Hydrogel Adsorbents of Poly(N-isopropylacrylamide-co-methacryloyloxymethyl-12-crown-4) for Li+ Recovery Prepared by Droplet Microfluidics

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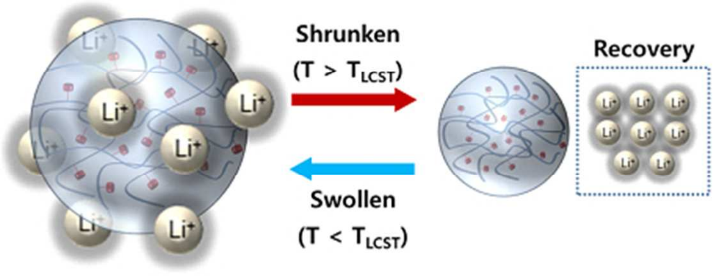
Graphic Abstract



Graphical Abstract
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Hydrogel Adsorbents of Poly(*N*-isopropylacrylamide-*co*-methacryloyloxymethyl-12-crown-4) for Li^+ Recovery Prepared by Droplet Microfluidics

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Abstract

This article describes the synthesis and application of hydrogel adsorbents for lithium ion (Li^+) recovery from seawater. The monodisperse hydrogel adsorbent particles of crosslinked poly(*N*-isopropylacrylamide-*co*-methacryloyloxymethyl-12-crown-4) [P(NIPAAm-*co*-M12C4)] were prepared using droplet microfluidics. For selective binding of Li^+, methacryloyloxymethyl-12-crown-4 (M12C4) was synthesized from 2-hydroxymethyl-12-crown-4 and methacrylyol chloride. M12C4 was then used as a comonomer in the photo-polymerization of aqueous droplets containing *N*-isopropylacrylamide (NIPAAm) and *N*,*N*'-methylenebisacrylamide (MBA) in the presence of 2,2-diethoxyacetophenone (DEAP) under 365 nm UV irradiation. The chemical composition and morphology of P(NIPAAm-*co*-M12C4) hydrogel adsorbents were analyzed by IR, NMR, optical microscopy, and SEM techniques. Inductively coupled plasma mass spectrometry (ICP-MS) and optical emission spectrometry (ICP-OES) analyses revealed 89% Li^+ adsorption efficiency with high selectivity among several different metal ions from artificial seawater and a maximum adsorption of 1.4 mg Li^+/g hydrogel adsorbent achieved within 20 min.

Keywords: Lithium ion, Adsorbent, Recovery, Hydrogel, Droplet microfluidics, Seawater

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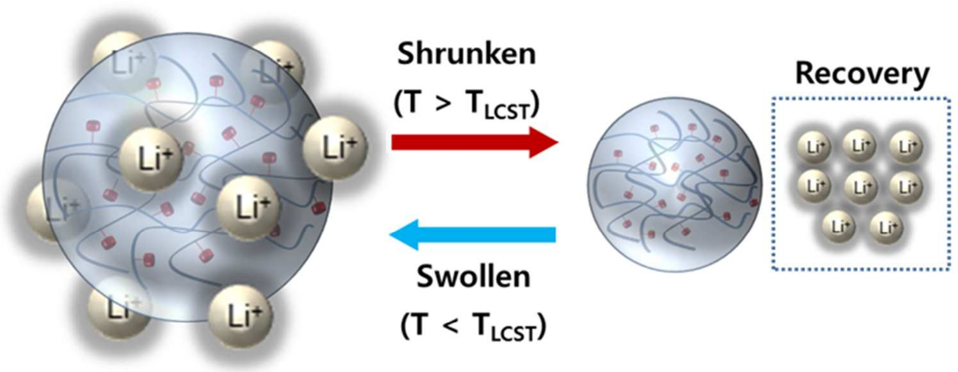


Introduction

Lithium and its complexes are widely used for a variety of applications including rechargeable batteries for mobile electronic gadgets and vehicles, alloys for aircrafts, hydrogen storage and fuel, and nuclear fusion.[1-3] Despite their versatility, securing sources of lithium at a national level has increased importance because of the limited amount of lithium available. However, 230 billion tons of lithium is dissolved in seawater,[4] and which is much greater than quantities present in mines and salt lakes. Unfortunately, concentrations of sodium (~10,800 ppm) and other metal ions are much higher in seawater than lithium (0.1-0.2 ppm). Therefore, a selective method for the recovery of lithium should be developed.

For the selective recovery of lithium ions (Li^+) from the seawater, several methods, such as adsorption,[5-6] solvent extraction,[7] and co-precipitation,[8] have been developed so far. Among them, the adsorption method seems quite attractive but most of the research have focused on inorganic materials. One well-known adsorbent, spinel-type manganese oxides (λ-MnO_2), have a high selectivity for Li^+, and which is selectively adsorbed by topotactic extraction. This adsorbent can be prepared from lithium manganese oxide ($Li_xMn_2O_4$) by exchanging Li^+ for H^+ (e.g., 1M HCl with $[Li^+]:[H^+] = 1:40$). However, the recovery of Li^+ requires strong acids (e.g., H_2SO_4 or HCl), which is not eco-friendly,[9-10] and it takes a long adsorption/desorption cycle from a couple of days to several weeks. It has already been known that the crown ether of 12-crown-4 forms a complex with Li^+; however, there were few studies on the lithium recovery of crown ether-functionalized polymeric (organic) adsorbent. Chu group reported reversible aggregation and fluctuation dependent on colloidal stability with metal complexion of P(NIPAAm-co-18C6) microspheres prepared by precipitation copolymerization.[11-12]

In this work, we report the development of a hydrogel adsorbent made by UV-photo copolymerization of methacryloyl crown ether (12-crown-4) and *N*-isopropylacrylamide (NIPAAm) in a tubular microfluidic device. The hydrogel adsorbent developed selectively adsorbs lithium ions in seawater and can be regenerated by facile volume phase transition (VPT) of the PNIPAAm above a lower critical solution temperature (LCST) without acidic treatment. This work is, therefore, the first article for selective and eco-friendly lithium recovery from seawater by using polymeric hydrogel adsorbents.

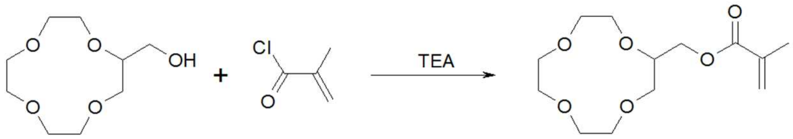
Experimental

Reagents and materials

NIPAAm was purchased from Aldrich (97%, St. Louis, MO, USA) and purified by recrystallization with a mixture of hexane and acetone (50/50, v/v). *N*,*N*'-methylenebisacrylamide (MBA, 99%), methacrylyol chloride, magnesium sulfate ($MgSO_4$), hexadecane, dry diethyl ether (>99.0%), acetone and triethylamine (TEA) were all reagent grades, purchased from Aldrich (St. Louis, MO, USA), and used without purification. Hydrochloric acid (HCl, 35%) and acetone were purchased from Duksan Chemical (South Korea). 2-Hydroxymethyl-12-crown-4 and 2,2-diethoxyacetophenone (DEAP) were purchased from TCI (Tokyo, Japan). Span 80 was purchased from Junsei Chemical (Tokyo, Japan). Artificial sea salt (under water vision and quality control) was purchased from Marine Research (Sunnyvale, CA, USA) for lithium adsorption analysis. Double-distilled and deionized (DDI) water was used for all procedures.

Preparation of methacryloyloxymethyl-12-crown-4 (M12C4)

Scheme 1 shows the synthesis of M12C4. A solution of 2-hydroxymethyl-12-crown-4 (0.83 g, 4 mmol) and TEA (0.5 g, 5 mmol) in dry diethyl ether (10 mL) was added dropwise to methacryloyl chloride (0.42 g, 4 mmol) at 0 °C for 5 min and the reaction mixture was stirred for 60 min at room temperature. The mixture was then extracted five times with dilute (5 vol%) aqueous HCl, once with excess DDI water, and dried over $MgSO_4$. After filtration, the ether layer was evaporated under reduced pressure. The yield of methacryloyloxymethyl-12-crown-4 (M12C4) was about 83%.



Scheme 1. Synthesis of methacryloyloxymethyl-12-crown-4 (M12C4).

Preparation of crosslinked P(NIPAAm-co-M12C4) hydrogel adsorbents

For the adsorbent particle preparation, we used droplet microfluidics. This is a good candidate for uniform microparticle (over 100 μm diameter) preparation, as compared with suspension, soap-free emulsion or dispersion polymerizations in terms of size distribution control and reaction time. In addition, a broad size distribution ranged from nanometer to millimeter size may be an obstacle to easy recovery of adsorbents and precise measurement of Li adsorption. For microfluidic particle preparation,[13-16] a 30 gauge needle (NanoNC, Seoul, South Korea) was inserted into Tygon® microbore tubing (UV-permeable, 0.02-inch I.D. with ca. 30 cm length, Cole-Parmer, IL, USA). The flow rates of the continuous and disperse phases were maintained by using two micro-syringe pumps (Legato 200, kd Scientific, South Korea). A schematic illustration of the microfluidic device is shown in **Fig. 1**.

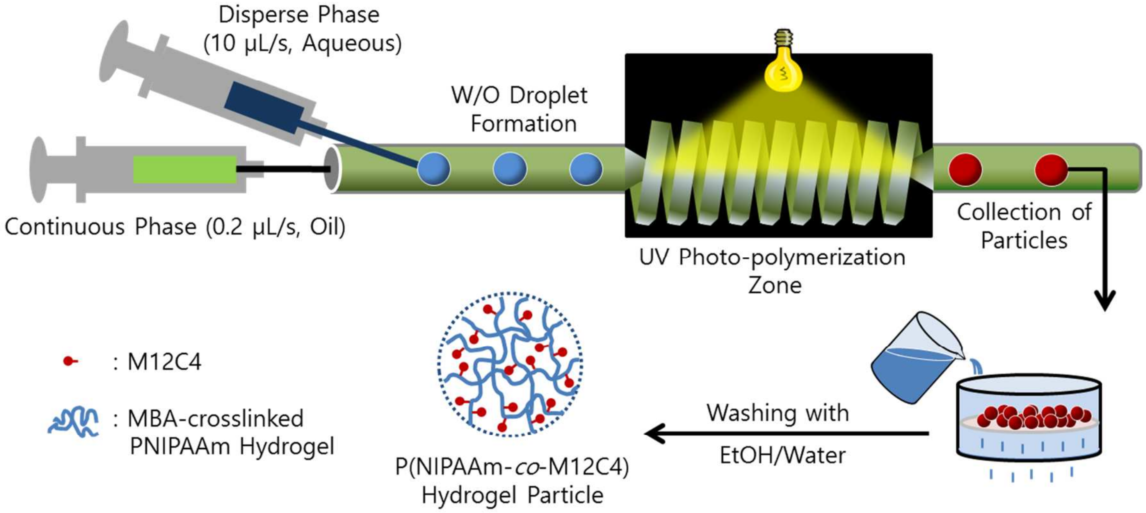


Fig. 1. Schematic illustration of a simple microfluidic device for the preparation of crosslinked P(NIPAAm-*co*-M12C4) hydrogel adsorbents.

The disperse phase was made by mixing NIPAAm (0.25 g) and MBA (0.05 g) in DDI water (5 mL). A mixture of DEAP (0.05 g) and M12C4 (0.25 g) in acetone (5 mL) was then added to the disperse phase. The molar concentration of M12C4 monomer of 26.5 mol% (in recipe) had been optimized by comparing the monomer conversion in each batch, since the monomer conversion was decreased as the M12C4 concentration was increased. The concentration of MBA was also tuned by studying the mechanical property of the adsorbent, which was also affected by the monomer conversion. The continuous phase was a mixture of hexadecane (20 mL), DEAP (0.05 g), and Span 80 (0.50 g). For UV photo-polymerization, DEAP was added into both continuous and dispersed phases for high monomer conversion, and which increased mechanical strength of adsorbent particles. When DEAP was added only into continuous phase, the adsorbent particles were damaged during washing. We could overcome this problem by adding DEAP into both phases, and which was effective because of the water-solubility of DEAP (= 0.16 g/L water, 25°C).

The two immiscible fluids, disperse and continuous phase, were injected into Tygon® microbore tubing and photo-polymerized under UV irradiation (365 nm, 100 W, 2000 mW/cm^2, SPOT UV/Inno-cure, Lichtzen, South Korea) for 0.5 h. After polymerization, unreacted monomer and surfactant were washed with DDI water and ethanol on a 20 μm-mesh sieve, and the purified particles were collected. The number-average size of hydrogel particles in the shrunken and swollen state was approximately 283 μm and 310 μm, respectively, at 50 ºC (> T_{LCST} of PNIPAAm) and 25ºC. The number-average sizes were obtained from the optical microscopic images by measuring the diameters of over 50 randomly selected hydrogel adsorbents. The size distribution of the particles was expressed as a coefficient of variation (CV, %) and the CV (%) value of adsorbent at 25°C was ca. 5%.

Characterization of adsorbents

A scanning electron microscope (SEM, S-4300, Hitachi, Japan) and an optical microscope (Eclipse LV100D, Nikon, Tokyo, Japan) were used to determine particle morphology. The chemical structures of M12C4 and P(NIPAAm-*co*-M12C4) microspheres were confirmed by nuclear magnetic resonance (NMR, Avance III 500, Bruker, Germany) and Fourier transform infrared spectrophotometer (IR, Tensor 27, Bruker, Germany).

Adsorption/desorption experiments

For Li^+ adsorption analyses, 100 mg hydrogel adsorbent was added in a 10 mL artificial seawater solution (the concentration of sea salt was 3.64 g/L water). Prior to ICP-MS analysis (NexION 300, Perkin-Elmer, USA), the major cations (Na^+, Mg^{2+}, Ca^{2+}, and K^+) with high concentrations were filtered off through iminodiacetic acid (IDA) chelating columns (Elemental Scientific, USA) to measure Li^+ ions in this work. It was confirmed that the artificial seawater solution contained Li (0.2 ± 0.03 mg/L), Co (0.07 ± 0.04 mg/L), In (< 0.05 mg/L), and Cr (< 0.06 mg/L) ions after minimizing the seawater-related polyatomic interferences. For the maximum Li^+ adsorption measurements, a standard lithium solution (1000 ± 3 mg/L, Inorganic Ventures, Virginia, USA) was used, and the adsorption was measured using ICP-OES (Optima 8300, Perkin-Elmer, USA). The adsorption (%+Li^+) efficiency, desorption (%–Li^+) efficiency, and amount of Li^+ uptake in the adsorbents were calculated with Eq. (1), (2), and (3), respectively:

$$\% + Li^+ \ \ efficiency = \frac{C_0 - C_{eq}}{C_0} \times 100 \qquad (1)$$

$$\% - Li^+ \ \ efficiency = \frac{C_{re}}{C_0 - C_{eq}} \times 100 \qquad (2)$$

$$Li^+ \quad uptake \ \ (mg \quad Li^+ / g \quad adsorbents) = \frac{(C_0 - C_{eq})V}{m} \qquad (3)$$

where C_0 and C_{eq} are the Li^+ concentrations (mg/L) in the seawater solution before and after lithium ion adsorption, respectively. V is the volume of the solution (liter) and m is the mass of adsorbent (g). After Li^+ uptake, the adsorbents were removed from the solution and redispersed in DDI water (10 mL), as shown in **Fig. 2**. The dispersion was heated to 50 °C (>T_{LCST} of

PNIPAAm) for desorption of Li^+ from the adsorbent and magnetically stirred for 50 min. The adsorbents were then filtered and collected using a 20 µm-mesh sieve at 50 °C. C_{re} is the concentration of Li^+ in DDI water after redispersion, as shown in Eq. (2).

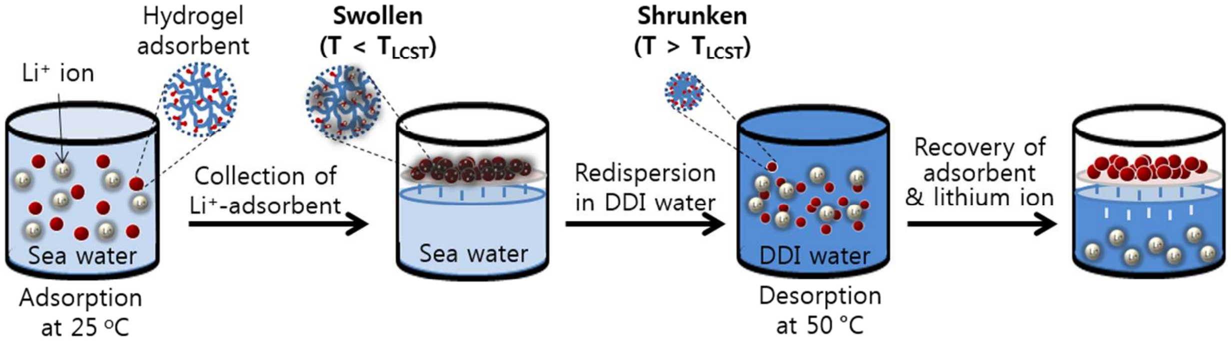


Fig. 2. Schematic illustration of the adsorption and desorption processes for Li^+ recovery using hydrogel adsorbents.

Results and Discussion

For hydrogel adsorbent preparation, the disperse phase (aqueous, W) was injected through a needle connected to the tube in which the continuous phase (oil, O) is constantly flowing. The W/O droplets were generated at the needle tip in this typical co-flow regime with flow rates of 10 and 0.2 µL/s for the continuous and disperse phases, respectively. The resultant droplets were then photo-polymerized and crosslinked within the UV irradiation zone (see **Fig. 1**).

Due to a short polymerization time of 0.5 h, the final conversion of total monomer measured by gravimetric analysis was ca. 70%. Unfortunately, we could not get the number/ratio of M12C4 per one particle empirically because the composition of the polymer adsorbent drifted and the partial monomer conversion was not studied. If we could assume that all NIPAAm and MBA monomers were completely polymerized, then only 34% of M12C4 monomer might be polymerized (this would satisfy 70% total monomer conversion in the photo-polymerization and give 0.142 g M12C4/g adsorbent). After collection of the particles, they were purified with DDI water and ethanol to remove the residual monomer. The production rate of adsorbent particle in the single tubing could be calculated as 4.6×10^4 particles/h, and which corresponds to ~0.03 g/h.

IR spectra of M12C4 (lithium ionophore) are shown in **Fig. 3**. The strong peak in the range 1120-1250 cm^{-1} was assigned to the ether functional group (C–O–C) in 12-crown-4. A typical C–H bond stretch was found at 2859 cm^{-1} and the C=O bond stretching frequency for an ester appeared at 1735-1750 cm^{-1}. The C=C bond of the methacryloyl group in M12C4 was confirmed by a C=C bond stretch at 1635 cm^{-1}.

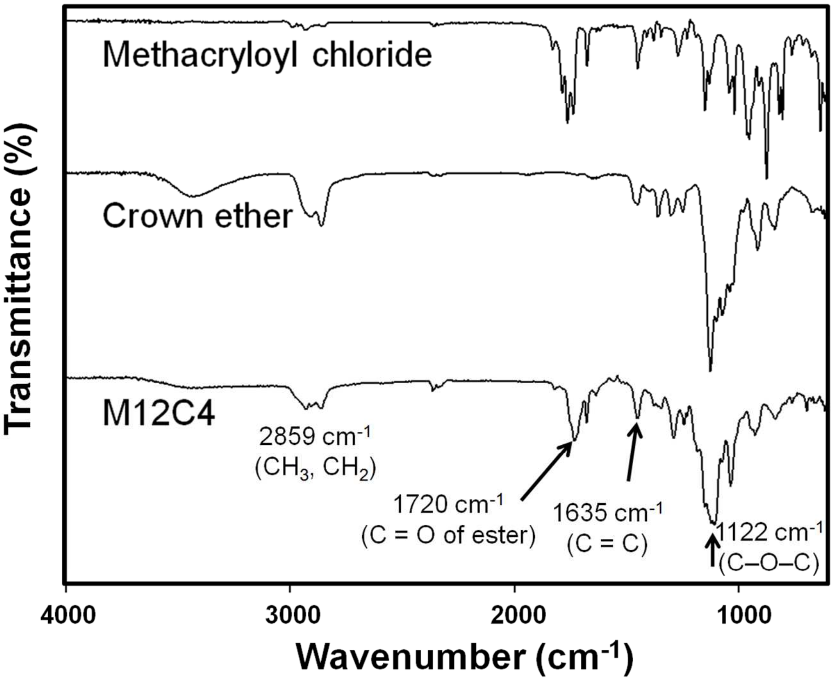


Fig. 3. IR spectra of methacryloyl chloride, 2-hydroxymethyl-12-crown-4, and M12C4 lithium ionophore.

M12C4 lithium ionophore was further confirmed by ^{13}C-NMR in $CDCl_3$ and the spectrum is shown in **Fig. 4(a)**. The methyl group, carbonyl (C=O) peak, carbon double bond (C=C), and carbon adjacent to the crown ether were assigned at 18, 172, 125, and 64 ppm, respectively. Aliphatic CH_2 carbons of the crown ether appeared in the range 70-73 ppm. Structural analysis of P(NIPAAm-*co*-M12C4) hydrogel was also performed by ^{13}C-NMR in solid state, which is shown in **Fig. 4(b)**. The peak marked with an asterisk in the solid state ^{13}C-NMR spectrum was assigned to the carbonyl groups of the NIPAAm units. The methylene carbons of the 12-crown-4 groups in M12C4 were observed at approximately 70 ppm.

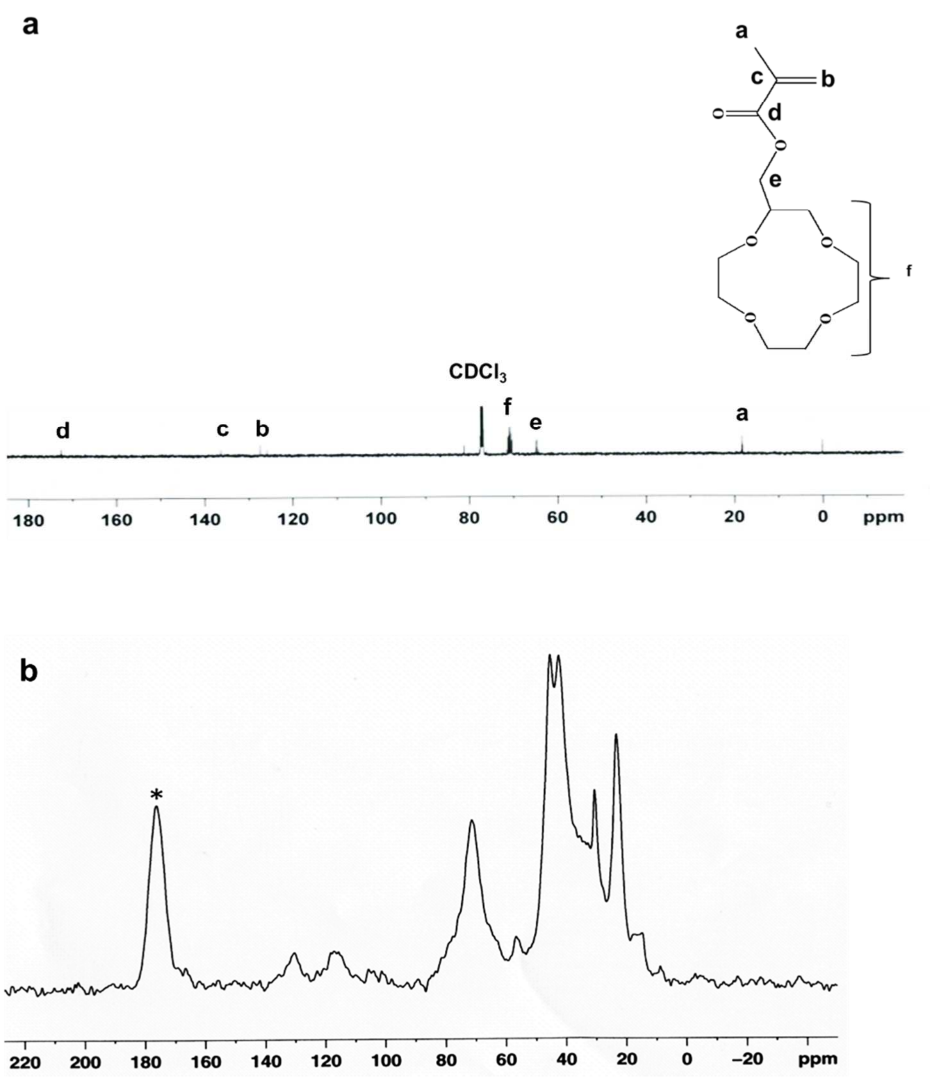


Fig. 4. ^{13}C-NMR spectra of (a) M12C4 lithium ionophore and (b) crosslinked P(NIPAAm-*co*-M12C4) hydrogel adsorbents in solid state.

Photographic images of P(NIPAAm-*co*-M12C4) hydrogel adsorbents are shown in **Fig. 5(a)**. The swollen hydrogel adsorbents at 25 °C have an average diameter of 310 μm with 5% CV. Regarding the VPT behavior of adsorbent particles against the temperature change, the diameter change of the particle was observed, as shown in **Fig. 5(b)**. The temperature change of an adsorbent particle was controlled by a heating glass (Live Cell Instr., USA) and the diameter change was completed within several minutes. In this work we didn't study the response time or rate for VPT behavior of the adsorbent but the response time would be short, and which were reported in several references.[17-18]

At 50 °C the diameter of the hydrogel adsorbents shrunk from 310 to 283 μm because the temperature is over the LCST. The volume decrease was only 24%, which was attributed to a crosslinked structure due to addition of MBA. For large volume changes (i.e., VPT), 0.03 and 0.01 g of MBA were added in the hydrogel adsorbents preparation; however, addition of less than 0.05 g of MBA produced poor mechanical properties for the hydrogel adsorbents.

The SEM images of P(NIPAAm-*co*-M12C4) hydrogel adsorbents are shown in **Fig. 6**. **Fig. 6(a-c)** depict the morphology of the hydrogel adsorbents in a dried state at several magnifications, and a porous surface structure for hydrogel was confirmed in SEM image **6(c)**. To observe the inner structure of the adsorbent, the hydrogel adsorbents were fully dried in a freeze dryer after immersion in liquid N_2. From **Fig. 6(d)** and the high magnification (×50,000) insert, the porous nature of the inner adsorbent particle was observed. The pore size at the particle surface appears to be bigger and more irregular than the inner pore.

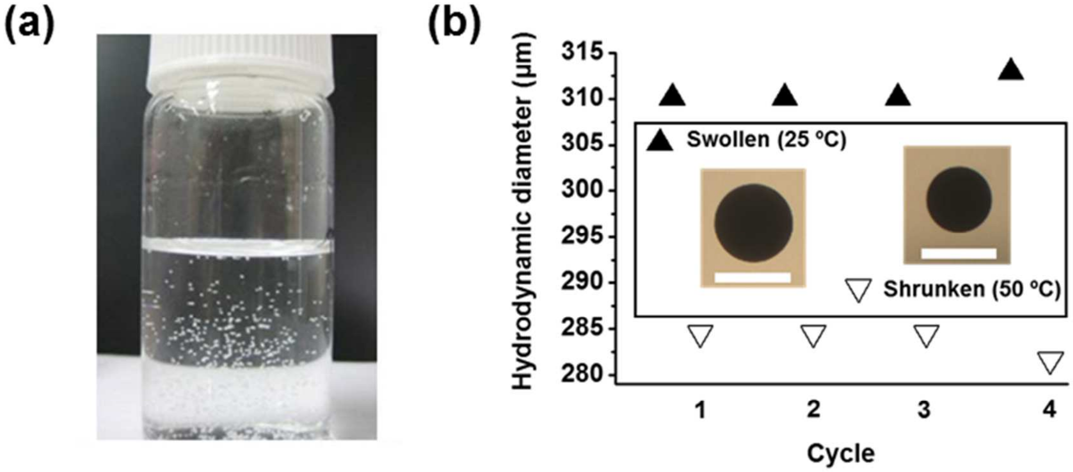


Fig. 5. (a) Photographic image of P(NIPAAm-*co*-M12C4) hydrogel adsorbent particles in DDI water. (b) Variation of the hydrodynamic diameter of the hydrogel adsorbents in DDI water at 25 °C and 50 °C (>T_{LCST}). The photographic images on the left and right sides correspond to the swollen and shrunken states of hydrogel adsorbents, respectively.

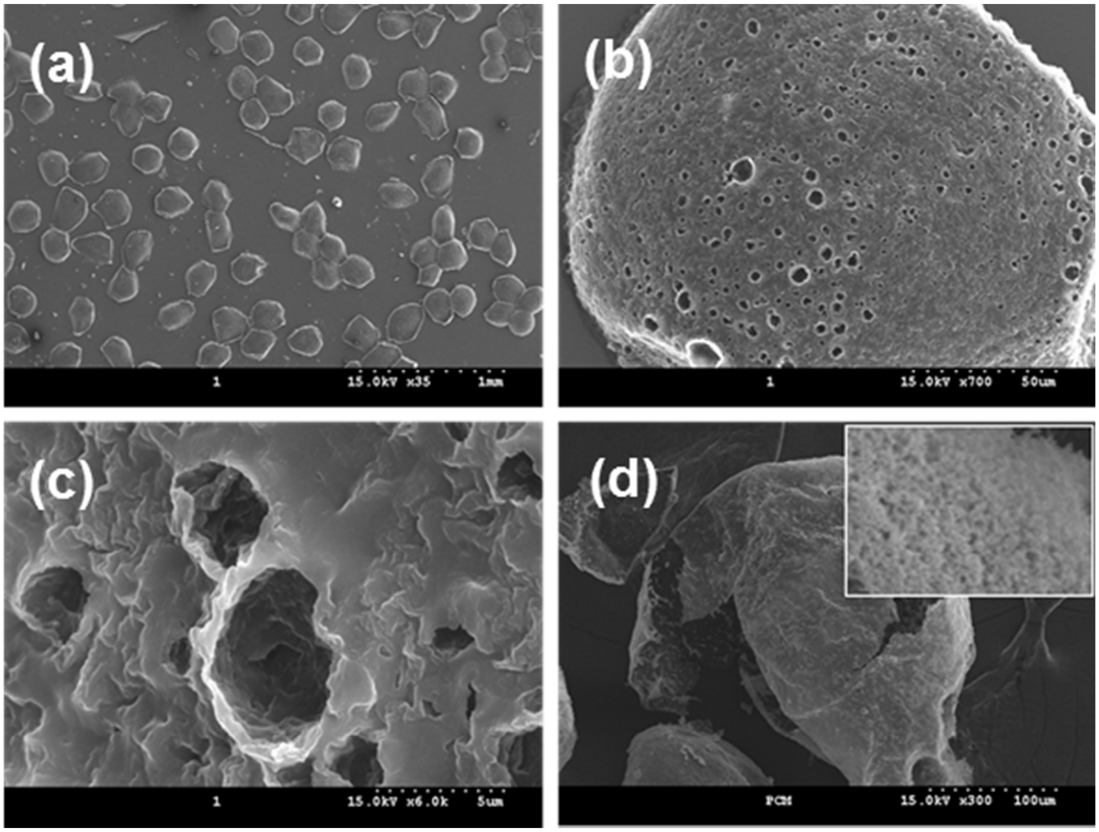


Fig. 6. (a, b, and c) SEM images of adsorbent hydrogel particles (×35, ×700, ×6,000 magnification, respectively), and (d) SEM image of the particles after freeze-drying (inset: magnified inner structure of the particle at ×50,000).

The Li^+ adsorption and desorption efficiencies of the particle were measured and the results are shown in **Fig. 7(a)**. Within 1 h, a high Li^+ selectivity was found among the four different metal ions contained in the artificial seawater, which was attributed to selective binding of M12C4 with Li^+. In addition, 89% adsorption efficiency indicates a high loading capability for Li^+. However, 2.0% of Cr ions were also detected from the ICP analyses, as shown in the inset of **Fig. 7(a)**. This may be due to Cr ions strong affinity for the amine and ester groups in PNIPAAm crosslinked with MBA and M12C4.

After collecting Li^+ in the hydrogel adsorbent, the Li^+ were recovered in DDI water using the method described in **Fig. 2**. As shown in **Fig. 7**, 69% of the Li^+ adsorbed were recovered, which means that 31% of the Li^+ remained in the hydrogel particles after the desorption process. This result may be explained because the hydrogel particles at room temperature are swollen by hydration of neighboring water molecules, which is driven by the balance between the loss of entropy of the water molecules and the gain of enthalpy of hydrogen bonding between the water molecules. Increasing the temperature above the LCST causes a cut-off in hydrogen bonding, [19-21] which leads to dehydration and shrinkage of the adsorbent. Simultaneously, Li^+ coordinated with the M12C4 group dissociate from the adsorbent. This desorption occurs because of a structural change in the cohesion of the neighboring isopropyl groups as well as thermal motion in the lithium complex. In addition, the structure of the main polymer chain is distorted by the thermal volume change of the hydrogel particles, potentially inducing displacement of the lithium ions from their original positions. However, we assume that Li^+ coordinated at the outer surface of the adsorbent particles and residual Li^+ inner particle are not fully affected by the change in the structure motion, leading the remnant of 31% Li^+.

The maximum Li^+ adsorption for the hydrogel adsorbent was determined by ICP analysis with a standard aqueous solution containing a Li^+ concentration of 1000 mg/L. The adsorption data were plotted as a function of time, as shown in **Fig. 7(b)**. The results showed that 1.4 mg Li ion was adsorbed onto 1 g adsorbent particles. The amount of 1.4 mg Li corresponds to 0.202 mmol, and which can be the same as the moles of M12C4 ionophore as long as the adsorption is carried out with 1:1 ratio. By assuming 34% of M12C4 was polymerized, we could estimate the concentration of M12C4 ionophore (= 0.517 mmol/g particles). Therefore, we can suggest that at least 39% of ionophores adsorbed Li ions. Within 20 min, 1.4 mg of Li^+ was adsorbed in 1 g of

P(NIPAAm-*co*-M12C4) hydrogel particles, which is remarkable compared to Li^+ recovery based on lithium manganese oxide (~1 mg/g within 1 day). [22] This result can be rationalized by the highly porous and fast swelling nature of the hydrogel particles. Therefore, Li^+ recovery method based on VPT of PNIPAAm above the LCST is a suitable candidate for metal ion adsorption, which avoids the use of strong acids for the regeneration of the adsorbent, i.e., an environmentally friendly process.

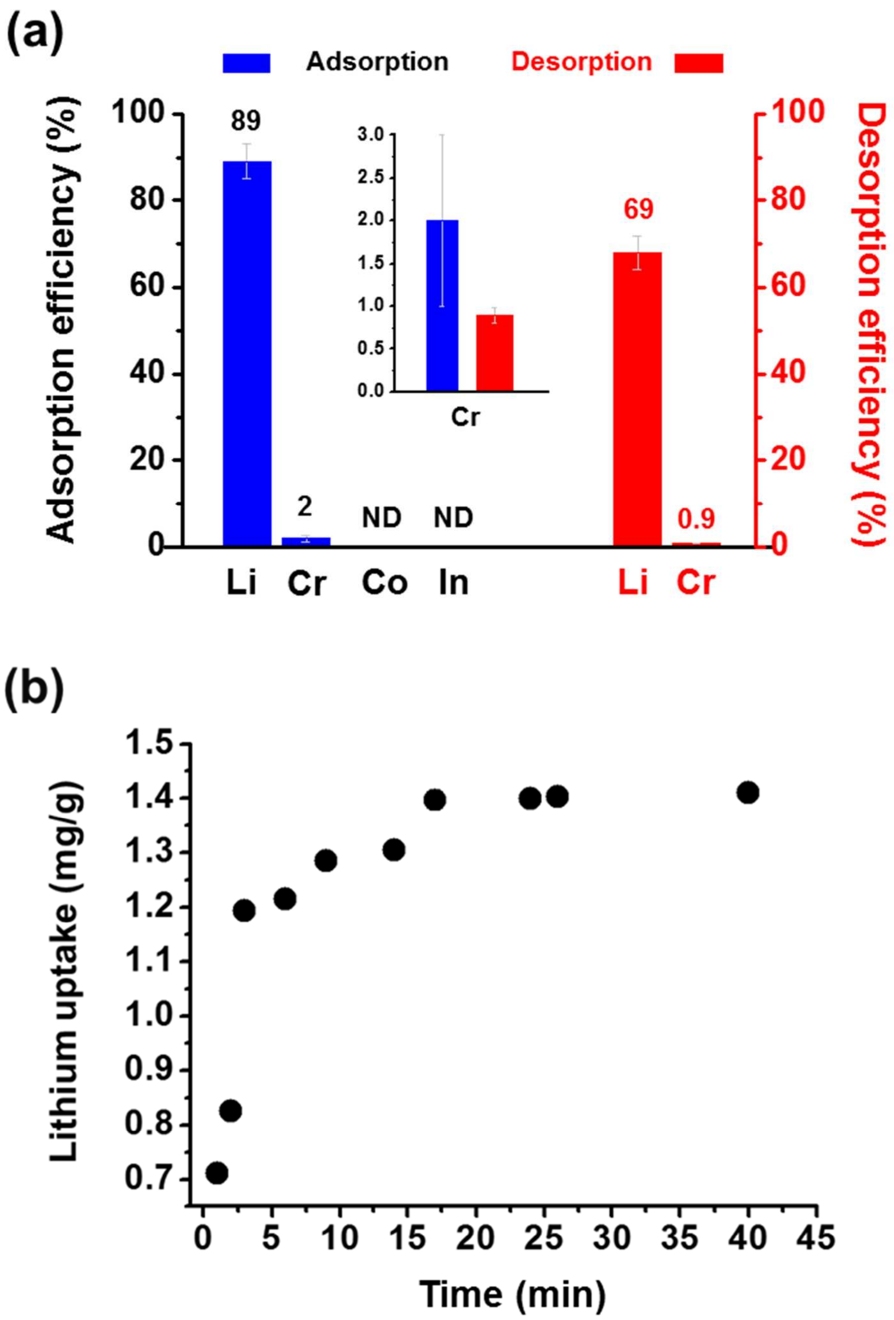


Fig. 7. (a) Lithium ion adsorption and desorption efficiencies for P(NIPAAm-*co*-M12C4) hydrogel adsorbent particles. ND indicates that the ion was not detected. Desorption was performed at 50 °C. (b) The lithium ion adsorption curve for P(NIPAAm-*co*-M12C4) using a single lithium ion solution at room temperature.

Conclusions

In summary, we have developed a simple microfluidic-based synthesis of uniform and thermo-responsive P(NIPAAm-*co*-M12C4) hydrogel adsorbent particles via UV photo-polymerization. The hydrogel particles were used as an adsorbent for lithium ions from artificial seawater. The adsorbent undergoes a VPT from swollen to shrunken states in the particle size range from 310 μm to 283 μm when the temperature is increased from 25°C to 50°C. The adsorbent afforded a lithium ion adsorption efficiency of 89% and desorption efficiency of 69%. In addition, the adsorption of lithium ions was fast, with a maximum adsorption of 1.4 mg Li^+/g adsorbent particle achieved within 20 min. Based on these results, we believe this concept may be applied to the preparation of smart adsorbents for a wide range of potential applications including metal ion recovery from seawater, waste water, and ion exchange resin and column catalysis. These results also suggest a new approach for sustainable lithium resource recovery.

Acknowledgements

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Notes and references

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