Direct Lithium Recovery from Aqueous Electrolytes with Electrochemical Ion Pumping and Lithium Intercalation
Ernesto Julio Calvo*

ABSTRACT: In this mini-review, we provide an account of recent developments on electrochemical methods for the direct extraction of lithium (DEL) from natural brines, geothermal fluids, seawater, and battery recycling electrolytes by ion-pumping entropy cells. A critical discussion of selected examples with the LiMn$_2$O$_4$ lithium intercalation battery cathode material is presented, with emphasis on the operation parameters, some experimental results and multiscale simulations, some limitations and challenges, and conditions for industrial scaleup.

INTRODUCTION
The increasing demand for lithium for energy storage in electric vehicles, renewable intermittent energy, and portable electronics has led to the search for new extraction methods from two lithium sources: high altitude salt flats (brine) and hard rock, with a total world production at present just above 300,000 t/y of lithium carbonate equivalent (LCE). Liexiviation of hard rock such as LiAl(SiO$_3$)$_2$ (spodumene) produces large volumes of waste at a higher cost as compared to the lithium recovery from salt flat brines. The lime-soda evaporation technology employed nowadays to extract lithium from natural brines under solar radiation is very slow with water loss at a very large scale and chemical pollution. Slow evaporation (2400 mm/y at Hombre Muerto, Argentina or 3200 mm/y at Atacama, Chile) in shallow ponds with huge surfaces comparable to the size of 1000 football stadiums results in 6 g/L LiCl liquor over a one-year period. The fraction recrystallization method results in the sequential precipitation of salts to enrich the liquid in LiCl over a period of 12 to 18 months: Halite (NaCl), Sylvinite (NaCl + KCl), Carnalite (K$_2$MgCl$_3$·H$_2$O), and Bischofite (MgCl$_2$·6H$_2$O) precipitate sequentially. Calcium and magnesium are removed by precipitation with lime and Solvay (soda ash), borates by solvent extraction, and finally lithium carbonate precipitates after addition of sodium carbonate at 85 °C to yield finally battery-grade material after thoroughly washing and drying the resulting solid Li$_2$CO$_3$. While precipitation of Li$_3$PO$_4$ is more efficient with much lower solubility (0.39 g/L at 25 °C),\textsuperscript{2} the chemistry of each brine is peculiar, and it determines the extraction strategy (see Table 1). For instance, the high Mg/Li ratio in magnesia sulfate-type brines in China and Bolivia presents limitations due to high consumption of chemicals, loss of lithium, and waste generation.\textsuperscript{1,3}

Direct lithium extraction (DLE) methods from brines as an alternative to the slow solar evaporation and lime soda process include solvent extraction, ion-exchange resin, inorganic absorbents such as spinel lithium manganese oxide (LMO), spinel lithium titanium oxide (LTO), and lithium aluminum layered double hydroxide (LiCl·2Al(OH)$_3$), nanofiltration, and phosphate precipitation followed by electrodialysis.\textsuperscript{1}

Electrochemical methods are sustainable since they use electrons as reactants in electrolysis or electrodialysis processes. They are faster than the evaporation technologies and avoid the use of chemicals, loss of water, and production of waste. The methods based on lithium ion pumping and insertion into battery cathode materials are highly selective and have low cost for lithium recovery from natural brines, seawater, geothermal fluids,\textsuperscript{4–9} and battery recycling liquids.\textsuperscript{2} There has been an increasing interest in these electrochemical methods.

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methods for lithium extraction as described in recent reviews.\textsuperscript{1,10−15}

This mini-review describes ion-pumping methods, electrochemical flow reactors including modeling and digital simulation of the electrode processes and mass transport, and the resulting operation parameters for scaleup into the industrial large scale.

\section*{ELECTROCHEMICAL ION PUMPING}

Lithium extraction by ion pumping takes advantage of the selective intercalation in lithium battery cathode materials such as LiMn\textsubscript{2}O\textsubscript{4} (LMO), LiNi\textsubscript{0.5}Mn\textsubscript{1.5}O\textsubscript{4} (LNMO), or LiFePO\textsubscript{4} (LFP) and the concentration difference between the lithium source electrolyte and the recovery solution. These electrochemical methods are environmentally benign, highly specific, and efficient and they consume a low amount of energy. They combine the high lithium insertion specificity (compared to Na\textsuperscript{+} and Mg\textsuperscript{2+} ions) with the use of electrons as reactant, thereby neither producing waste material nor consuming water.

Lithium ions can be extracted by chemical treatment from LiMn\textsubscript{2}O\textsubscript{4} within the cubic spinel structure by acid to yield $\lambda$-MnO\textsubscript{2}, and lithium can be recovered from aqueous solutions using an electrochemical Pt/$\lambda$-MnO\textsubscript{2} cell as reported by Kanoh\textsuperscript{16} with Li\textsuperscript{+} insertion into the $\lambda$-MnO\textsubscript{2} cathode and oxygen evolution at the Pt anode. However, in brines with high chloride concentration the evolution of chlorine gas is a problem for large-scale operation as well as the pH change during the electrolysis. To solve this problem, the Ag/AgCl/Cl\textsuperscript{−} counter electrode was introduced as the chloride ion reversible electrode. Pasta et al. described an ion pumping method based on mixed entropy cells (concentration electrochemical cells based on salinity difference) with a Li\textsuperscript{+} ion-capturing FePO\textsubscript{4} cathode and a chloride-capturing Ag anode immersed in 5 M NaCl solution simulating brine to convert a sodium-rich solution (Li/Na = 1:100) into a lithium-rich solution (Li/Na = 5:1) at low energy cost. The overall reaction 1 is as follows:

$$\text{FePO}_4 + \text{Ag} + \text{Li}^{+} + \text{Cl}^{-} \rightleftharpoons \text{LiFePO}_4 + \text{AgCl}$$  \hspace{1cm} (1)

Alternatively, the lithium ion capturing LiFePO\textsubscript{4} can be replaced by the Li\textsuperscript{+} battery cathode LiMn\textsubscript{2}O\textsubscript{4} and the Ag anode by the anion selective polypyrrole (PPy) modified electrode for the electrochemical selective recovery of LiCl from natural brines,\textsuperscript{17} with the overall reaction 2 being:

\begin{table}[h]
\centering
\caption{Chemical composition of South American Brines}
\begin{tabular}{lccccccccc}
\hline
 & g/L Li & Na & K & Mg & Cl & sulfate & borate & Mg/Li \\
\hline
Uyuni & 0.350 & 87.50 & 27.20 & 6.50 & 156.90 & 8.50 & 0.20 & 18.6 \\
Hombre Muerto & 1.268 & 103.24 & 14.20 & 3.09 & 182.00 & 11.38 & 1.62 & 2.4 \\
Olarox & 1.280 & 115.60 & 107.8 & 2.62 & 84.98 & 11.33 & 0.78 & 2.0 \\
Atacama & 1.480 & 100.70 & 19.90 & 9.80 & 156.00 & 14.09 & N/A & 6.6 \\
\hline
\end{tabular}
\end{table}
The overall ion capture with the LiMn$_2$O$_4$–PPy lithium ion recovery process involves two electrochemical reactions and two electrolyte exchange operations. In the first electrochemical step, the capture of lithium ions from the brine takes place at the lithium deficient battery cathode material and chloride ions at the polypyrrole anode (see Figure 1). After rinsing the electrodes, the brine is exchanged by a dilute LiCl recovery solution, and the release of lithium and chloride ions from the LiMn$_2$O$_4$ and PPy electrodes, respectively, takes place by reversing the electrode polarity (second electrochemical step). Finally, we flush the feed solution into the reactor to restart the cycle.

The first step (LiCl capture) is a spontaneous process producing energy analogous to a battery discharge, but the second electrochemical step (LiCl release) consumes energy like in battery charging. Likewise, electrolyte exchange steps consume mechanical energy by pumping of liquids.

The specific energy consumed during LiCl extraction and recovery (Wh·mol$^{-1}$) can be calculated from the integration of the voltage vs charge curve from the initial voltage $E_i$ to the final voltage $E_f$ as follows:

$$W = - \int_{E_i}^{E_f} \Delta E_R \, dq$$

For $\Delta E_R > 0$, the process is spontaneous and produces energy, while for $\Delta E < 0$, energy must be supplied to continue the recovery of lithium. The specific energy consumption for the lithium recovery using LSEs in different configurations ranges 1–10 Wh/mol.$^{13}$

Trocoli has recently reviewed the different counter electrodes employed with lithium selective electrodes (LSE) for lithium recovery.$^{18}$ An alternative to the ion capture method is the ion selective exchange method$^{19}$ with the chloride capturing Ag/AgCl anode replaced by a cation exchanger nickel hexacyanoferrate anode which releases $M^+$ (a cation different to Li$^+$ such as K$^+$ or Na$^+$ with lithium ion exclusion$^{18}$)

$$\text{FePO}_4 + \text{MKNi}[\text{Fe}^{III}(CN)]_6 + \text{Li}^+$$

$$= \text{LiFePO}_4 + \text{KNi}[\text{Fe}^{III}(CN)]_6 + \text{M}^+$$

Trocoli has described that the ion (salt) capturing and selective exchange methods have different thermodynamic and kinetic contributions to the two-step overall processes.$^{20}$

The ion exchange configuration can be accomplished by a pair of symmetrical Li$^+$ intercalation electrodes such as LiFePO$_4$ or LiMn$_2$O$_4$ with different degrees of lithium intercalation (see Figure 1), separated by an anion exchange membrane in contact with natural brine and recovery electrolyte, respectively.$^{5,7,21}$ With the symmetric rocking-chair battery-like mechanism was introduced by Zongwei Zhao$^{22}$ with LiFePO$_4$/LiFePO$_4$ further applied to LiMn$_2$O$_4$/Li$_{1-x}$Mn$_x$O$_{24.5}$ and tested in flow-through$^{23}$ and flow-by reactors.

This configuration includes an anion selective membrane that separates both source and recovery solutions. When the source of lithium is natural brine with very high salt concentration, i.e., $>5$ M, Donnan breakdown occurs and the membrane is no longer highly selective. This has led to lower selectivity of Li$^+$ with respect to Mg$^{2+}$ in spite of the high selectivity of the capturing lithium intercalation electrode material.

Figure 2 shows experimental results for the application of lithium ion exchange recovery from Uyuni brine using the rocking chair system Li$_{1-x}$Mn$_2$O$_4$ ($x = 0.9$) cathode and LiMn$_2$O$_4$ ($x = 0$) anode. The electrode potential at the lithium-deficient Li$_{1-x}$Mn$_2$O$_4$ cathode decreases, while the potential of the LiMn$_2$O$_4$ anode increases according to the reactions$^{10}$

$$\text{Li}_{1-x}\text{Mn}_x\text{Mn}^{III}_1\text{Mn}^{IV}_1\text{O}_4 + y\text{Li}^+ + y\text{e}$$

$$\rightarrow \text{Li}_{1-x}\text{Mn}_x\text{Mn}^{III}_1\text{Mn}^{IV}_1\text{O}_4$$

$$\Delta E_{cell} > 0.$$
Besides its high cost, the silver anode readily dissolves in natural brines, seawater, and geothermal fluids with high chloride ion concentration. Marchini et al. replaced the Ag anode with the anion selective polypyrrole modified electrode for the electrochemical selective recovery of LiCl from natural brines from high altitude salt flats in northwest Argentina.\textsuperscript{17} The undivided electrochemical cell was composed of a Li-deficient Li$_{1−x}$Mn$_2$O$_4$ ($\lambda$-LMO) cathode and a polypyrrole (PPy) anode, which upon oxidation to the radical cation PPy takes up chloride ions from the electrolyte. A polypyrrole (PPy) anion selective counter electrode operates at lower overpotential than carbon, which is used in a similar hybrid LiMn$_2$O$_4$/carbon supercapacitor for energy storage.

The highly selective LiMn$_2$O$_4$ battery cathode material has been employed in combination with several counter electrodes: platinum, carbon, zinc, silver, polypyrrole, hydrogen electrode (PtH$_2$), and polyaniline. The study of X-ray reflections at different states of charge of LiMn$_2$O$_4$ in NaCl solutions has shown that Na$^+$ does not intercalate into the spinel structure even in brine with 5 M large Na$^+$ excess. However, electrochemical impedance and XPS studies have shown that Na$^+$ adsorbs at the crystal surface and decreases the rate of lithium intercalation probably blocking surface Li$^+$ tetrahedral adsorption sites.\textsuperscript{6}

It should be noted that the high selectivity for Li$^+$ vs other monovalent ions is the result of dehydration of Li (OH)$_2$$_4^-$, (solvated ionic radius 7.64 Å) in the solution into Li(O$_2$)$_{tetra}^-$ (ionic radius 1.20 Å) in the crystal tetrahedral site of the intercalation electrode. The loss of the hydration shell represents at the same time an important activation barrier for the interfacial intercalation process. The high hydration Gibbs enthalpy of Li$^+$ in aqueous solutions, i.e., $\Delta G^0_{hyd} = −475$ kJ/mol due to the Li$^+$ small ionic radius, results in a high activation energy for the interfacial intercalation reaction as depicted in Figure 3. Note that the slow Li$^+$ dehydration process also results in the slow rate of other direct lithium recovery methods such as electro-nanofiltration and solvent extraction.

![Figure 3](https://doi.org/10.1021/acs.omega.1c05516)

**Figure 3.** Scheme of the activation free energy profile for the insertion of hydrated Li(OH)$_2$$_4^-$ from aqueous electrolyte into tetrahedral sites in the cubic LiMn$_2$O$_4$ spinel crystal structure.

The electrode reactions for lithium capture and lithium exchange have been shown to be understood at the laboratory bench scale. However, in order to increase the recovery capacity to reach large-scale lithium extraction flow, electrochemical reactors are needed.

### Electrochemical Flow Reactors

The electrolyte flow plays an important mixing role, reaching homogeneous concentrations in 3D porous electrodes when the flow rate is such that the convective mass transport is larger than diffusion and migration contributions. Palagonia et al. have shown important flow effects at low lithium concentration and low flow rate where concentration polarization of lithium in the electrolyte is important.\textsuperscript{28−30} The effect of current density and active material mass loading on the performance of flow-through electrodes for lithium recovery has also been described by these authors.

Electrochemical reactors for the extraction of lithium have been described in recent years, both in flow-through\textsuperscript{23,28−31} and flow-by\textsuperscript{25,32} configurations (see Figure 4). Experiments with a flow-through electrochemical reactor with a symmetric two Li$_{1−x}$Mn$_2$O$_4$ (0 ≤ x ≤ 1)/LiMn$_2$O$_4$ electrodes and anion exchange membrane have been described for the capture and release of lithium from brine into recovery electrolyte.\textsuperscript{23} Digital simulation\textsuperscript{33} has confirmed the experimental results of Palagonia et al.;\textsuperscript{29} a larger amount of lithium could be captured per unit mass at higher flow rate increasing the mass loading of the lithium-capturing electrode. The same result was obtained when the applied current density was decreased because of the limitations in the Li$^+$ ion insertion kinetics and diffusion in the crystal as observed in lithium ion batteries.

A flow-through reactor with mesoporous LiMn$_2$O$_4$ coated on three-dimensional graphite felt (GF) for the recovery of Li$^+$ from brines with a high Mg$^{2+}$/Li$^+$ ratio was reported with an extraction rate of 75.06 mg/h per gram of LiMn$_2$O$_4$, a Li−Mg separation coefficient of 45.58, and an energy consumption of 23.38 Wh/mol under constant potential mode. It has been shown that constant potential operation results in higher energy consumption than constant current conditions in capacity deionization.

The active intercalation material mass loading is limited in flow-by reactors with thin porous electrodes and electrolyte channels as has been shown from the maximum applied current, the current efficiency, and the specific lithium recovery in flow-by electrochemical experiments compared to flow-through configuration.\textsuperscript{24} Therefore, the flow-by configuration with a small mass loading of intercalation material requires an important increase of electroactive area which can be achieved with spiral swiss roll configuration such as in commercial capacitive deionization or reversal electrodialysis reactors. A porous three-dimensional electrode in flow-through configuration lends itself to industrial scaleup at moderate flow rates with filter press reactors. However, the former presents less ohmic drop than the latter.

Digital simulation is a powerful tool for the study of multiscale processes at porous three-dimensional packed bed electrodes with flow of electrolyte. Romero et al. have described flow-through ion capture reactors using a one-dimension model similar to the approach to lithium ion batteries (Li$^+$ selective LiMn$_2$O$_4$ and PPy selective to Cl$^-$) with a porous separator\textsuperscript{31} and a two-dimensional model with forced convective flow conditions.\textsuperscript{35} Also, the ion exchange configuration has been simulated in three-dimensional porous packed-bed symmetrical LiMn$_2$O$_4$/Li$_{1−x}$Mn$_2$O$_4$ electrodes in brine and recovery electrolyte separated by anion exchange membrane.\textsuperscript{23} A mathematical model that takes into account three-dimensional porous packed-bed electrodes in contact with natural brine and dilute recovery electrolyte considers
lithium diffusion in LiMn$_2$O$_4$ particles, interfacial reaction kinetics, Nernst–Planck diffusion, and migration of different ions in the electrolyte and electrolyte flow to describe the potential and concentration fields. The simulations were performed by a finite element method under the COMSOL environment, and the model predictions have been validated with experimental $\Delta E_{\text{Reactor}}$ vs time (charge) electrodes at constant current. The model used no free adjustable parameters, while it captures the overall reactor voltage–time evolution and describes the concentration distribution and time evolution of Li$^+$, Cl$^-$, and all the non-intercalating ions in the electrolytes, the Li$^+$ concentration at the LiMn$_2$O$_4$ crystal surface at different positions in the reactor, as well as the electrical potential gradients and their time evolution. The simulations showed that the degree of lithium insertion in the lithium-deficient Li$_{1-x}$Mn$_2$O$_4$ electrode determines the Li$^+$ recovery efficiency and the effect of flow rate on the electrolyte concentration distribution and on the specific lithium extraction capacity with a maximum of 148 mAh/g or 38 mg/g at a flow of 60 mL/min. A critical flow rate value is needed to offset the diffusion concentration profiles and to achieve an homogeneous concentration distribution in the reactor.

Joo and co-workers reported experimental results and follow the digital simulation of Romero et al.$^{23,31,33}$ for a flow-by electrochemical reactor with thin porous $\lambda$-MnO$_2$/LiMn$_2$O$_4$ electrodes in a symmetric rocking-chair configuration with anion selective membrane.$^7$ Since the maximum lithium recovery capacity is given by the stoichiometry of LiMn$_2$O$_4$, i.e., 38 mg per gram of LiMn$_2$O$_4$, a thin layer of intercalation material limits the mass loading and thus the amount of lithium that can be extracted from the circulating brine. The observed recovery capacities, i.e., 11 to 35.5 mg/g,$^{13,15}$ are lower than 38 mg/g due to kinetic limitations of the interfacial reaction with a loss of four water molecules in the Li$^+$ hydration shell, which are adsorbed at tetrahedral surface sites in the cubic O$^{2-}$ sublattice with simultaneous Mn$^{IV}$ ion reduction to Mn$^{III}$.

### Operation Parameters

The group of Yoon$^{34}$ discussed key limiting factors for lithium recovery with regard to the rate of Li$^+$ supplied from the electrolyte and described three distinctive stages in the LiMn$_2$O$_4$ crystal from experimental evidence using X-ray techniques: depletion, transition, and saturation regions. The recovery capacities are strongly influenced by the current density, the lithium concentration in the source electrolyte, and the intercalation material crystal size.$^{34}$ The authors found enhancement of the overall lithium recovery by increasing the density of electrode/electrolyte interface.

Since the intercalation capacity of LiMn$_2$O$_4$ is only 3.8% (similar to other absorbers such as gibbsite or LiFePO$_4$), a large mass loading of intercalation electrode material is needed in practical applications. Each gram of LiMn$_2$O$_4$ corresponds to a maximum electrical charge of 148 mAh to yield a maximum 38 mg of lithium; therefore the time needed to recover a given mass of lithium from brine is determined by the total charge circulated at a constant applied current. However, under operation conditions less mass of lithium can be recovered per gram of LiMn$_2$O$_4$ the higher the applied current and the lower the lithium ion concentration.$^{34}$

Another limitation is the maximum current that can be applied to the reactor. This current is limited by the rate of the overall extraction process measured by the local current density at the LiMn$_2$O$_4$ crystal surface. The local current density is given by the interfacial rate of insertion coupled to the Li$^+$ diffusion in the crystal and can be expressed by the Butler–Volmer equation:
With state of lithium intercalation, \(\theta = \frac{c_i}{c_{i,max}}\), the ratio of lithium surface concentration in the particle to the maximum concentration in the crystal, \(k_0 = \frac{c_{i,max} - c_i}{c_{i,max} - c_{i,ref}}\), the reference lithium concentration \(c_{i,ref} = 1 \text{ mol.m}^{-3}\) and \(\alpha = 0.5\). Typical values of \(i_{LOC} = 1 \mu A\text{.cm}^{-2}\) are equivalent to a lithium flux of \(3.6 \text{ mol.m}^{-2}\text{.h}^{-1}\), which is similar in other direct lithium extraction technologies, such as membrane electro-nano-filtration (2 mol.m\(^{-2}\).h\(^{-1}\)) or MOF membrane lithium selective filtration (6 mol.m\(^{-2}\).h\(^{-1}\)).

The total applied current in the reactor is the product of the local current density at the LiMn\(_2\)O\(_4\) particle surface \(i_{LOC}\) (A.cm\(^{-2}\)), and the total electroactive surface area of the intercalation material. Therefore, to sustain an applied current of 100 mA we require a minimum electroactive area \(\geq 5 \times 10^8\) cm\(^2\), which corresponds to a volume specific electro-active area, \(S_i \geq 1.42 \times 10^7\) cm\(^{-1}\) in the 3D porous electrode volume of 35 cm\(^3\) with 50% porosity.\(^{23,31,33}\)

Larger applied currents can be achieved by decreasing the LiMn\(_2\)O\(_4\) crystal size and increasing the volume fraction (mass loading) of the lithium manganese oxide in the porous electrode so that the electroactive area is increased. Yoon and co-workers have shown experimentally the effect of particle size on the operation current densities for different Li\(^+\) ion concentrations.\(^{34}\) They correlated lithium recovery capacity (mg/g LiMn\(_2\)O\(_4\)) with current density plots at different Li\(^+\) ion concentrations, with typical values ranging 2–25 mg/g.

Several lithium intercalation nanomaterials have been developed which resulted in shorter diffusion length in the crystal and larger area to volume ratio, examples of which are hydrothermal nanowires or the mesoporous LiMn\(_2\)O\(_4\).

The increase in the applied current to recover a larger mass of lithium, on the other hand, poses a penalty in the total reactor ohmic drop due to the electrolyte resistance and the contact resistance between solid particles that defines the overall reactor voltage and energy consumption. This is worse for the dilute recovery electrolyte.

Unlike lithium ion batteries with few-micrometers-thick insertion electrodes and milliohm resistances, the lithium recovery porous electrodes are thicker and require fine-tuning of their electrical resistance.

### SUMMARY AND OUTLOOK

There has recently been a large amount of experimental work on the direct extraction of lithium using electrochemical ion pumping. The electrochemical lithium recovery methods (ELR) from aqueous electrolytes have proven successful at the laboratory scale with high selectivity for lithium ion, low energy cost, environmental benefits of the electrochemical extraction, and faster extraction as compared to present evaporation methods. The flow of the electrolyte has been shown to be very important to offset lithium diffusion concentration gradients, thereby increasing the specific recovery efficiency. For large-scale operation, the flow-through configuration is preferred over the flow-by method with low mass loading of electroactive material.

Numerical simulations are very useful to understand complex multiscale phenomena such as lithium intercalation in nanosized particles simultaneous to electrical charge circulated in the electrolyte embedded in porous three-dimensional electrodes with coupled interfacial kinetics. After validation with experimental data, the simulation concentration and potential space profiles and their time evolution are very useful to understand the complex phenomena and to design more efficient reactors.

Some limitations such as the mass loading of electroactive intercalation material, local current density, and ohmic drop need to be considered in the scaling up of efficient sustainable electrochemical lithium recovery systems.

There are a number of operational parameters such as the total applied current, reactor resistance, lithium concentration in the source electrolyte, current density, intercalation material particle size that play an important role over the recovery rate, specific recovery capacity, energy consumption, and Li/Mg selectivity. The modeling and understanding of these interconnected phenomena would find a solution for the sustainable recovery of lithium from primary sources and battery recycling.

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Notes

The author declares no competing financial interest.

Biography

Ernesto Julio Calvo is Professor of Physical Chemistry at the Universidad de Buenos Aires (UBA) and Permanent Research Staff member at the Consejo Nacional de Investigaciones Científicas y Técnicas. His research focuses on wiring redox enzymes to electrodes; layer-by-layer redox polyelectrolytes; and oxygen reduction on oxides, enzyme functionalized surfaces, and in Li–air cathodes. Calvo received first prize in the 2017 Bright Minds Challenge for inventing a lithium extraction method powered by solar energy that is quicker and cleaner than existing technology. Calvo is an ECS Emeritus Member and Fellow of the ECS; Fellow of the Royal Society of Chemistry and International Union of Pure and Applied Chemistry; and member of the Latin America Academy of Science. Among the accolades garnered by his research are the 2020 Argentine National Academy of Exact, Physical and Natural Sciences Prize; 2017 Personality of the Year in Science and Technology; 2017 Schumacher Prize in Physical Chemistry of the Argentine Chemical Society; 2005 National Award in Science from the Argentine Ministry of Education and Science; 2003 Konex Award in Science and Technology; and 2000 John Simon Guggenheim Award. Calvo completed an MS in Chemistry at Universidad de Buenos Aires (1975) and PhD in Chemistry at the Universidad Nacional de La Plata (1979) under Prof. David J. Schiffrin. As a Postdoctoral Research Fellow in Chemistry and Materials Science at Imperial College London from 1979 to 1982, he worked with Profs. Wyndham John Albery and Brian C. H. Steele, and then with Prof. Ernest B. Yeager as a Senior Research Associate at Case Western Reserve University. He was Director of INQUIMAE at UBA from 2008 to 2018. He served as the
Vice President of the International Society of Electrochemistry from 2009 to 2011. Calvo has an h-index of 52 and has published some 180 research papers in peer-reviewed international journals. He has supervised 20 chemistry PhD students.

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