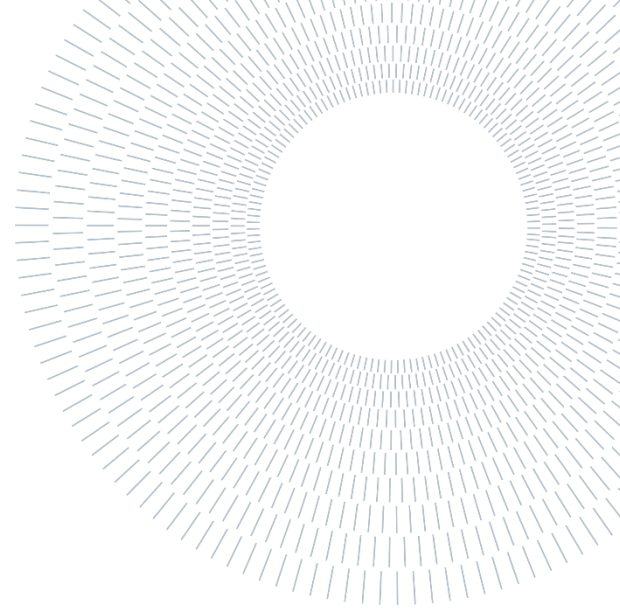




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EXECUTIVE SUMMARY OF THE THESIS

# Insight into the cycling behaviour of metal anodes for rechargeable batteries, enabled by systematic electrochemical testing, enhanced with mathematical modelling

TESI MAGISTRALE IN ENERGY ENGINEERING – INGEGNERIA ENERGETICA

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## 1. Introduction

The target of this thesis is the investigation of shape-change and passivation issues of metallic anodes in battery context, under real operating conditions. This study is based on the systematic combination of experimental data of high statistical quality with PDE-based mathematical modelling. This approach is not common in the literature since anodic and cathodic responses are generally studied in isolation, and, on the other hand, when cycling data is considered, quantitative use of electrochemical time series is very rare and only time-to-failure is taken into account. In addition, this thesis has, as an ancillary target, the study of the behaviour of new electrolyte materials for Zn and Li batteries. In particular, we were inspired by new studies that have set the aim of describing the profiles of chronopotentiometric transients through models that describe the electrochemical response in terms of electrokinetic, mass-transport and material evolution parameters. The experimental

platform adopted is the 2032 symmetrical coin cell with Zn and Li electrode (Zn|Zn, Li|Li).

## 2. Next-generation electrolytes for Zn and Li batteries

As far as electrolyte choice is concerned, our contribution targets the latest developments of battery research, aiming at better durability and safety. Regarding Zn, the key prospective is that of moving from alkaline environments to low-acid aqueous electrolytes. Specifically, we addressed the scantily investigated topic of organic additives for the suppression of dendrite growth, quaternary ammonium salt (QAS), in particular. In addition, we investigated Deep Eutectic Solvents (DESs) [1] as a prospective replacement of aqueous solutions, in view of improved Zn shape control. DESs are eutectic mixtures formed by a QAS and a hydrogen-bond donor compounds such as amides, carboxylic acids or polyols. Eutectic formation results from hydrogen bonding, leading to the lowering of the melting temperature below than that of the single components. A rich scenario of DESs has been investigated, consisting of a range of hydrogen

bond acceptors (such as choline chloride) and donors (such as urea and ethylene glycol). Unlike ILs, DESs have a number of advantages, including easy preparation, low cost, high biodegradability and stability in the presence of water. In keeping with this property, DESs containing a controlled quantity of water are starting to be considered as battery electrolytes [2]. Specifically, if the quantity of water inside the DES is below 40 mol%, it becomes part of the DES lattice itself and increases conductivity. Our study thus competes weakly acidic aqueous solutions with QAS additives and two types of DES, characterized by different hydrogen donors (urea and ethylene glycol) and with different quantities of water. We thus investigated Zn with the following electrolytes, denominated with the symbols specified below: AQ for the aqueous series, ChU0.1 and ChU0.3 for U-based DES with two different contents of Zn salt and water, AChU with the same Zn salt content of ChU0.3 but without water and ChEG for EG-based DES with the same Zn salt content of ChU0.3. Water in DES is controlled by adding the hydrated salt  $\text{Zn}(\text{SO}_4)\cdot 7\text{H}_2\text{O}$ .

With regard to cells with Li electrodes, we considered the traditional LP30 electrolyte as a benchmark, against which we tested a polymeric one and a polymer/IL mixture. Polymer-based electrolytes exhibit many desirable electrolyte properties, such as: compatibility with the electrodes, no leakage, better thermal and mechanical stabilities. ILs are considered as promising LIB electrolytes, allowing anode stability and effective  $\text{Li}^+$  transport. Specifically, we studied the PEGDME polymeric electrolyte and the same with added Pyr14TFSI IL [3]. We denominated the cells with Li electrodes as: LP30, PGDM for polymer:LiTFSI system and PGDM-IL for polymer:LiTFSI:IL.

### 3. Electrochemical testing and modelling

For each type of electrolyte and each current density (CD), three replicated 2032 coin-cells were tested. Electrochemical testing was centered on galvanostatic charge-discharge cycling (GCDC) and EIS was used as a method to assess the state of the cells before and after GCDC. Reproducibility of the measurements with the replicated cells was accurately checked and sample statistic were derived, for a rigorous quantitative treatment.

GCDC data were modelled along the lines proposed in [4]. This mode consists of a PDE system, coupling the material balance for the electroactive metal species and the potential of the electrolyte phase (by modelling the coin cell in 1D geometry with an adequate approximation). With this approach, the time-dependence of the solutions of parameters can be separated into a fast and a slow regime. The fast regime involves the timescale of a single galvanostatic interval (a half period of the galvanostatic square wave) and controls the shape of each individual chronopotentiometric transient. We followed experimental data by assigning numerical values to two key model parameters: diffusivity  $D$ , number density of nuclei and passivation rate  $k_{\text{pass}}$ . The slow regime, instead, involves the timescale of the whole measurement, that is generally controlled by passivation-induced termination, and defines the evolution of the potential over several galvanostatic periods, defined by the outgrowth rate  $F_c$  and the passivation rate  $k_{\text{pass}}$ . EIS data were modelled accurately with the equivalent-circuit approach, taking care of accounting for the totality of spectral features, including instrumental ones.

To test practically relevant operating regimes, we cycled the AQ Zn cells at  $1 \text{ mA cm}^{-2}$ , the DES Zn cells at 0.1, 0.2, 0.5 and  $1 \text{ mA cm}^{-2}$ ; anodic and cathodic conditions in each cycle were held for 30 min. For the Li cells, we cycled LP30 at 0.1 and  $10 \text{ mA cm}^{-2}$  ( $C = 1 \text{ mAh cm}^{-2}$ ) and the PEGDME cells without and with IL at 0.05 and  $1 \text{ mA cm}^{-2}$  ( $C = 0.1 \text{ mAh cm}^{-2}$ ), fixing the temperature to  $60 \text{ }^\circ\text{C}$ .

## 4. Results and discussion

EIS spectra were measured for the cells in pristine conditions. Calendar-ageing effects were taken into account and quantified. For the Li case, it has been noted that after only 24 h from the first EIS, this doubles and subsequently it remains constant (1 week of observation time), but the data is currently unavailable due to technical problems; they will be available in the future version of this report. The variance of the Li cells is slightly larger than that of the Zn-containing ones – coherently with the higher reactivity of this metal.

In Figures 1 and 2 the EIS data and their fits for pristine Zn and Li cells are reported. The fitting

parameters for the EIS curves of Figure 3 are reported in Tables 1 and 2. The differences among electrolytes can be straightforwardly rationalized in terms of viscosity and conductivity. For Zn cells, it was noted that AQ is the one with the lowest  $R_o$  and  $R_{CT}$ : electrolyte is mainly characterized by Zn salt dissolved in water which makes the system with a very low viscosity and very high conductivity. The DES ranking is the following: ChEG < ChU0.3 < ChU0.1 < AChU, valid for both  $R_o$  and  $R_{CT}$ . In the ChU0.1 and AChU systems, the low conductivity, together with the high viscosity, leads to mass-transport control. The most evident effect is this the impact of water content in the DES: in fact, among the four systems studied, the best-performing are ChEG and CHU0.3, which, apart from the difference in H-bond donor, exhibit a very similar behavior. ChEG appears to be slightly more performing since it is made with ethylene glycol a liquid component which, compared to urea, makes DES less viscous, with higher conductivity.

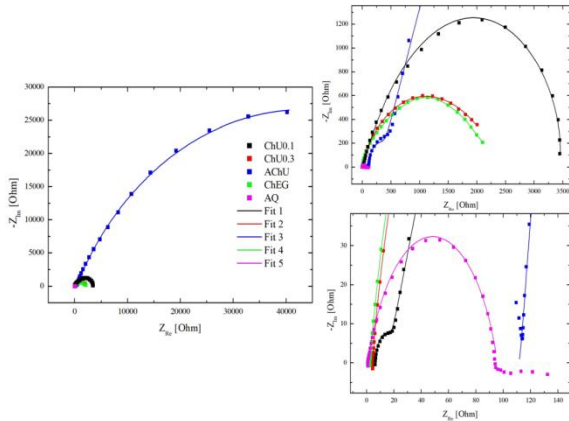


Figure 1: Pristine EIS for Zn electrolytes

For Li the EIS curves of Figure 2 rank in the following order: LP30 < PGDM-IL < PGDM. The best-performing electrolyte, in this is LP30. The polymeric electrolyte has the highest  $R_o$ , coherently with its conductivity, resulting from highly viscous chain ethers. It is worth noting that, despite their promising characteristics, such as electrochemical stability, high temperature stability and non-flammability, nevertheless show some degree of reactivity with respect to Li, that leads to resistance increase. Addition of IL is considered to improve the performance of polymeric electrolytes, thanks to anode stability, high conductivity and effective  $Li^+$  transport,

especially if the anion of IL is the same as the Li salt.

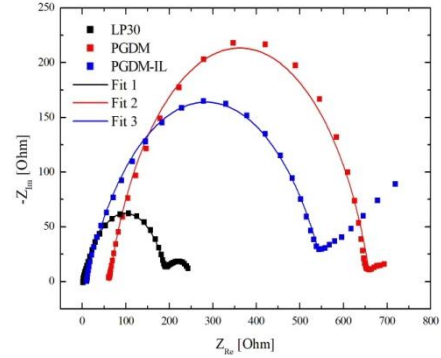


Figure 2: Pristine EIS for Li electrolytes

Zn	AQ	CHU0.3	AChU
$R_o$ [ $\Omega$ ]	0.799±0.246	4.86±0.32	120.74±24.82
$R_{CT}$ [ $\Omega$ ]	82.26±33.58	(1.92±0.48)e <sup>3</sup>	157.53±76.69
$\tau_{DL}$ [s]	(6.75±1.60)e <sup>-3</sup>	0.039±0.023	(2.01±2.08)e <sup>-5</sup>
$\alpha_{DL}$ [-]	0.735±0.030	0.892±0.065	0.883±0.071
$\tau_o$ [s]	-	0.386±0.176	-
$\alpha_o$ [-]	-	0.412±0.062	-
$R_{MT}$ [ $\Omega$ ]	-	-	(96.18±31.46)e <sup>3</sup>
$\tau_{MT}$ [s]	-	-	1.744±0.518
$\alpha_{MT}$ [-]	-	-	0.658±0.039

Table 1: Fitting parameters of Zn electrolytes

Li	LP30	PGDM	PGDM-IL
$R_o$ [ $\Omega$ ]	2.23±0.65	60.56±5.34	9.74±0.90
$R_{CT}$ [ $\Omega$ ]	187.38±37.31	759.4±238.1	676.34±209.51
$\tau_{DL}$ [s]	(1.68±0.47)e <sup>-3</sup>	(3.57±0.86)e <sup>-3</sup>	(5.19±1.13)e <sup>-3</sup>
$\alpha_{DL}$ [-]	0.762±0.021	0.769±0.026	0.729±0.026
$R_{SEI}$ [ $\Omega$ ]	39.66±11.20	-	-
$\tau_{SEI}$ [s]	0.307±0.095	-	-
$\alpha_{SEI}$ [-]	0.688±0.059	-	-

Table 2: Fitting parameters of Li electrolytes

GCDCs are traditionally analyzed in terms of time to failure and failure mode. In our case, two failure modes are observed: short circuit and passivation. The short circuit mainly characterizes the U-based and AQ systems, which are therefore subject to the formation of dendrites, while passivation is found for ChEG.

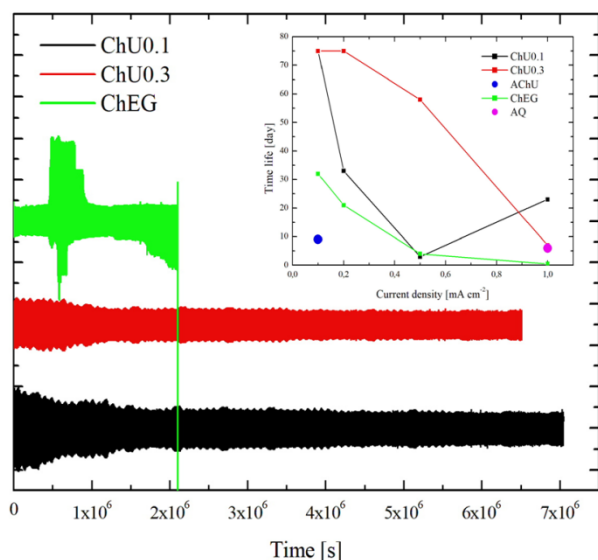


Figure 3: Typical GCD cycles and time life of Zn cells

Owing to time-constraints, less extended cycling was possible for the Li cells, that, nevertheless, allowed to obtain a sufficiently well-defined scenario. More prolonged cycling is currently in progress and will be reported in subsequent work. Regarding LP30, at  $0.1 \text{ mA cm}^{-2}$ , after 40 cycles a very stable behaviour is observed, without signs of either passivation or outgrowth. At  $10 \text{ mA cm}^{-2}$ , on the other hand, the measurements start with a fairly regular and constant period of ca. 20 transients, after which the onset of passivation can be noticed. After reaching a peak of  $\pm 1 \text{ V}$ , the amplitude of the transients begins to decrease (as a result of metal outgrowth) until it reaches ca.  $\pm 0.75 \text{ V}$ . Eventually, all cell voltage undergoes a gradual, passivation related, increase.

The voltage transients obtained with GCDC can be rationalized with the model presented in [4]. Results for the Zn cells are shown in Tab. 3. We found that the transient shapes are controlled by diffusivity that grows from DES-based electrolyte to AQ. It should be noted that U-based DESs maintain the same shape throughout the transient, denoting stability and stripping/plating reversibility. ChEG instead, presents regions in which transient amplitude is different; in addition, it does not manifest the same shape among transients, suggesting again instability.

SEM/ $r_{\max}$	transient/D

Table 3: Zn fast regime parameters

Li-systems, instead, are characterized mainly by periods with irregular transients, caused by formation and destruction of dendrites above the metal surface.

After termination of the GCDC experiments, EIS spectra were measured. Non correlation could be established among the electrochemical operating conditions, the time to failure and the failure mode, and EIS behaviour is in all cases controlled by passivation. However, clear differences were found among different types of electrolytes, showing their impact on passivation mode. Once again water has a key role. For ChU0.1 there is less dispersion, mainly due to the lower presence of water. The same is shown for AChU, that has also the smallest deviation from the pristine EIS: the reasons are that AChU is a completely anhydrous system.

*Post-mortem* analysis of the structure and morphology of Zn electrodes cycled at  $1 \text{ mA cm}^{-2}$  in three different electrolytes (AQ, ChU0.3, ChEG) was carried out by SEM. It can be noticed that the Zn deposited from the U-based liquid exhibits a globular morphology, with an almost homogeneous crystallite distribution. A very different Zn morphology occurs when aqueous or ChEG systems are used. Indeed, Zn metal grain are covered by thin amorphous plate that can be attributed to the formation of ZnO. In the latter two cases, the overall morphology of the samples



is due to the electrodeposited Zn grain (produced during charge process) that are then covered by layers of ZnO (produced during discharge). DESs have a high solubility for metal salts; unusually, this also includes metal oxides and hydroxides, which gives these systems an advantage over aqueous and organic based electrolytes. However, in the absence of literature data, by dissolution tests, we showed that ZnO solubility in ChU0.3 is much larger than in ChEG. This outcome clearly correlates with the overvoltages measured during GCDC and with the SEM morphology. In fact, the higher solubility of ZnO in ChU, leads U-series to have more regular transients and fail due to short circuit, while EG-series transients remain more irregular especially at high CDs, then failing due to passivation.

The conclusion that passivation is the prevailing phenomenon, is confirmed also for Li, by the EIS measured for cycled LP30. Polymer-based electrolytes are still cycling.

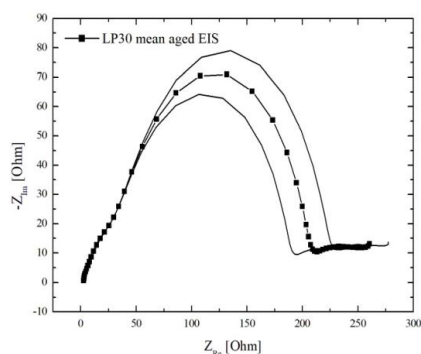


Figure 4 LP30 aged EIS

## 5. Conclusion

A systematic characterization of the pristine coin-cells was made by EIS was made, leading to the conclusion that the AQ series for Zn and LP30 for Li are the best performing.

As shown by EIS analyses of cells that have reached the end of live, regardless of the failure mode or the specific chemistry, all aged cells show passivation as the final outcome of calendar ageing, the quantitative aspects of which depend on the type of electrode and electrolyte GCDC shows that ChU0.3 allows the best stability, while ChEG gives rise to passivation at high CDs. For Li, relatively good behaviour of LP30 was found, in comparison with polymer-

and IL-based systems. Morphochemical modelling of GCDC time-series allowed a transparent rationalization of the observed electrochemical performance and SEM microscopy in terms of simple, but highly diagnostic physico-chemical parameters, as exemplified in Table 3 for a prototypical case, or GCDCs dominated by diffusive effects (parameter D) and micromorphology controlled by the number density of nuclei (parameter  $r_{max}$ ).

## References

- [1] A. P. Abbott, G. Capper, D. L. Davies, H. L. Munro, R. K. Rasheed, V. Tambyrajah, "Preparation of novel, moisture-stable, Lewis-acidic ionic liquids containing quaternary ammonium salts with functional side chains", *Chem. Commun.*, **2001**, 2010-2011.
- [2] T. Zhekenov, N. Toksanbayev, Z. Kazakbayeva, D. Shah, F. S. Mjalli, "Formation of type III Deep Eutectic Solvents and effect of water on their intermolecular interactions", *Fluid Phase Equilibria*, **2017**, 441 43-48.
- [3] D. Devaux, R. Bouchet, D. Glé, R. Denoyel, "Mechanism of ion transport in PEO/LiTFSI complexes: effect of temperature, molecular weight and end groups", *Solid State Ionics*, **2012**, 227, 119-127.
- [4] F. Rossi, L. Mancini, I. Sgura, M. Boniardi, A. Casaroli, A. P. Kao, B. Bozzini, "Insight into the cycling behaviour of metal anodes, enabled by X-ray tomography and mathematical modelling", *ChemElectroChem*, **2022**, 9, 1-8.

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