Selective Lithium Extraction from Brine and Seawater: An LLTO-Based Electrodialysis Approach

Ali Alfaraj, Xin Wang

Ali.alfaraj.1@kaust.edu.sa, Xin.Wang.2@kaust.edu.sa

Abstract

Lithium demand keeps climbing while the cheapest reserves, concentrated brines and hard-rock ores, are running down, so extracting lithium from harder feeds like oilfield brine is becoming necessary. We built an electrodialysis cell that uses a LLTO-loaded polyurethane (LLTO-PU) membrane as the selective layer, letting an applied electric field pull Li^+ through while blocking the far more abundant Na^+, Mg^{2+}, K^+, and Ca^{2+} ions. XRD and TGA confirm the membranes were cast correctly, with the LLTO staying crystalline and its content tracking the intended loading. Testing membranes at 20–50% LLTO/PU loading against real oilfield brine, a synthetic Mg–Li solution, and a LiCl solution shows that a 30% loading gives the best lithium selectivity in real brine, reaching a Li/Mg selectivity of 1765.5 and a Li/Na selectivity of 483.7, both far above the 20% membrane. Lithium flux across the membrane depends heavily on which feed is used, peaking at different loadings for brine, LiCl, and the synthetic Mg–Li solution, which points to a percolation-driven trade-off between ceramic loading and membrane defects rather than a simple "more ceramic is better" relationship. The takeaway: LLTO-PU membranes can selectively extract lithium from real oilfield brine, but the loading that performs best depends on the complexity of the feed, so membranes optimized on simplified test solutions should still be validated against the real brine before scale-up.

- **Date:** August 21, 2026

Contents

1 Introduction 2

2 Related Work 3

3 Methodology 4

3.1 Method details . . . 4

3.2 Membrane Fabrication . . . 6

3.3 Evaluation Procedure . . . 7

4 Results 8

4.1 Membrane Characterization . . . 8

4.2 Ion Selectivity in Oilfield Brine . . . 9

4.3 Li/Mg Selectivity in a Synthetic Mg–Li Solution . . . 10

4.4 Lithium Flux . . . 10

5 Discussion 11

6 Limitations and Future Work 13

7 Conclusion 13

1 Introduction

Problem Motivation and Real-World Impact

The push toward electric vehicles, grid storage, and portable electronics keeps pushing lithium demand higher every year. The problem is that most of today's supply still comes from hard rock mining or evaporation ponds, and neither is fast: pond extraction alone can take 12 to 18 months, and both routes use a lot of water and land while being concentrated in just a handful of places, mainly the "Lithium Triangle" spanning Chile, Argentina, and Bolivia. At the pace reserves are being drawn down, current estimates put global lithium supplies running out around 2080. Seawater and brine are the two big alternatives worth going after: seawater because there's effectively an unlimited amount of it, and brine, including produced oilfield brine, because it's often already being pumped to the surface as part of other operations and can carry meaningful lithium content of its own. The catch is concentration. In seawater it's tiny (about 0.17 ppm), and even in richer brines the lithium is still mixed in with far more abundant competing ions like Na^+, Mg^{2+}, K^+, and Ca^{2+}. Pulling lithium out selectively from either source is the hard part, and it's what makes a faster, more targeted extraction method worth pursuing.

Why In-Kingdom Sources Matter

For Saudi Arabia specifically, this problem carries some extra weight. Vision 2030 leans on mining and mineral processing as a new pillar of the economy, with plans reportedly targeting more than $2.5 trillion in untapped mineral resources and aiming to grow mining's share of GDP several times over by 2030. Lithium sits right in the middle of that push. Aramco has projected that domestic lithium demand could grow roughly twentyfold between 2024 and 2030 as the Kingdom builds out electric vehicles and renewable energy storage, and Aramco and Ma'aden have already reported pulling lithium from oilfield brine in early trials, with commercial-scale production targeted as soon as 2027 through a joint venture between the two. A KAUST spinout, Lihytech, is chasing a similar idea already, using ceramic membranes paired with electrodialysis to pull lithium out of low-grade brine. None of this guarantees a system like the one in this project will scale, but it does mean the timing lines up: working with brine that's already available from Kingdom operations, rather than importing concentrate from the other side of the world, is a real option worth having ready.

Problem Statement

We need a way to pull lithium ions out of seawater or brine that's dominated by other cations, and do it without burning through energy, wearing out the membrane, or taking forever, while still ending up with a lithium product that's concentrated and pure enough to use downstream.

Key Assumptions or Limitations

- How the LLTO membrane holds up over long operation, fouling, or real brine and seawater conditions like biofouling and scaling isn't something lab-scale testing fully captures. Our longest single run here was measured in hours, not the weeks or months a real deployment would run for.
- We haven't demonstrated scale-up from bench-scale to an industrial throughput. The cell used in this project processes a small volume at a time, and nothing here speaks directly to how performance holds up once the active membrane area gets much larger.
- Getting good lithium selectivity over sodium and magnesium remains a limiting factor, especially since real brine carries several competing ions at once rather than the single ion

a simplified test solution isolates.

Summary of the Proposed System

The system we're building around is electrodialysis with LLTO membranes standing in as the selective layer instead of a typical ion-exchange membrane. LLTO is a solid, lithium-conductive ceramic with a perovskite structure, and its lattice essentially only lets Li^+ hop through while blocking bulkier or differently charged ions like Na^+, Mg^{2+}, and K^+, which is exactly the kind of selectivity a brine or seawater feed demands. With an electric field applied across the cell, lithium ions migrate through the membrane from the feed side into the product side, so the product gets steadily more concentrated while the competing ions stay behind. In effect, this pairs the selectivity you'd get from a solid-state lithium conductor with the continuous, scalable operation electrodialysis is known for, aiming for something quicker and less resource-heavy than evaporation ponds, whether the feed is produced brine or seawater.

2 Related Work

Lithium demand has researchers looking at brine extraction from a few different angles, and three approaches keep coming up: conventional soda-lime evaporation, electrodialysis, and the decoupled membrane-free cell (DCMF). None of them is a clear winner; each comes with its own catch.

- **Conventional soda-lime evaporation:** It's the most established method out there, but it falls apart economically once the brine's lithium content is low.
- **Decoupled membrane-free cell (DCMF):** Li et al. [2] built a cell that shuttles lithium between iron-phosphate electrodes instead of relying on a selective membrane at all, which sidesteps membrane fouling and works even at very high Mg/Li ratios, and a pilot-scale version recovered 84% of the lithium from real Dead Sea brine. Selectivity and scalability are both strong here, but the capacity fades with use, so in practice it ends up running as a slow, batch-style process rather than continuously.
- **Electrodialysis:** This one runs continuously and selects for lithium well, but the flux is painfully slow. Li et al. [1] used a dense LLTO ceramic membrane to enrich lithium from Red Sea water by more than 40,000-fold with a Li/Mg selectivity above 45 million, but the process took multiple 20-hour stages to get there and the extraction rate was on the order of tens of milligrams per square meter per hour. On top of that, keeping the membrane stable over time is a real challenge, and there's an inherent tension between pushing for high purity and keeping energy use reasonable.

Zhang et al. [3] recently reviewed this broader class of lithium superionic conductor (LSIC) membranes, including LLTO, and note that ion transport in these materials happens by lithium hopping between lattice vacancies, which is what gives them their sharp size- and charge-based selectivity over Na^+, Mg^{2+}, and Ca^{2+} in the first place. The same review flags membrane brittleness and long-term stability in water as the main open problems, which lines up with why we chose to embed LLTO particles in a flexible PU matrix rather than casting it as a standalone ceramic membrane.

Beyond these three approaches, a wider field of direct lithium extraction (DLE) technology has been picking up momentum outside the lab too. Sorbent-based methods, which use a solid material that selectively binds lithium ions and then releases them into a fresh solution on demand, are already being commercialized in several countries, with some reporting recovery

rates approaching 99% under favorable conditions. Ion-exchange resins work on a related principle, swapping lithium for another cation on a fixed matrix. Compared to those, a ceramic membrane like LLTO trades away some of that plug-and-play simplicity: sorbents and resins can usually be dropped into existing brine-handling infrastructure with minimal redesign, while a membrane cell needs its own dedicated compartments and electrodes. What LLTO gains in return is a higher ceiling on selectivity, since separation happens through the crystal lattice itself rather than through surface sites that can saturate, foul, or wear out after repeated cycles. Which family of methods ends up winning out is likely to depend on the feed: a simple, concentrated brine might favor a sorbent for its ease of deployment, while a complex, dilute feed with many competing ions, like the oilfield brine used in this project, is exactly the kind of case where a membrane's sharper selectivity should matter most.

3 Methodology

3.1 Method details

Why Electrodialysis

Of the three approaches compared in Related Work, electrodialysis was the starting point for this project mainly because it is the only one of the three that runs continuously and pairs naturally with a solid ceramic membrane as the selective layer. Evaporation ponds were ruled out early since they depend on open-air area and sunlight rather than a compact reactor, which is not practical for brine handled on-site at an oilfield. The decoupled membrane-free cell sidesteps membrane problems entirely, but its batch-like operation means the system has to be periodically stopped and reset, which adds downtime and complexity that a continuous process avoids. Electrodialysis keeps a steady flow going as long as the field is on, and pairing it with LLTO instead of a standard ion-exchange membrane was meant to fix electrodialysis's traditional weak point, its flux and selectivity, since LLTO's crystal lattice offers much sharper ion selectivity than a polymer membrane can manage on its own. Embedding the LLTO in a flexible PU matrix rather than using it as a standalone ceramic film, the way earlier work has, was a deliberate choice too: standalone LLTO membranes are known to be brittle, and a polymer-ceramic composite should hold up better to handling and repeated use even if it costs a bit of raw ion conductivity.

Overview

The cell we built has four compartments. Brine flows through one, carrying the mix of cations and anions that get pulled apart once the field is on. A separate product compartment collects the lithium as it crosses over. Two more compartments, one on each side, circulate an electrode solution whose job is just to keep the charge balanced on both ends of the cell.

Two different membrane types keep these compartments apart. Between the electrode compartments and everything else sits an anion exchange membrane (AEM), letting negative ions through. Between the brine and product sides sits the LLTO membrane, the one doing the actual selective work, since it's built to let lithium through and stop everything else.

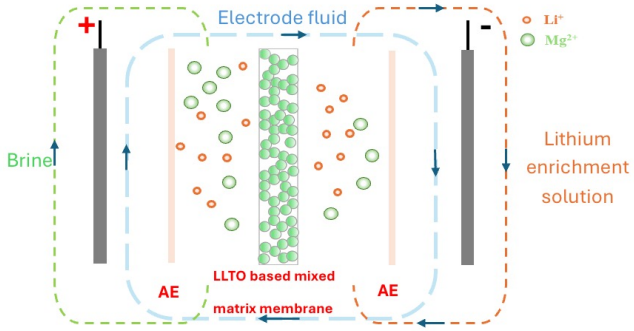


Figure 1 The process's schematic.

Process Description

1. **Adjust and apply current.** Once the setup is dialed in, we run 0.2 mA across the two electrodes to get the field going.



Figure 2 Cell layout after the current is applied: cathode, product, feed (brine), and anode compartments separated by the AEM and LLTO membranes.

2. **Brine enters, ions separate.** Brine flows into its compartment, and the field immediately starts pulling the cations and anions apart, sending them in opposite directions.



Figure 3 Brine enters the feed compartment and ions begin separating under the applied field.

3. **Selective transfer.** The cations head for the LLTO membrane: lithium gets through into the product side, while the larger competing cations just pile up against it. Meanwhile the anions move the other way, crossing the AEM into the electrode solution.



Figure 4 Selective transfer: Li^+ crosses the LLTO membrane into the product compartment while Na^+/Ca^{2+} are blocked and stack up; anions move through the AEM toward the electrode compartments.

4. **Charge balance.** As lithium builds up on the product side, the electrode solution circulating around the outside supplies anions that cross the AEM into the product compartment, keeping everything charge-balanced.



Figure 5 Charge balance: anions supplied from the electrode compartments pass through the AEM into the product compartment alongside the enriched Li^+.

Legend: Li^+ is the ion we're after; Na^+ and Ca^{2+} are the competing cations the LLTO membrane blocks; Cl^- and A^- are the anions moving through the system.

3.2 Membrane Fabrication

The LLTO-loaded membranes come from blending ceramic LLTO particles into a polyurethane (PU) matrix, casting that mixture into a film, and letting the solvent evaporate off. Honestly, the chemistry isn't the hard part. Getting an even, defect-free membrane comes down to how carefully the mixing is handled, since LLTO particles clump together if you're not careful rather than spreading evenly through the polymer.

Building the solution takes a few stages. We start with a PU stock solution, made by dissolving PU pellets in NMP solvent under gentle heat until it turns into a clear, uniform liquid with no gel bits left, and since this stock keeps, it gets reused across batches. Separately, the LLTO particles get dispersed in their own solution and broken apart with sonication, which uses sound waves to knock clumps apart so the ceramic ends up suspended as fine, individual particles instead of aggregates.

Before combining everything in bulk, though, there's an intermediate step: a small amount of PU gets mixed into the LLTO dispersion first and left stirring at room temperature. This "priming" coats each particle with a thin layer of polymer, which stops them from re-clumping once full mixing starts. Only after that coating step does the primed LLTO dispersion get slowly

added into the rest of the PU solution, which is kept warm to thin it out and stirred for hours so the filler spreads evenly instead of settling or clustering.

Last comes degassing. The ceramic loading makes the mixture prone to trapping tiny air bubbles while it's being stirred, so the blend goes under vacuum in repeated cycles: pulling vacuum, releasing it, pulling again, until bubbles stop rising to the surface. It's worth the trouble: any bubble left behind turns into a pinhole once the film dries, and that's basically a shortcut for ions to slip through the membrane uncontrolled.

Once the solution looks clear and bubble-free, it's ready to be cast. Rather than just pouring it out freely, we dose a set volume into molds, since the volume poured is what actually controls how thick the finished membrane ends up once it dries. Getting that volume right matters: too thin and the membrane is fragile and easier to damage, too thick and ion transport slows down more than it needs to. From there the cast film is left to dry into the finished membrane. Scaling to a different LLTO loading is just a matter of changing how much ceramic dispersion goes in relative to the PU solution, while the mold volume stays what sets the thickness.

3.3 Evaluation Procedure

We evaluated the system in two ways: testing the ion concentrations in solution, and characterizing the membrane itself.

The Sample Testing

We measured ion concentrations in the brine and product solutions with Inductively Coupled Plasma (ICP) analysis. The sample gets turned into a fine mist and shot through argon plasma at extremely high temperature, which strips it down to individual atoms and ions. Each element then gives off light at its own characteristic wavelength, and how bright that light is tells you how much of the element is there. Since Li^+, Na^+, Mg^{2+}, K^+, and Ca^{2+} can all be read out from the same sample this way, ICP is what we used to track how much lithium was being enriched and how well the other ions were being rejected throughout the run. The technique is sensitive down to parts-per-billion for most metals, which matters here since the product side starts out with barely any lithium at all and only builds up gradually as the run progresses. It also has an edge over older single-element methods like flame photometry, since one injection reads out every ion of interest at once instead of needing a separate pass for each, which matters when the same sample has to be checked for five different ions every time.

The Membrane's Characterisation

To check the LLTO membranes themselves, we relied on X-ray Diffraction (XRD) and Thermogravimetric Analysis (TGA).

X-ray Diffraction (XRD): XRD tells us whether the LLTO inside the membrane still has its correct crystal structure. The technique works by firing X-rays at the sample and reading the angles at which they bounce back constructively, which only happens where the spacing between atomic planes matches a specific relationship between the X-ray wavelength and the diffraction angle. A material with an ordered, repeating crystal structure, like LLTO, produces sharp peaks at specific angles, while a disordered material scatters X-rays diffusely in every direction instead. That is exactly the contrast we see: plain polyurethane on its own just gives a broad, featureless signal with no real structure to it, whereas membranes loaded with LLTO show sharp peaks lining up with the reference LLTO pattern, and those peaks get more pronounced as more LLTO goes in, which is good evidence the ceramic actually made it into the membrane intact.

Thermogravimetric Analysis (TGA): TGA answers a simpler question: how much LLTO is

actually in there. The sample gets heated while a scale tracks its weight the whole time. The polyurethane burns off, but the LLTO doesn't, so whatever weight is left once the temperature climbs high enough is essentially the LLTO content. This works because organic polymers like PU decompose and burn away at a few hundred degrees Celsius, breaking down into gases that leave the sample entirely, while a ceramic oxide like LLTO is thermally stable across that same range and simply stays put. Tracking the sample's weight continuously as the temperature climbs, rather than just weighing it before and after, also shows the exact temperature range where the polymer burns off, which is a useful check that nothing unexpected is happening in the sample beyond straightforward decomposition. The numbers we got back lined up with what we'd intended to add, which is a good sign the membranes were made correctly.

4 Results

4.1 Membrane Characterization

XRD confirms that the LLTO filler keeps its crystal structure once it is cast into the PU membrane. The plain PU film gives only a broad, featureless hump around 20°, with no sharp features at all. Every LLTO-loaded membrane, from 20% up to 60%, shows a set of sharp peaks that line up with the reference LLTO pattern (PDF#87-0935), and those peaks grow more intense as the loading increases. None of the LLTO peaks shift or disappear at higher loading, so the ceramic is not reacting with the polymer or losing crystallinity during casting.

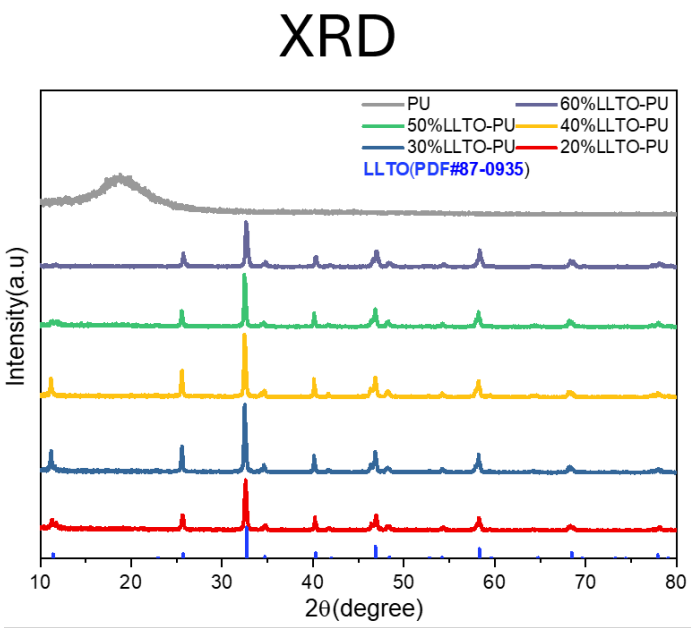


Figure 6 XRD patterns of the plain PU membrane and LLTO-PU membranes at 20–60% LLTO loading, compared against the reference LLTO pattern (PDF#87-0935).

TGA gives the actual ceramic content. Plain PU burns off almost completely by 450°C, leaving close to 0% residual mass. The loaded membranes lose weight over the same range but level off at a residue that tracks the amount of LLTO added: about 6% left over for the 20% LLTO membrane, 24% for 30%, 32% for 40%, and 35% for 50%. The residual mass rises with loading but not in a straight line; the gain between 20% and 30% is much larger than the gain between 40% and 50%.

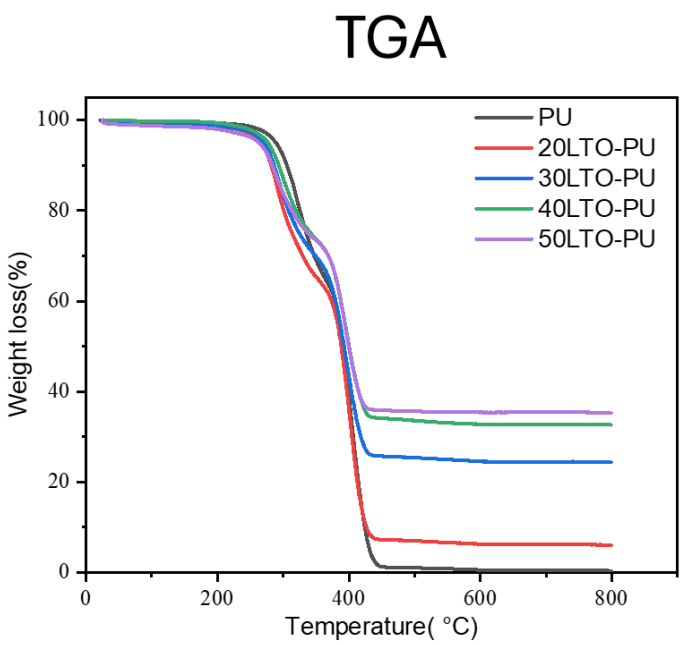


Figure 7 TGA weight-loss curves for plain PU and LLTO-PU membranes at 20–50% nominal LLTO loading.

4.2 Ion Selectivity in Oilfield Brine

Table 1 and Figure 8 show Li/Mg and Li/Na selectivity measured directly in oilfield brine as a function of LLTO/PU ratio. Selectivity is not a monotonic function of loading: it jumps sharply from 20% to 30% loading, then drops off at 40% before partially recovering at 50%. The 30% membrane gives the best separation by a wide margin, with a Li/Mg selectivity of 1765.5 and a Li/Na selectivity of 483.7, roughly 30 times and 20 times higher than the 20% membrane, respectively. Across every loading tested, Li/Mg selectivity is consistently higher than Li/Na selectivity, by a factor of about 2.5 to 4.

Table 1 Li/Mg and Li/Na selectivity in oilfield brine at different LLTO/PU ratios.

LLTO/PU ratio	Li/Mg selectivity	Li/Na selectivity
20%	59.5	23.5
30%	1765.5	483.7
40%	772.6	251.3
50%	951.0	231.0

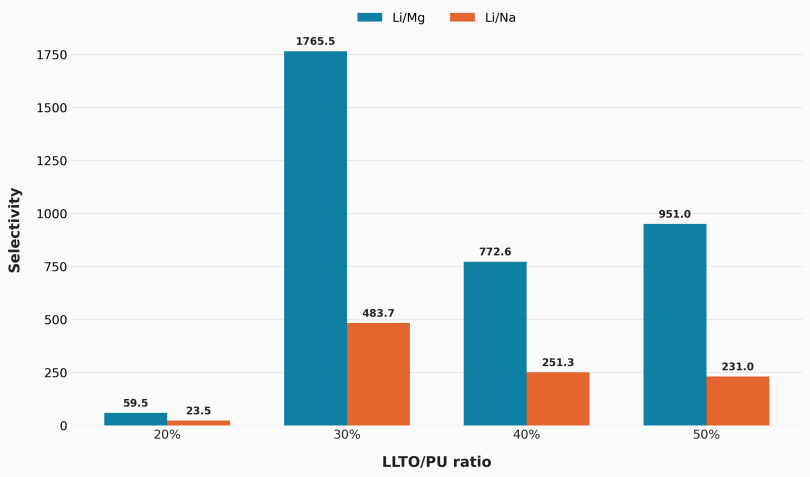


Figure 8 Li/Mg and Li/Na selectivity measured in oilfield brine across LLTO/PU ratios of 20–50%.

4.3 Li/Mg Selectivity in a Synthetic Mg–Li Solution

We ran the same loading series on a synthetic Mg–Li solution to isolate Li/Mg selectivity without the rest of the brine's ion background. Here the trend looks different from the brine result: selectivity is 31.9 at 20% loading, falls to 8.4 at 30%, then climbs to its highest value of 39.4 at 40% before easing slightly to 35.2 at 50%. The 30% membrane, which gave the best selectivity in real brine, gives the worst selectivity in this simpler solution.

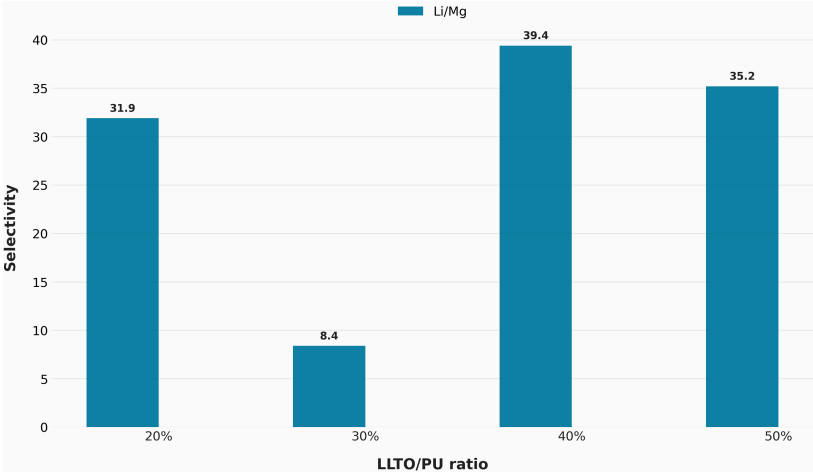


Figure 9 Li/Mg selectivity in a synthetic Mg–Li solution across LLTO/PU ratios of 20–50%.

4.4 Lithium Flux

Figure 10 reports lithium flux across the membrane for three feed types, oilfield brine, a LiCl solution, and the Mg–Li solution, at each loading. In oilfield brine, flux rises steadily with loading, from 4.2 mmol/m^2·h at 20% to a peak of 88.1 mmol/m^2·h at 40%, then drops back to 36.4 mmol/m^2·h at 50%. The LiCl solution behaves differently: flux peaks earlier, at 30% loading (86.7 mmol/m^2·h), and is noticeably lower at 40% and 50% (40.6 and 41.2 mmol/m^2·h). The Mg–Li solution gives the lowest flux of the three feeds at every loading past 20%, and flux there falls steadily as loading increases past 30%, ending at just 9.0 mmol/m^2·h at 50%.

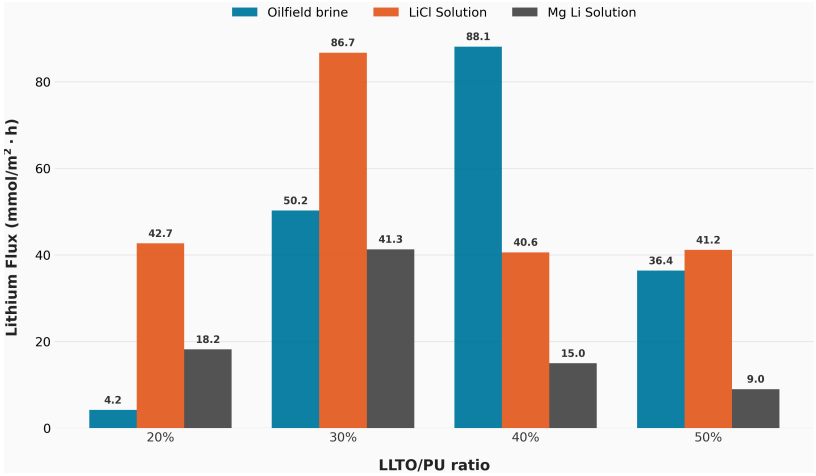


Figure 10 Lithium flux across LLTO-PU membranes for oilfield brine, LiCl solution, and Mg–Li solution feeds, at LLTO/PU ratios of 20–50%.

5 Discussion

The XRD and TGA data together confirm that the membranes were made correctly before we even get to performance. XRD shows the LLTO stays crystalline once it is mixed into PU and cast into a film, so the fabrication process is not damaging the ceramic or letting it react with the polymer matrix. TGA backs this up from a different angle: the residual mass after burning off the PU tracks the intended loading closely enough to trust that the amount of LLTO we set out to add is the amount that actually ended up in the membrane. The one wrinkle is that the residue does not scale linearly with the target loading, the jump from 20% to 30% is much bigger than the jump from 40% to 50%. That flattening at higher loading is consistent with the membrane approaching a practical ceiling on how much ceramic the PU matrix can hold before particles start crowding each other rather than dispersing.

That same ceiling effect is a likely explanation for why selectivity and flux both peak somewhere in the middle of the loading range instead of increasing all the way to 50%. At low loading (20%), there simply isn't enough LLTO to form a well-connected network of lithium-conducting pathways through the membrane, so ions leak through the PU matrix around the ceramic rather than being forced through it. As loading increases, more of these pathways connect up, which is why both selectivity and flux jump sharply between 20% and 30% in the brine measurements. Past that point, though, packing more ceramic into the same PU matrix likely reintroduces defects, aggregation, or the kind of pinholes we deliberately tried to avoid during degassing, and that would explain why 40% and 50% loading give worse brine selectivity than 30%, even though the LLTO content is higher. In other words, membrane performance here looks like it depends on how well the ceramic percolates through the polymer, not just how much of it is present.

The most surprising result is that the loading which performs best in real oilfield brine (30%) performs worst in the simplified Mg–Li solution, where 40% wins instead. Since both membranes come from the same fabrication process, the difference has to come from the feed itself. Oilfield brine carries a much more complex ion background, including Na^+, K^+, and Ca^{2+} alongside Mg^{2+}, along with a higher overall ionic strength than the two-ion synthetic solution. It is possible that in the synthetic solution, with nothing else competing for space at the membrane surface, Mg^{2+} crowds the 30% membrane's less-defined pathways more effectively than it does in brine, where the other competing cations may already be occupying or blocking some of those

same weak points. This would mean the synthetic Mg–Li test is not simply a cleaner stand-in for brine performance, it is measuring something a little different, and selectivity numbers from one feed should not be assumed to carry over to the other without direct testing.

The flux data point to a similar trade-off between how much LLTO is loaded and how the membrane behaves under different feeds. Brine flux keeps climbing up to 40% before falling at 50%, while LiCl flux peaks earlier, at 30%, and then declines. Since LiCl is a much simpler, more concentrated single-salt solution, it likely doesn't need as much ceramic loading to hit its transport ceiling, so extra LLTO past 30% just adds transport resistance without adding benefit. Brine, being more dilute in lithium and more crowded with competing ions, may benefit from the extra pathways up to a higher loading before the same resistance effect takes over. The Mg–Li solution is the odd one out here too: its flux is the lowest of the three feeds at almost every loading, and it falls steadily past 30% rather than peaking. Given that this solution gave the highest selectivity at 40%, a low flux there is not entirely unwelcome, since it points to the membrane being highly selective for Li^+ over Mg^{2+} at the cost of overall throughput, a trade-off that shows up often in ion-selective membranes generally.

Taken together, these results suggest that 30% loading is the practical sweet spot for actual brine feeds, balancing decent flux with the strongest Li/Mg and Li/Na selectivity we measured, while higher loadings only pay off for less complex feeds or where selectivity against Mg^{2+} specifically matters more than throughput. The gap between the brine and synthetic-solution trends is the finding that most needs following up: it suggests that testing membranes only in idealized single- or two-ion solutions can give a misleading picture of how they will perform once real, multi-ion brine is involved.

It's worth putting these numbers next to what has been reported elsewhere for similar ceramic membranes. Li et al. [1] reported a Li/Mg selectivity above 45 million using a dense, standalone LLTO membrane on Red Sea water, several orders of magnitude higher than the 1765.5 measured here for the 30% LLTO-PU membrane in real oilfield brine. Two things likely explain most of that gap. First, that result came from a dense ceramic film with no polymer diluting the ion-conducting pathway, while embedding LLTO in PU necessarily leaves some fraction of the membrane as non-conductive polymer, which caps how selective the composite can get no matter how well it is made. Second, it took multiple 20-hour stages of operation to reach that level of enrichment, while the measurements here come from a single pass, so the comparison is not entirely apples to apples. The PU composite trades away some of that ceiling for a membrane that is far less brittle and easier to handle and scale, which may matter more than raw selectivity once the question shifts from whether this can work in a lab to whether it can survive being built into a real system.

These results also point to a practical path for scale-up rather than just a lab curiosity. Since 30% loading was the best performer specifically in real oilfield brine, and not in the simplified test solutions, it is a reasonable starting point for a pilot built around actual produced water rather than one optimized on synthetic feeds and re-tuned later. That matters for a project motivated by processing brine that is already available from Kingdom oilfield operations, since it means the membrane composition tested here does not need to be re-validated from scratch before moving to real feedstock: it already was validated on real feedstock. The remaining gap is throughput. Even at the best-performing loading, the flux measured here is still well below what a commercial-scale system would need, and closing that gap, alongside the membrane-stability and electrode improvements discussed next, is the main work standing between this result and a system that could plausibly run continuously outside the lab.

6 Limitations and Future Work

One of the main things standing in the way of taking this system to a larger scale is how stable the membrane actually is. LLTO dissolves fairly easily in water, so not long after the process starts running, the membrane begins to degrade, gradually but steadily. That degradation doesn't just weaken the material itself, it also hurts how well the membrane can tell lithium apart from the competing cations, since the selectivity depends on that crystal structure staying intact in the first place. Our plan is to coat the membrane with aluminum oxide, using an intergrowth structure that still lets lithium move through freely while keeping the LLTO from ever sitting in direct contact with the brine. If it works as intended, this should let the membrane hold onto its lithium selectivity and mobility for much longer without paying for it in stability.

There's a similar issue on the electrode side. Right now the setup still risks triggering hydrogen evolution at the cathode, and once that side reaction kicks in, it starts wasting energy that should be going toward moving lithium instead. To deal with that, we plan to swap the electrode solution for potassium ferricyanide, $K_3Fe(CN)_6$. Instead of splitting water, it runs on a reversible $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ redox couple, so the electrode reactions can happen at a noticeably lower voltage. That should cut down on how much energy the process consumes overall, without requiring any changes to the rest of the cell.

There's also the question of how long these numbers hold up. Every result in this report comes from a single run at each loading, over a timescale of hours, not the weeks or months a real deployment would need to run continuously. Lithium flux, in particular, is still well below what a commercial system would require even at the best-performing loading, and it isn't yet clear whether that flux stays steady over longer operation or drifts as the membrane and electrodes age. Before this system could move past the lab, the next round of testing needs to run each promising loading for much longer stretches, on a larger cell, and track how selectivity and flux change over time rather than relying on a single snapshot measurement. Pairing that longer-duration testing with the aluminum oxide coating and the ferricyanide electrode swap described above would give a much clearer picture of whether this membrane chemistry can hold up outside a controlled lab setting.

7 Conclusion

This project set out to test whether an LLTO-loaded polyurethane membrane could selectively pull lithium out of oilfield brine using electrodialysis, and the results say yes, with a clear best operating point. Getting there took building the electrodialysis cell itself, working out a fabrication process that could reliably embed LLTO ceramic into a flexible PU film without trapping defects, and then testing the resulting membranes both on their own and as part of the full separation.

XRD and TGA showed the membranes were fabricated as intended, with crystalline LLTO present at every loading tested and ceramic content tracking what was added, which means the performance differences measured afterward can be attributed to the loading itself rather than to inconsistent fabrication. Among the loadings tested, 30% LLTO/PU gave by far the strongest lithium selectivity in real brine (Li/Mg of 1765.5, Li/Na of 483.7), beating both lower and higher loadings by a wide margin, while lithium flux depended on loading differently depending on which feed solution was used, peaking at 40% for brine and earlier, at 30%, for the simpler LiCl solution.

The clearest lesson from the work is that selectivity measured in a simplified synthetic solution does not reliably predict selectivity in real, multi-ion brine: the 30% membrane that per-

formed best in brine was the worst performer in the synthetic Mg–Li solution. That gap matters beyond just this project. It suggests that membrane development in this space should lean on real, multi-ion feeds for screening rather than idealized single- or two-ion solutions, even though the latter are easier to prepare and control in a lab setting.

Set against the broader picture, this result lands at a useful moment. Saudi Arabia's push to develop domestic lithium sources, through Aramco and Ma'aden's early brine trials and Vision 2030's broader mineral strategy, needs exactly this kind of validated, brine-tested membrane chemistry to build on, rather than results that only hold up under idealized lab conditions. A 30% LLTO/PU membrane that already performs best on real oilfield brine, not just on a synthetic stand-in, is a small but concrete step in that direction.

That said, this is still a lab-scale result. Membrane stability under prolonged exposure to real brine, throughput at scale, and the energy efficiency of the electrode reaction are all open questions this project did not resolve, and they are the reason the membrane-stability and electrode improvements outlined above are worth pursuing on real brine feeds rather than idealized ones, continuing from a foundation that has already been shown to work where it matters most.

References

[1] Zhen Li, Chunyang Li, Xiaowei Liu, Li Cao, Peipei Li, Ruicong Wei, Xiang Li, Dong Guo, Kuo-Wei Huang, and Zhiping Lai. Continuous electrical pumping membrane process for seawater lithium mining. *Energy & Environmental Science*, 14(6):3152–3159, 2021. doi: 10.1039/D1EE00354B.

[2] Zhen Li, I-Chun Chen, Li Cao, Xiaowei Liu, Kuo-Wei Huang, and Zhiping Lai. Lithium extraction from brine through a decoupled and membrane-free electrochemical cell design. *Science*, 385(6716):1438–1444, 2024. doi: 10.1126/science.adg8487.

[3] Qianxi Zhang, Qiuyue Wang, Zhouyou Wang, Ze-Xian Low, Zhaoxiang Zhong, Weihong Xing, and Huanting Wang. Direct lithium harvesting via superionic conductor membranes. *Advanced Functional Materials*, 36:e20068, 2026. doi: 10.1002/adfm.202520068.