_a=9.9\pm 0.4 \text{ kJ mol}^{-1}$; $\Delta H^\ddagger = 8.0\pm 0.4 \text{ kJ mol}^{-1}$; $\Delta S^\ddagger = -146\pm 2 \text{ J mol}^{-1} \text{ K}^{-1}$.

COMPETITIVE NMR STUDY OF THE nCOMPLEXATION OF SOME ALKALINE EARTH AND TRANSITION METAL IONS WITH 12-CROWN-4, 15-CROWN-5 AND BENZO-15-CROWN-5 IN ACETONITRILE SOLUTION USING THE LITHIUM-7 NUCLEUS AS A PROBE

Journal of Coordination Chemistry, Volume 52, Issue 2, 2000, pages 139-149

Mojtaba Shamsipur^a & Tayyebeh Madrakian^a

Abstract

⁷Lithium NMR measurements were used to determine the stoichiometry and stability of Li^+ complexes with 12-crown-4, 15-crown-5 and benzo-15-crown-5 in acetonitrile solution. A competitive ⁷Li NMR technique was also employed to probe the complexation of Mg^{2+} , Ca^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} and Cd^{2+} ions with the same crown ethers. In all cases, the stability of the resulting 1:1 complexes was found to decrease in the order 15-crown-5 > benzo-15-crown-5 > 12-crown-4. Ca^{2+} and Cd^{2+} ions formed the most stable complexes in the series.

Lithium-7 NMR and ab initio calculation studies of complexation of Li⁺ ions with 12-Crown-4, Benzo-12-Crown-4, 15-Crown-5, Benzo-15-Crown-5 and Dibenzo-15-Crown-5 in binary nitromethane-acetonitrile

Polish Journal of Chemistry, 2007, Vol. 81, p1743-174

Shamsipur, M., Alizadeh, N., Rofouei, M.K. and Alizadeh, K.

Abstract

Complexes of 12-crown-4 (12C4), benzo-12-crown-4 (B12C4), 15-crown-5 (15C5), benzo-15-crown-5 (B15C5) and dibenzo-15-crown-5 (DB15C5) with Li⁺ ion were investigated by lithium-7 NMR in a number of nitromethane (NM)-acetonitrile (AN) binary mixtures. In all cases, the exchange between the free and complexed lithium ion was fast on the NMR time scale and a single population average resonance was observed. Both 1:1 and 2:1 (sandwich) complexes were observed between lithium ion and 12C4 and B12C4 in pure nitromethane solution. Stepwise formation constants of the 1:1 and 1:2 (metal/ligand) complexes were evaluated from computer fitting of the NMR mole ratio data to equations which relate the observed metal ion chemical shifts to formation constants. There is an inverse linear relationship between the logarithms of the stability constants and the mole fraction of acetonitrile in the solvent mixtures. The stability of the complexes varies inversely with the Gutmann donor number of the solvent. The stability order of the complexes was found to be 15C5.Li⁺ > B15C5.Li⁺ > DB15C5.Li⁺ > 12C4.Li⁺ > B12C4.Li⁺. The optimized structures of the free ligands and their 1:1 and 2:1 complexes with Li⁺ ion were predicted by ab initio theoretical calculations using the Gaussian 98 software, and the results are discussed.

Nuclear magnetic resonance study of the stoichiometry and stability of lithium ion complexes with two small size crown ethers in binary nitromethane-acetonitrile mixtures

Journal of Inclusion Phenomena and Macrocyclic Chemistry (2010) 68(3-4) 431-436

Alizadeh N and Shamsipur M

Abstract

Lithium-7 NMR spectrometry was used to study the complexation reaction between lithium ions and different small size crown ethers 12-crown-4 (12C4), benzo-12-crown-4 (B12C4) in a number of binary nitromethane (NM)-acetonitrile (AN) mixtures. The exchange between the free and complexed lithium ion was fast on the NMR time scale and a single population average resonance was observed. Both 1:1 and 2:1 (sandwich) complexes were observed between lithium ion and 12C4 and B12C4 in pure nitromethane solution. Stepwise formation constants of the 1:1 and 2:1 (ligand/metal) complexes were evaluated from computer fitting of the NMR-mole ratio data to equations which relate the observed metal ion chemical shifts to formation constants. There is an inverse linear relationship between the logarithms of the stability constants and the mole fraction of acetonitrile in the solvent mixtures. The stability order of the 1:1 and 2:1 complexes was found to be 12C4.Li⁺ > B12C4.Li⁺. The optimized structures of the free ligands and their 1:1 and 2:1 complexes with Li⁺ ion were predicted by ab initio theoretical calculations using the Gaussian 98 software, and the results are discussed.

A comparison of complexation of Li⁺ ion with macrocyclic ligands 15-crown-5 and 12-crown-4 in binary nitromethane–acetonitrile mixtures by using lithium-7 NMR technique and *ab initio* calculation

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, Volume 78, Issue 1, January 2011, Pages 488-493

Nina Alizadeh

Department of Chemistry, University of Guilan, Namjoo Street, Rasht 41335-1914, Iran

Abstract

Lithium-7 NMR measurements were used to investigate the stoichiometry and stability of Li⁺ complexes with 15-crown-5 (15C5), benzo-15-crown-5 (B15C5), dibenzo-15-crown-5 (DB15C5) and 12-crown-4 (12C4) in a number of nitromethane (NM)–acetonitrile (AN) binary mixtures. In all cases, the exchange between the free and complexed lithium ion was fast on the NMR time scale and a single population average resonance was observed. While all crown ethers form 1:1 complexes with Li⁺ ion in the binary mixtures used, both 1:1 and 2:1 (sandwich) complexes were observed between lithium ion and 12C4 in pure nitromethane solution. Stepwise formation constants of the 1:1 and 2:1 (ligand/metal) complexes were evaluated from computer fitting of the NMR-mole ratio data to equations which relate the observed metal ion chemical shifts to formation constants. There is an inverse linear relationship between the logarithms of the stability constants and the mole fraction of acetonitrile in the solvent mixtures. The stability order of the 1:1 complexes was found to be 15C5·Li⁺ > B15C5·Li⁺ > DB15C5·Li⁺ > 12C4·Li⁺. The optimized structures of the free ligands and their 1:1 and 2:1 complexes with Li⁺ ion were predicted by *ab initio* theoretical calculations using the Gaussian 98 software, and the results are discussed.

A Comparison of Complexation of Li⁺ Ion with Macrocyclic Ligands 15-Crown-5 and Benzo-derivatives in Binary Nitromethane-Acetonitrile Mixtures by Using Lithium-7 NMR Technique and *Ab Initio* Calculation

Applied Magnetic Resonance (2011) 40(3) 303-310

Alizadeh N

Abstract:

Lithium-7 nuclear magnetic resonance (NMR) measurements were used to investigate the stoichiometry and stability of Li⁺ complexes with 15-crown-5 (15C5), benzo-15-crown-5 (B15C5) and dibenzo-15-crown-5 (DB15C5) in a number of nitromethane (NM)-acetonitrile (AN) binary mixtures. In all cases, the exchange between the free and complexed lithium ion was fast on the NMR time scale and a single population average resonance was observed. While all crown ethers form 1:1 complexes with Li⁺ ion in the binary mixtures used, stepwise formation constants of the 1:1 (ligand/metal) complexes were evaluated from computer fitting of the NMR-mole ratio data to equations which relate the observed metal ion chemical shifts to formation constants. There is an inverse linear relationship between the logarithms of the stability constants and the mole fraction of AN in the solvent mixtures. The stability order of the 1:1 complexes was observed to be 15C5·Li⁺ > B15C5·Li⁺ > DB15C5·Li⁺. The optimized structures of the free ligands and their 1:1 complexes with the Li⁺ ion were predicted by *ab initio* theoretical calculations using the Gaussian 98 software.

Enrichment of ${}^6\text{Li}$ using dispersive liquid–liquid microextraction as a highly efficient technique,

Annals of Nuclear Energy, Volume 62, December 2013, Pages 499-503

Mehrdad Davoudi and Mohammad Hassan Mallah

Nuclear Fuel Cycle Research School, Nuclear Science & Technology Research Institute, Atomic Energy Organization of Iran, End of North Karegar Ave., Tehran, Iran

Abstract:

Isotope separation of lithium by the dispersive liquid–liquid micro-extraction system $\text{H}_2\text{O}/\text{C}_2\text{Cl}_4/\text{C}_3\text{H}_6\text{O}$ is investigated using benzo-15-crown-5 for finding an efficient way for the enrichment of ${}^6\text{Li}$. Samples collected in the best and worst conditions were used for the isotopic analysis by inductively coupled plasma–mass spectrometry. The maximum isotope enrichment factor ϵ_{max} for ${}^6\text{Li}/{}^7\text{Li}$ obtained in the present study was 0.082 ± 0.0021 . As a result, the lighter isotope, ${}^6\text{Li}$, was concentrated in the receiving phase, whereas in most of cases the heavier isotope, ${}^7\text{Li}$, was enriched in the source phase.

(Mehrdad Davoudi received his PhD in May 1994 from Carleton University, Canada and then returned to the Department of Chemistry, Imam Hossein University where he continued to perform research on lithium ion chemistry.)

Comparison of the selectivity of $[\text{M}(12\text{-Crown-4})]^+$ ($\text{M} = \text{Li}^+, \text{Na}^+, \text{K}^+$) complexes for halide anions and some neutral molecules; a computational study

J. Theor. Comput. Chem. **14**, 1550057 (2015) [16 pages]

Faranak Dastineh¹, Sadegh Salehzadeh¹, Mehdi Bayat¹ and Yazdan Maghsoud¹

¹Faculty of Chemistry, Bu-Ali Sina University Hamedan, Iran

Abstract:

A theoretical study on the selectivity of a series of $[\text{M}(12\text{C4})]^+$ ($\text{M} = \text{Li}^+, \text{Na}^+, \text{K}^+$, 12C4 = 12-crown-4) complexes for F^- , Cl^- and Br^- anions and a number of neutral molecules (CH_3CN , CH_3OH , NH_3 , H_2O , py, and 12C4) is reported. At first, it was shown that in the gas phase among all studied halide anions and neutral molecules, halides have much more bonding interaction with all $[\text{M}(12\text{C4})]^+$ cations. Calculated interaction energies of above anions and $[\text{M}(12\text{C4})]^+$ cations decrease from F^- to Br^- . Also the interaction energy of halide anions with $[\text{M}(12\text{C4})]^+$ complexes, decreases from $[\text{Li}(12\text{C4})]^+$ to $[\text{K}(12\text{C4})]^+$. The electron decomposition analysis showed that the bond between $[\text{M}(12\text{C4})]^+$ complexes and both the neutral and anion guests is mainly electrostatic in nature. Then the selectivity of $[\text{M}(12\text{C4})]^+$ complexes for studied anions and neutral molecules are compared in methanol, acetone, acetonitrile, and nitromethane solutions. It was shown that both the desolvation process of reactants and the strength of host–guest interactions have significant effect on the selectivities. Thus the selectivity of $[\text{Li}(12\text{C4})]^+$ cation for NH_3 and H_2O neutral molecules in solution, in contrast to the gas phase, is higher than that for bromide anion. The results of calculations showed that all $[\text{M}(12\text{C4})]^+$ complexes, specially $[\text{Li}(12\text{C4})]^+$, have high selectivity for F^- over other halide anions and neutral molecules.

Section V: Lithium Ceramics Properties for Tritium Breeders

Conference Papers:

X-ray diffraction technique investigation: phase stabilization study of hydrothermally synthesized lithium silicates nano materials

The 2nd Asian Symposium on Electromagnetics and Photonics Engineering

August 28-30, 2013, Tabriz, Iran

ASEPE 2013-Poster, PFr20

Abdolali Alemi 1, Shahin Khademinia 1,* , Sang Woo Joo², Mahboubeh Dolatyari 3, Akbar Bakhtiari 4,

Hossein Moradi⁵, Sorayya Saeidi

1 Department of Inorganic Chemistry, Faculty of Chemistry, University of Tabriz, Tabriz, Iran

2 School of Mechanical Engineering WCU Nano Research Center, Yeungnam University, Gyeongsan 712-749, South Korea

3 Laboratory of Crystal Engineering & Nano Structured Materials, School of Engineering Emerging Technologies, University of Tabriz, Tabriz, Iran

4 Department of Chemistry, Faculty of Basic Sciences, Payame Noor University, PO Box 19395-3697, Tehran, Iran

5 Department of Chemistry, Faculty of Basic sciences, University of Azad, Branch of Ardabil, Ardabil, Iran

6 Department of Geology, Faculty of Science of Nature, University of Tabriz, Tabriz, Iran

1alemi.aa@gmail.com; 1 shahinkhademinia@gmail.com; 2swjoo@yu.ac.kr;*

3m.dolatyari@tabrizu.ac.ir;

4bakhtiari.a1@gmail.com; 5hmoradi84@gmail.com; 6sorayyasaeidi@gmail.com

Abstract-

Highly crystalline lithium silicates nano-materials were synthesized via hydrothermal method at 180°C with using various reaction times and raw materials. In this study we discuss about reaction time, Li:Si molar ratio and raw material type effects on lithium silicate nano materials phase stabilization. Powder X-ray diffraction technique (PXRD) was used to investigate the phase stability of the formed lithium silicates in different reaction times and Li:Si molar ratios. Hydrothermally synthesized lithium silicates in Li:Si molar ratios of 1:1, 1:2, 2:3, 1:3, 1:4, 1:5 with various raw materials types and reaction times of 48, 72, 96 and 120 h were used for the phase stabilization study.

Journal Articles:

Low temperature nanostructured lithium titanates: controlling the phase composition, crystal structure and surface area

Journal of Sol-Gel Science and Technology volume 55, pages19–35(2010)

M. R. Mohammadi^{1,2} & D. J. Fray²

Abstract

Low temperature lithium titanate compounds (i.e., $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and Li_2TiO_3) with nanocrystalline and mesoporous structure were prepared by a straightforward aqueous particulate sol–gel route. The effect of Li:Ti molar ratio was studied on crystallisation behaviour of lithium titanates. X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) revealed that the powders were crystallised at the low temperature of 500 °C and the short annealing time of 1 h. Moreover, it was found that Li:Ti molar ratio and annealing temperature influence the preferable orientation growth of the lithium titanate compounds. Transmission electron microscope (TEM) images showed that the average crystallite size of the powders annealed at 400 °C was in the range 2–4 nm and a gradual increase occurred up to 10 nm by heat treatment at 800 °C. Field emission scanning electron microscope (FE-SEM) analysis revealed that the deposited thin films had mesoporous and nanocrystalline structure with the average grain size of 21–28 nm at 600 °C and 49–62 nm at 800 °C depending upon the Li:Ti molar ratio. Moreover, atomic force microscope (AFM) images confirmed that the lithium titanate films had columnar like morphology at 600 °C, whereas they showed hill-valley like morphology at 800 °C. Based on Brunauer–Emmett–Taylor (BET) analysis, the synthesized powders showed mesoporous structure containing pores with needle and plate shapes. The surface area of the powders was enhanced by increasing Li:Ti molar ratio and reached as high as 77 m²/g for the ratio of Li:Ti = 75:25 at 500 °C. This is one of the smallest crystallite size and the highest surface areas reported in the literature, and the materials could be used in many applications such as rechargeable lithium batteries and tritium breeding materials.

IRANIAN JOURNAL OF CRYSTALLOGRAPHY AND MINERALOGY SUMMER 2013
, Volume 21 , Number 2; Page(s) 243 To 252.

Paper:

SYNTHESIS AND STRUCTURAL STUDIES OF LITHIUM METASILICATE (Li_2SiO_3) NANOPARTICLES VIA HYDROTHERMAL METHOD

Author(s): AHMADPOUR S.*, ALEMI A.A., KHADEMINIA SH.

* CHEMISTRY DEPARTMENT, TABRIZ UNIVERSITY, TABRIZ, IRAN

Abstract:

The hydrothermal method due to advantages of low reaction temperatures and achieving fine particles in synthesized samples was used. Li_2SiO_3 has orthorhombic structure with Cmc21 space group and cell parameters $a=9.392$, $b=5.397$ and $c=4.660\text{Å}$. The structure, size and morphology of nano particles were investigated by XRD, FT-IR and SEM analysis methods. In

addition, the cell parameters of lithium metasilicate nano particles were determined by CELREF software version 3. Optical properties of synthesized silicates were investigated by UV-vis and PI analysis methods.

Low temperature nanostructured lithium titanates: controlling the phase composition, crystal structure and surface area

Journal of Sol-Gel Science and Technology, volume 55, pages 19–35 (2010)

M. R. Mohammadi^{1,2} & D. J. Fray²

Abstract

Low temperature lithium titanate compounds (i.e., $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and Li_2TiO_3) with nanocrystalline and mesoporous structure were prepared by a straightforward aqueous particulate sol-gel route. The effect of Li:Ti molar ratio was studied on crystallisation behaviour of lithium titanates. X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) revealed that the powders were crystallised at the low temperature of 500 °C and the short annealing time of 1 h. Moreover, it was found that Li:Ti molar ratio and annealing temperature influence the preferable orientation growth of the lithium titanate compounds. Transmission electron microscope (TEM) images showed that the average crystallite size of the powders annealed at 400 °C was in the range 2–4 nm and a gradual increase occurred up to 10 nm by heat treatment at 800 °C. Field emission scanning electron microscope (FE-SEM) analysis revealed that the deposited thin films had mesoporous and nanocrystalline structure with the average grain size of 21–28 nm at 600 °C and 49–62 nm at 800 °C depending upon the Li:Ti molar ratio. Moreover, atomic force microscope (AFM) images confirmed that the lithium titanate films had columnar like morphology at 600 °C, whereas they showed hill-valley like morphology at 800 °C. Based on Brunauer-Emmett-Taylor (BET) analysis, the synthesized powders showed mesoporous structure containing pores with needle and plate shapes. The surface area of the powders was enhanced by increasing Li:Ti molar ratio and reached as high as 77 m²/g for the ratio of Li:Ti = 75:25 at 500 °C. This is one of the smallest crystallite size and the highest surface areas reported in the literature, and the materials could be used in many applications such as rechargeable lithium batteries and tritium breeding materials.

INTERNATIONAL NANO LETTERS (INL) FEBRUARY 2013 , Volume 3 , Number 3;
Page(s) 1 To 11.

**LITHIUM METASILICATE AND LITHIUM DISILICATE NANOMATERIALS:
OPTICAL PROPERTIES AND DENSITY FUNCTIONAL THEORY CALCULATIONS**

Author(s): ALEMI ABDOLALI, KHADEMINIA SHAHIN*, WOO JOO SANG, DOLATYARI MAHBOUBEH, BAKHTIARI AKBAR

* DEPARTMENT OF INORGANIC CHEMISTRY, FACULTY OF CHEMISTRY,
UNIVERSITY OF TABRIZ, TABRIZ, IRAN

Abstract:

UV–vis and photoluminescence spectra of the hydrothermally synthesized crystalline lithium metasilicate (Li_2SiO_3) and lithium disilicate ($\text{Li}_2\text{Si}_2\text{O}_5$) nanomaterial's are studied. The intensity of the bands in the emission spectra increases with increasing reaction time in both compounds. The electronic band structure along with density of states calculated by the density functional theory (DFT) method indicates that Li_2SiO_3 and $\text{Li}_2\text{Si}_2\text{O}_5$ have an indirect energy band gap of 4.575 and 4.776 eV respectively. The optical properties, including the dielectric, absorption, reflectivity, and energy loss spectra of the compounds, are calculated by DFT method and analyzed based on the electronic structures.

INITIAL SINTERING KINETICS OF LITHIUM META TITANATE AT CONSTANT RATES OF HEATING

Iranian Journal of Material Science & Engineering , 2013; 10 (3) :44-53

A.R. Abbasian, M. R. Rahimpour , Z. Hamnabard

Abstract:

In order to evaluate the sintering behavior of lithium metatitanate (Li_2TiO_3) powder, the shrinkage of powder compact was measured under constant rates of heating. Densification curves for Li_2TiO_3 have been constructed with the help of shrinkage powder measured at different heating rates. The activation energy at the initial stage of sintering was determined by analyzing the densification curves and the value of $Q=377$ kJ/mol was obtained. The diffusion mechanism at the initial sintering stage was determined by the analytical method applied to the constant rates of heating data. This analysis exhibited that the dominant mechanism for initial sintering stage of Li_2TiO_3 is volume diffusion from grain boundary and surfaces.

Part I: Lithium metasilicate (Li_2SiO_3)—mild condition hydrothermal synthesis, characterization, and optical properties

International Nano Letters, 2015, Vol. 5, pp15-20

Alemi, Abdolali and Khademinia, Shahin

Abstract:

Using LiNO_3 and SiO_2 as raw materials, Li_2SiO_3 nano-powders were synthesized via a nonstoichiometric 2:3 Li:Si molar ratio hydrothermal reaction at 180 °C for 48, 72, and 96 h in a NaOH aqueous solution system. The synthesized materials were characterized by powder X-ray diffraction technique and Fourier transform infrared spectroscopy. To investigate the effect of the reaction time on the morphology of the obtained materials, the morphologies of the synthesized materials were studied by field emission scanning electron microscopy technique. The technique showed that on increasing the reaction time, the morphology of the as-prepared samples changed from belt structures to flower structures. Ultraviolet-Visible spectra analyses showed that the nanostructured lithium silicate powders had good light absorption properties in the ultraviolet light region. Also, photo luminescence spectra and cell parameter refinement of the obtained materials were studied.

PART II: LITHIUM DISILICATE ($\text{Li}_2\text{Si}_2\text{O}_5$): MILD CONDITION HYDROTHERMAL SYNTHESIS, CHARACTERIZATION AND OPTICAL PROPERTIES

Author(s): ALEMI ABDOLALI, KHADEMINIA SHAHIN*, SERTKOL MURAT

* DEPARTMENT OF INORGANIC CHEMISTRY, FACULTY OF CHEMISTRY, UNIVERSITY OF TABRIZ, TABRIZ, IRAN

Abstract:

Lithium disilicate nano-powders were synthesized via a mild condition hydrothermal reaction at 180°C for 48 and 72 h with a non stoichiometric 1: 2 Li: Si molar ratio in NaOH aqueous solution using Li_2CO_3 and $\text{SiO}_2\cdot\text{H}_2\text{O}$ as raw materials. The synthesized materials were characterized by powder X-ray diffraction (PXRD) technique and Fourier transform infrared (FTIR) spectroscopy.

The XRD data showed that the obtained materials crystallized in a monoclinic crystal structure with a space group of Ccc2. The morphologies of the synthesized nanomaterials were studied by field emission scanning electron microscope (FESEM).

Ultraviolet–visible spectra showed that the nanostructured lithium disilicate powders had good light absorption properties in the ultraviolet light region. Photo luminescence spectra of the obtained materials were investigated in an excitation wavelength of 281 nm. Cell parameter refinement data of the obtained materials showed that with increasing the reaction time, parameters a and b were increased. So there is an expansion in the unit cell.

Part III: Lithium metasilicate (Li_2SiO_3)—mild condition hydrothermal synthesis, characterization and optical properties

International Nano Letters, 2015, Vol. 5, pp77-83

- Alemi, Abdolali, Khademinia, Shahin and Sertkol, Murat
-

Abstract

Li_2SiO_3 nanopowders were synthesized via a non-stoichiometric 2:3 (S_1), 1:3 (S_2), 1:4 (S_3) and 1:5 (S_4) Li/Si molar ratios via hydrothermal reaction for 72 h at 180°C in an aqua solution using Li_2CO_3 and H_2SiO_3 as raw materials. The synthesized materials were characterized by powder X-ray diffraction (PXRD) technique and Fourier transform infrared spectroscopy. PXRD data showed that the crystal structure of the obtained materials is orthorhombic with the space group of Cmc2₁. Also, to investigate the effect of the Li/Si molar ratio on the morphology of the obtained materials, the morphologies of the synthesized materials were studied by field emission scanning electron microscopy. The technique showed that with changing the Li/Si molar ratio from S_1 to S_4 , the morphology of as-prepared samples changed from flower structures to microrod-microsphere and then to a non-homogenous layer-like structure. Ultraviolet-visible spectra showed that the nanostructure lithium silicate powders had good light absorption properties in the ultraviolet light region. It showed that with changing the Li/Si molar ratio from

S_1 to S_4 , the calculated band gap was decreased. Also, cell parameter refinement showed that with changing the Li/Si molar ratio from S_1 to S_4 the cell parameters decreased. Photoluminescence analysis of the obtained materials was studied at the excitation wavelength of 247 nm. It showed that the emission spectra of the obtained materials had a blue shift from S_1 to S_4 .

Activation Energies for Initial and Intermediate Stage Sintering of Li_2TiO_3 Determined by a Two-Stage Master Sintering Curve Approach

Advances in Engineering Mechanics and Materials

A. R. Abbasian is with Ceramic Department, Materials and Energy Research Center, Karaj, 31787-316, Iran (corresponding author to provide phone: 98-263 628 0040; e-mail: abbasian@merc.ac.ir).

M. R. Rahimipour is with Ceramic Department, Materials and Energy Research Center, Karaj, 31787-316, Iran (e-mail: m-rahimi@merc.ac.ir).

Z. Hamnabard is with the Lasers and Optics Research School, NSTRI, Tehran, 11365-8486, Iran (e-mail: zhamnabard@nrcam.org).

Abstract:

Lithium meta titanate (Li_2TiO_3) is considered as one of the most promising breeder materials for the fusion power. In this study, the activation energy and sintering kinetics of the Li_2TiO_3 is determined with the help of the master sintering curve (MSC). It was found that a better representation of the sintering behavior could be achieved by constructing MSC over two consecutive densification stages with the relative density of 66% set as the boundary. From the activation energy values of the two stages obtained, lattice diffusion enhanced with surface diffusion and solely lattice diffusion mechanisms were identified for the dominant sintering mechanism at initial and intermediate stages of the Li_2TiO_3 sintering, respectively.

Hydrothermal Synthesis of Lithium Meta Titanate Nanocrystallites

Procedia Materials Science, Volume 11, 2015, Pages 336-341

A.R.Abbasian^a, M.R.Rahimipour^b and Z.Hamnabard^c

a

Material Research School, Nuclear Science and Technology Research Institute, PO Box 81465-1589, Isfahan, Iran

b

Department of Ceramics, Materials and Energy Research Center, PO Box 31787-316, Karaj, Iran

c

Lasers and Optics Research School, Nuclear Science and Technology Research Institute, PO Box 11365-8486, Tehran, Iran

Abstract:

Lithium meta titanate (Li_2TiO_3) is one of the most promising tritium breeding candidate materials. In this study, the nanocrystallites lithium-titanate with hexagonal and cubic crystal structures were synthesized at low temperature, 200°C for 12 h by the hydrothermal method. The results showed that the monoclinic phase of Li_2TiO_3 nanostructure with high purity can be

synthesized by further heat treatment of the hydrothermal synthesis powder above 700°C. In despite the heat treatment, electron microscope and X-ray diffraction analysis showed that the synthesized compounds had grain size smaller than 120 nm. Li_2TiO_3 was also prepared by a solid-state reaction in order to study the influence of the synthesis rout on the morphology and particle size.

Phase transformation during sintering of Li_2TiO_3 nanocrystallites synthesised by hydrothermal method

Micro & Nano Letters (Volume: 11 , Issue: 12 , 12 2016), **Page(s):** 822 - 824

Ahmad Reza Abbasian

Nuclear Science and Technology Research Institute – NSTRI, Iran

Mohammad Reza Rahimipour

Materials and Energy Research Center, Iran

Zohreh Hamnabard

Nuclear Science and Technology Research Institute – NSTRI, Iran

Abstract:

Lithium meta titanate (Li_2TiO_3) is a major compound in the Li-Ti-O ternary system. In this work, the monoclinic-cubic transformation is studied during the sintering process of Li_2TiO_3 nanocrystallites by means of dilatometry analysis, for the first time. The minimum temperature for transformation of stoichiometric Li_2TiO_3 has been so far reported to be about 1150°C, while this study found that the transformation temperature of Li_2TiO_3 nanocrystallites synthesised by hydrothermal method was determined in this work to be about 900°C or even less.

Hydrothermal Synthesis of Monoclinic - Cubic Li_2TiO_3 Hybrid Nanocomposite Microspheres

International Journal of New Chemistry, Winter 2019, Vol. 6(1)., pp58-65

- Ahmad Reza Abbasian¹
- Mohammad Reza Rahimipour²
- Zohreh Hamnabard³

¹ Department of Materials Engineering, Faculty of Engineering, University of Sistan and Baluchestan, Zahedan, Iran

² Department of Ceramics, Materials and Energy Research Center, PO Box 31787-316, Karaj, Iran

³ Lasers and Optics Research School, Nuclear Science and Technology Research Institute, PO Box 11365-8486, Tehran, Iran

Abstract:

Li_2TiO_3 compound is one of the most important tritium breeding ceramics for industrial application in the nuclear fusion reactor. The use of the hydrothermal method for preparing ceramic composite materials is new trend. In this work, hybrid nanocomposite microspheres of the nanocrystallites Li_2TiO_3 were prepared at low temperature 400°C. Nanocomposite powders synthesized by the batch supercritical hydrothermal method for 12 hours under pressure 12MPa. The raw materials were used containing tetrabutyl titanate ($\text{Ti}(\text{C}_4\text{H}_9\text{O})_4$) as a titanium source,

lithium nitrate (LiNO_3) as a lithium source, citric acid as a chelating agent and nitric acid as pH controller. The samples were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) and X-ray diffraction (XRD). The SEM micrographs showed the synthesized powders have microsphere shape with range size 1 to 3.5 micrometers. XRD result illustrates the microspheres are nanostructure with cubic and monoclinic crystal structures. According to XRD results and using known Scherrer's equation, the crystallite size of monoclinic phase about 18 nm and monoclinic about 14 nm were determined. The TEM results show that two type of particles morphologies are present in the synthesized microspheres. The first is a spherical shape with a particle size smaller than 100 nm and second is an irregular shape with a particle size between 100 to 200 nm.

Sintering Behavior of Lithium Meta Titanate Nanocrystallites

Iranian Journal of Material Science and Engineering, Volume 16, Issue 4 (December 2019), pp43-52

A. R. Abbasian , M. R. Rahimpour, Z. Hamnabard

Abstract:

In this work, lithium meta titanate (Li_2TiO_3) nanocrystallites were synthesized by hydrothermal method and subsequent heat treatment. The shrinkage of the powder compact was measured under constant heating rate in order to study the sintering behavior of the synthesized powders. Densification curves of the synthesized powders were also constructed via the dilatometry analysis and evaluated at several heating rates. Two separate methods of analytical procedure and master curve sintering were employed to determine the activation energy of the initial sintering stage. The activation energy values were estimated based on these two distinct methods as 229 ± 14 and 230 kJ/mol respectively, consistenting with each other. Moreover, surface diffusion was determined as the dominant mechanism of densification on initial sintering of Li_2TiO_3 nanocrystallites.

Section VI: Tokamak Lithium Ceramic Breeder Studies

Conference Papers:

Experimental techniques for 14 MeV neutron benchmark studies

Scott, M.C.; Koochi-Fayegh, R.; Evans, N. (Birmingham Univ. (UK). Dept. of Physics)

Proceedings of specialist's meeting on nuclear data and benchmarks for reactor shielding, Paris, 27-29 October 1980 [en]

The use of proton-recoil proportional and scintillation counters for measurements with 14 MeV neutrons is discussed. Details are given of investigations into their performance and that of the unfolding codes used, and examples of their application in LiF and LiF-Be integral assemblies are presented.

Simulation of radiation damage of fusion reactor steel chamber by 14 MeV D-T fusion neutrons using heavy ions

International Conference on Fusion Reactor Materials, Decemner 10-14, 2007, Nice, France

F. Borlouri, F. Dini, S. Khorsani and R. Amrollahi

In order to study the effects of radiation damage caused by neutrons emitted from D-T reactions in a typical fusion reactor, one would need access to a robust high energy source.

Journal Articles:

Blanket Simulation and Tritium Breeding Ratio Calculation for ITER Reactor

Journal of Fusion Energy, volume 34, pages1365–1368(2015)

N. Zandi¹, H. Sadeghi¹, M. Habibi¹, I. Jalali¹ & M. Zare¹

Abstract:

In this study, the neutronic calculation to obtain tritium breeding ratio (TBR) in a deuterium–tritium fusion power reactor using Monte Carlo MCNPX is done. To this end Li_4SiO_4 was considered as the blanket module. In order to improve the distribution of power density in the blanket module, an arrangement of the neutron multiplier Be in the breeding zone has been optimized. Total TBR of 1.14 is achieved. Finally helium cooled pebble bed was designed as cooling system using COMSOL Multiphysics simulator.

Design and simulation of a blanket module for TOKAMAK reactors

Modern Physics Letters A, Vol. 34, No. 13, 1950103 (2019)

H. Sadeghi

Corresponding author.

Energy Engineering and Physics Department, Amirkabir University of Technology, Tehran, Iran

E-mail Address: hosseinsadeghi717@gmail.com

M. Habibi

Energy Engineering and Physics Department, Amirkabir University of Technology, Tehran, Iran

E-mail Address: mortezahabibi@gmail.com

Abstract:

In this paper, we simulated an appropriate model for an advanced breeding blanket of future TOKAMAK fusion reactors with solid breeder (Li_4SiO_4) building material in the form of pebble beds, ODS ferritic steel as structural material and Beryllium as neutron multiplier. With the MCNPX code, the efficiency of this proposed model for the production and self-sufficiency of tritium was investigated. Total tritium breeding ratio of 1.15 is achieved. The helium-cooled pebble bed system and parameters of temperature and pressure are investigated by COMSOL multiphysics simulating software. The temperature of helium as cooling gas never exceeded $530\text{ }^\circ\text{C}$ and the tolerable temperature of beryllium was obtained at $650\text{ }^\circ\text{C}$. In the proposed design, it is adequate to enrich the ^6Li to 40%.

Design and simulation of a blanket module with high efficiency cooling system of tokamak focused on DEMO reactor

Nuclear Engineering and Technology, Volume 52, Issue 2, February 2020, Pages 323-327

H.Sadeghi^a, R. Amrollahi^a, M. Zare^a and S.Fazelpour^{ab}

Abstract:

In this study, the neutronic calculation to obtain tritium breeding ratio (TBR) in a deuterium-tritium (D-T) fusion power reactor using Monte Carlo MCNPX is done. In addition, by using COMSOL software, an efficient cooling system is designed. In the proposed design, it is adequate to enrich up to 40% ⁶Li. Total tritium breeding ratio of 1.12 is achieved. The temperature of helium as coolant gas never exceed 687°C. As regards the tolerable temperature of beryllium (650°C), the design of blanket module is done in the way that beryllium temperature never exceed 600°C. The main feature of this design indicates the temperature of helium coolant is higher than other proposed models for blanket module, therefore power of electricity generation will increase.

Section VII: Indirect Drive Laser Fusion

Conference Presentations

Radiation Spectrum of Imploding Target

S. Khorasani, H. Mino, F. Dini, and R. Amrollahi

29th EPS Conference on Physics and Contributions to Physics, June 17-21 2002, ECA Volume 26B, D-.004

Abstract:

In a report on atypical inertial confinement fusion experiment, the x-ray emission of the compressing target apparently reduces when it shrinks. We verify that the plasma is actually for the Local Thermodynamic Equilibrium, by taking the shifting effect radiation law for Fermi Degenerate plasmas, as a natural subsequent of invalidity of atoms makes the distance among available energy states to become very large.

Journal Articles:

Reduction of Growth Rate of Rayleigh-Taylor Instability using Nano-Structured Porous Lining at ICF Target Shell

Rahimi Shamami, and A. Ghasemizad

European Physics Journal Plus, 2013, Volum 128(11), pp1-7

The Effect of Energy Leakage Probability on Burn Propagation in an Optically Thick Fusion Plasma

M. Mahdavi, T. Koohrorkhi, and Z. Barfarmi

ISRN High Energy Physics, 2012, Article ID 838394

Power Balance Consideration in the Design of Indirectly Driven Targets

Masoumi Mahboobeh, Ghasemizad Abbas, and Gholalzadeh Leila
Plasma Science and Technology, 2013, Volume 15(6), pp506-510

Abstract:

A preliminary design for a heavy ion driver inertial fusion target is presented. The effect of target material and dimensions on transfer efficiency and symmetrical irradiation in the hohlraum are investigated.

Effect of Target Materials on the Nonlinear Power Spectrum of Rayleigh-Taylor Instability in Inertial Confinement Fusion

Zahra Asadi, Abbas Behjat, and Leila Gholamzadeh

World Applications of Applied Computing, 2105, Volume 5(10) pp149-154

Section VIII: TRR Tritium Production Experiments

Producing Hydrogen-3 by irradiating lithium orthosilicate targets in a fission research reactor

International Journal of Hydrogen Energy

Volume 41, Issue 17, 11 May 2016, Pages 7181-7184

Short Communication

K. Hadad^a, M. Jabbari^a, Z. Tabadar^b and M. Hashemi-Tilehnoee^c

School of Mechanical Engineering, Shiraz University, Shiraz, Iran^a

Department of Nuclear Engineering, Faculty of Advanced Sciences & Technologies, University of Isfahan, Isfahan, Iran^b

Department of Nuclear Engineering, Aliabad Katoul Branch, Islamic Azad University, Aliabad Katoul, Iran^c

Abstract

Neutron flux in the eight irradiation boxes of the 5 MW Tehran low power research reactor computes by MCNP Monte Carlo N-Particle transport code. The lithium orthosilicate, an interesting material in fusion engineering, encapsulated by quartz cylindrical containers positioned in the irradiation boxes to produce tritium. According to the weight of the tritium produced in the Tehran research reactor in comparison with reference reactor, this type of low power reactor can be used as a source of external tritium supplier in the fusion research facility.

Section IX: Neutron Generator Research

Conference Presentation:

IEEE NPSS (Toronto), UOIT, Oshawa, ON, 25 & 26 June, 2010 International Workshop on Real Time Measurement, Instrumentation & Control [RTMIC] 2-1

Design and Construction of Deuterium Target for Fast Neutron Production

P.Tayyebi* Department of Radiation Application, Shahid Beheshti University, Velenjak, Tehran, Iran, F.Abbasi Davani *pooneh.tayyebi@gmail.com

Abstract:

In order to make deuterium targets (TiD), titanium layer with thickness 0.5 up to 2 μm and copper substrate have been used. Titanium coating on copper has been carried out by Ion coating method. Thicknesses of Targets have been measured by Rutherford Back Scattering (RBS) method and simulated by SIMNRA software. The targets, after thermal treatment, have been exposed to deuterium gas. For validation of deuterium diffusion in the targets they have been analyzed by ERD method. Then they have been bombarded with Deuterium ion (in the neutron generator) by different energies from 90 up to 140 keV and currents of 100 and 200 μA . Emitted neutrons from D-D reaction have been measured by BF₃ counter and neutron energy has been measured in zero angle respect to incident beam. A 2'' \times 2'' liquid scintillator, NE 213, has been used. In this experiment neutron and gamma spectra have been discriminated by pulse shape discriminator (P.S.D) and zero cross timing. Colrow and FORIST codes have been used for unfolding and the neutron energy has been measured that is 2.5 MeV. It is concluded from bombardment results that the best thickness of target which is made, is 1 μm .

Journal Articles:

JOURNAL OF NUCLEAR SCIENCE AND TECHNOLOGY 2006 , Volume - , Number 3 (38); Page(s) 36 To 41.

Paper:

MEASUREMENT OF 14.8 MEV NEUTRON FLUX OF A NEUTRON GENERATOR USING NEUTRON ACTIVATION TECHNIQUE

Author(s): KASHIAN S., RAHIGHI J.*, AZIZI SHAMAMI MEHRDAD, GHODS H.

* NUCLEAR SCIENCE RESEARCH SCHOOL, AEOI, TEHRAN, IRAN

Abstract:

Fast neutron flux (14.8 MeV) of a neutron generator has been measured by activation technique. The measurements performed using Cu and Ni threshold detectors. ⁶²Cu and ⁵⁷Ni were produced through ⁶³Cu (n, 2n) ⁶²Cu and ⁵⁸Ni (n, 2n) ⁵⁷Ni reactions. They decay by emitting 511 keV and 1377 keV gamma rays, respectively. The half life of ⁶²Cu is 9.74 min and that of ⁵⁷Ni is 36 hours. The flux of neutron has been calculated by measuring the activity after the irradiation time. Gamma spectroscopy of the activated foils was performed using a HPGe detector. By employing this technique the neutron flux of $2.64 \times 10^7 \pm 3\%$ n/s was obtained for 60 μA deuteron of 110keV energy, bombarding a solid target of ³H.

Comparison of physical sputtering and ion plating methods for investigation of hydrogen distribution into the hydrogen targets

Iranian Journal of Physics Research, 2011, Volume 10(4), pp287-293, In Farsi
P. Tayebi and Fereydoun Abbasi-Davani

Abstract:

In this paper, selection of proper method for titanium coating on copper substrate is studied to construct nuclear targets for neutron production in particle accelerators.

Section X: End Notes

Seoul says firm nearly sold Iran atomic booster

September 5, 2005

<https://iranfocus.com/en/wpen/nuclear/3626-seoul-says-firm-nearly-sold-iran-atomic-booster>

Watchdog cleared tritium shipment to Iran

Martin Mittelstaedt, March 23, 2006

<https://www.theglobeandmail.com/news/national/watchdog-cleared-tritium-shipment-to-iran/article/705544>

Non-Partisan Congressional Report Reveals India's Support for Iran's Nuclear Program

November 14, 2006

NIAG 6004: Dutch Response to Tritium Gas Shipment Demarche

March 19, 2008

NIAG 6004: Dutch Update on Tritium Gas Shipment

April 3, 2008

NIAG 8064: Iran Seeks Russian-Origin Neutron Generators Through Malaysia

May 16, 2008

Netherlands/Tritium: Shipment Details/IAEA Briefing

July 11, 2008

Tritium Gas Export to Iran: Germany Sends Back Kudos for Valuable Nonpapers

Date unavailable

On September 21, 2020 **Seyed Javad Ahmadi** was sanctioned by the Trump administration. Details of his research are contained in this bibliography and an earlier bibliography on Iranian Chemical Isotope Exchange Research: Boron, Lithium and Uranium

Feasibility Study of Uncontrolled Fission Chain Reaction

2004 International Nuclear Science and Technology Conference held in Shiraz, Iran

(Y. Zarei Yuzband, Tabriz Univ.)

Chain fission process completed during very short time in uncontrolled systems. In order to reach this quantity we used multigroup neutron transport calculation. Geometrical quantities of uncontrolled chain reaction systems such as buckling and critical radius have been evaluated. Number of generation and time of chain process in uncontrolled system computed. Study of the reduced amount of fissile material is underway.