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Lithium-ion battery recycling pre-processing with electrochemical discharge: Enhancing gas product analysis and pH monitoring

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ABSTRACT

Efficient discharge of Lithium-ion Batteries (LIBs) ensures safe recycling. Electrochemical discharge commonly uses NaCl solutions, causing severe corrosion of battery casing and a release of hazardous gases. This work proposes a novel setup to explore a gaseous product formation during electrochemical discharge processes with low gas quantities, in non-corrosive carbonates solutions (Na_2CO_3 and K_2CO_3). Two discharge setups were tested over 120 h: a conventional setup with a single battery completely immersed in the electrolyte; and a novel half-cells setup with two batteries in series, connected through a platinum wire, and partially immersed in the electrolyte. The two setups showed consistent discharge curves and pH trends, without corrosion. After 70 h, the residual voltage of new LIBs (3.8 V) dropped below the safety threshold (2V, 45 ± 1 % of initial voltage for Na_2CO_3 and 50 % ± 1 % for K_2CO_3). H_2 production was observed during the first 11 h for Na_2CO_3 (1722 ± 400 ppm/h) and 9 h for K_2CO_3 (1519 ± 670 ppm/h), with peaks at 2000–2300 ppm/h after 3–5 h while O_2 and CO_2 production was below the detection limit of the detector (0.1 %-vol for O_2, 50 ppm for CO_2). pH trends in the aqueous electrolytes (pH increased from 11.5 to 11.6 to 12.5 ± 0.48 pH units after 3 h in Na_2CO_3, and 12.06 ± 0.06 after 4 h in K_2CO_3) matched H_2 production and the formulation of the hydroxyl ions. The half-cell setup confirmed that H_2 release at negative half-cell, increasing the pH of discharge solution. These results presented a safe method for LIBs discharge, avoiding corrosion and hazardous gases release.

1. Introduction

Lithium ion batteries (LIBs) contribute to energy transition towards renewable sources and electrification of transport systems and play a key role in the achievement of decarbonization goals set by European regulations (European Commission, 2019, 2020). Recycling of end-of-life (EoL) LIBs is fundamental to limit the environmental impacts associated with the whole life-cycle of the battery (Dolganova et al., 2020; Sultana et al., 2022) and could lead to reducing greenhouse gasses emissions associated with battery production from 28 % (Bruno and Fiore, 2024) to 34 % (Hao et al., 2017).

If more advanced battery recycling methods are applied, the first stage in LIBs recycling is discharge, aimed at the reduction of residual voltage of EoL batteries (Garg et al., 2019; Kim et al., 2021; Mishra et al., 2022). Discharge is fundamental to ensure safe handling during recycling, avoiding short-circuits and possible fire hazards and explosions (Langner et al., 2021). As safety measure, the potential difference between the positive and negative poles of a battery cell should be below 2 V (Kwade et al., 2018) but not discharged at 0 V to avoid cell enlargement, which might lead to explosion (Lee et al., 2023). Nonetheless, no specific requirements for residual battery voltage are currently set by regulations about recycling processes (Rouhi et al., 2021). Discharge of EoL LIBs is currently performed either via connection to a controlled resistance (Langner et al., 2021) or, more commonly, by electrochemical discharge in saline solutions (Shaw-Stewart et al., 2019; Xiao et al., 2020; Kim et al., 2021). The salt most frequently applied in electrochemical discharge is NaCl (Shaw-Stewart et al., 2019; Yao et al., 2020; Punt et al., 2022). The residual voltage of LIBs discharged in NaCl is reduced below 1 V in 2 h (Yao et al., 2020) and to almost 0 V after 24 h (Shaw-Stewart et al., 2019) or 1.5 h when combined with ultrasonication (Torabian et al., 2022). However, NaCl solutions cause negative effects such as corrosion of battery casing (Kim et al., 2021; Rouhi et al., 2022) that can damage the active materials in the cells as well as chorine and alkane gaseous emissions (Wang et al., 2022), which are recognized harmful contaminants and can possess danger to humans and environment (Liu and Gao, 2021).

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Technical improvements of electrochemical discharge with NaCl have been previously explored. A recent study (Torabian et al., 2022) proposed a vertical parallel arrangement of the batteries in the discharge solutions to decrease the required contact time and to prevent corrosion. The main limitations of these approaches are that only pouch cells have the configuration required for the first design (Torabian et al., 2022). Alternatively, other authors developed an "ex-situ" discharge method (Rouhi et al., 2022) in which the battery electrodes are linked to platinum wires immersed in the discharge solutions, avoiding any contact between the solution and the batteries to prevent corrosion that are only suitable for academic purposes. A physical discharge process has been proposed (Yao et al., 2020) based on replacing the discharging solutions with conductive powders of copper or graphite, which provided a discharge rate equivalent to NaCl without any corrosion. Recent studies (Ojanen et al., 2018; Shaw-Stewart et al., 2019) investigated discharging solutions alternative to NaCl, as halogen salts (Cl^-, Br^- and I^-) and $Na_2S_2O_3$; however, they still caused corrosion of battery casing, especially nearly the positive electrode (Shaw-Stewart et al., 2019). Other studies tested sulfate-based electrochemical discharge solutions, achieving voltage reduction (70 % of initial voltage for $ZnSO_4$ (Fang et al., 2022), 60 % for $NaSO_4$ (Dagdougui et al., 2018; Wang et al., 2022), 50 % for $MnSO_4$ (Dagdougui et al., 2018) and 40 % for $MgSO_4$ (Torabian et al., 2022)) that are unsatisfactory compared with the almost complete discharge reached by NaCl (Ojanen et al., 2018; Torabian et al., 2022). However, they avoided corrosion, and the release of harmful compounds was not significant, e.g. the concentration of alkane gasses was 0 % during discharge with Na_2CO_3 and 0.8 % during discharge with NaCl (Wang et al., 2022). Thereby they have been listed as potentially "greener" alternatives to NaCl for LIBs electrochemical discharge (Yao et al., 2020).

Thus, it has been shown that there are also non-corrosive electrolytes, such as carbonates (Na_2CO_3 and K_2CO_3) (Shaw-Stewart et al., 2019; Rouhi et al., 2021) and electrochemical discharge with these electrolytes avoids damage to LIBs casing and prevents chlorine gas release as there is no chlorite ions present. Indeed, despite the high alkalinity of Na_2CO_3 and K_2CO_3 solutions, Shaw-Stewart et al. identified these solutions as the least corrosive alternatives among 26 other salt solutions. However, water splitting reaction still occur that forms of O_2 and H_2, which present considerable explosion hazard if not treated properly (Dagdougui et al., 2018). On the other hand, water electrolysis in alkaline solutions was proposed as viable method for H_2 production, as long as H_2/O_2 interaction is prevented (Chen et al., 2016). Thus, the development of gaseous products during LIBs discharge with non-corrosive solutions is a topic worthy of further investigation to better understand the reactions occurring in the electrolyte and to increase the safety of operation. The few available studies employed gas-chromatography to measure total gaseous release during electrochemical discharge but these studies did not analyse the trends of gaseous products that would be important to understand the different reactions occurring at different voltage ranges (Shiva Kumar and Himabindu, 2019; Yao et al., 2020). Previous research on monitoring of the produced gases from electrochemical discharge were limited to a few electrolyte such as NaCl (Shaw-Stewart et al., 2019; Yao et al., 2020; Punt et al., 2022; Torabian et al., 2022; Wang et al., 2022), Na_2SO_4 (Wang et al., 2022), $FeSO_4$ (Yao et al., 2020) and $MnSO_4$ (Yao et al., 2020; Wang et al., 2022). Moreover, recent studies proposed novel strategies to limit the environmental burden of LIBs recycling processes, considering the release of volatile organic components during mechanical treatments (Li et al., 2016) the application of organic acid during leaching (Nayaka et al., 2019) or the recovery of electrolyte solution in order to avoid the release of toxic hexafluorophosphate (Wu et al., 2024). However, the environmental impacts associated with the gaseous products generated during electrochemical discharge are yet understudied.

The general goal of this study was to understand better the LIBs behaviour during the electrochemical discharge in carbonate solutions. The elements of novelty are: (i) develop a system to analyse gaseous products (O_2, H_2, CO_2) as a function of the cell voltage from the electrochemical discharge of batteries in carbonate solutions; (ii) testing two discharge systems: a conventional setup, involving a single battery completely immersed in the electrolyte, according to previous literature; another, defined "half-cells" setup, was based on two batteries in series connected at opposite electrodes by a platinum wire, each battery partially immersed in separate electrolyte connected by a salt bridge. In both setups, the discharge curves and the pH change have been monitored during the tests; (iii) the "half-cells" setup allowed to investigate individually the behaviours of positive and negative electrodes during the electrochemical discharge tests.

2. Materials and methods

2.1. Materials

This study involved Cameron Sino CS- NCR18650 Panasonic batteries (3400 mAh; volumetric energy density 676 Wh/L; gravimetric energy density of 243 Wh/kg). Each battery weighed 47.5 g, measured 18.50 mm in diameter and 69 mm in length, and initial voltage was 3.8 ± 0.03 V. The choices of the salts used as the discharge electrolytes and their concentrations were based on the low corrosion behaviour that these electrolysers possess for LIBs casing corrosion explored in the previous (Rouhi et al., 2021). The electrolytes contained 5 %-wt. Na_2CO_3 (99.9 % purity, CAS: 497-19-8 VWR Chemical BDH), and 5 %-wt. K_2CO_3 (99 % purity, CAS: 20,961-9 Sigma-Aldrich) in Millipore deionized water.

2.2. Electrochemical discharge tests

The performances of 5 %-wt. Na_2CO_3 and K_2CO_3 solutions have been compared in two separate electrochemical discharge setups (Fig. 1), in the following defined conventional and "half-cells". In the conventional setup (Fig. 1A) a battery was completely immersed in the discharging solution as performed in various previous studies (Ojanen et al., 2018; Rouhi et al., 2021, 2022; Wang et al., 2022). The conventional discharge tests were performed in 250 mL Pyrex bottles with 30 mL headspace for the measurements of gaseous products. The conventional setup was used to monitor the discharge trend of the batteries, the pH of the discharging solutions and the release rate of gaseous products. In the "half-cells" setup (Fig. 1B), two batteries were connected in series by a platinum wire (CAS: 7440-06-4 ThermoFisher GmbH, 0.5 mm diameter, 99.997 %, purity) and partially immersed in separate electrolytes (100 mL) joined through a salt bridge. The "half-cells" set-up allowed to monitor the behaviour of the positive and negative electrodes in separated environments, by connecting with the platinum wire two LIBs and immersing the other extremities in different containers. The discharge tests lasted 120 h (5 days). The experiments have been performed in triplicates for both setup and both electrolytes.

The residual voltage of the batteries has been measured hourly using an 87V IMSK Fluke multimeter (10 μV resolution and ±1.05 % precision). The gaseous products from the system: CO_2 (ppm), O_2 (%vol.) and H_2 (ppm) have been monitored every 1–5 min with a G7c BlackLine Safety portable emissions detector measured CO_2, O_2 and H_2 concentrations released during the discharge tests (accuracy ±50 ppm for CO_2, ±0.1 %vol. for O_2, and ±400 ppm for H_2), and the hourly rate of gases was calculated as weighted average. Sensors connected to the portable gas detector were placed in the headspace of the glass bottle were discharge tests were conducted. The portable gas detector sampled gasses (CO_2, O_2 and H_2) concentration (ppm) automatically between every 3 and 10 min. In order to present consistent results, the H_2 release rate and the variation in H_2 concentration over a various periods of time were considered (according to the time periods between two samples have been collected). Eventually the plotted data have been obtained as the average of H_2 release rate weighted by their corresponding time

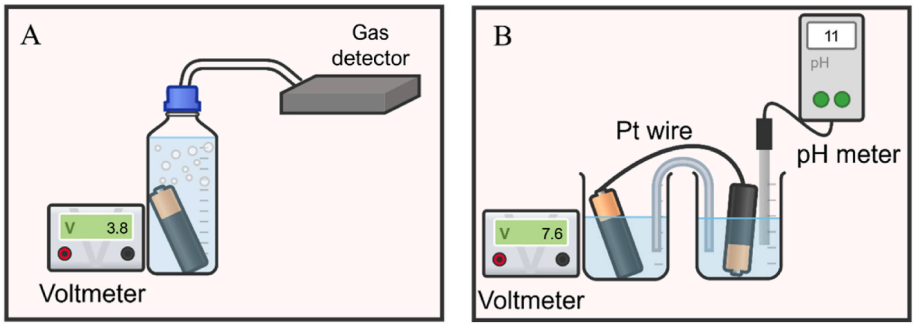

Fig. 1. Experimental setups employed in the electrochemical discharge tests: (A) conventional where the battery is submerged in one single electrolyte container and (B) "half-cells" setup where each of the poles can be studies separately.

periods within a span of 1 h.

The choice of the detector's sensors was based on the statement that the residual voltage during discharge was always above 1.7 V (Rouhi et al., 2021) which corresponds to the voltage required for water splitting (Yu et al., 2022). As a result, H_2 and O_2 gas should be released from the positive and negative electrodes, respectively. Moreover, because carbonate solutions were used as discharge medium, the risk of CO_2 generation was considered and therefore the CO_2 formation was also monitored. The initial headspace composition was 20.6 %vol. O_2, 450 ppm CO_2 and 0 ppm H_2. pH has been measured hourly for 8 h per day along the whole duration of the tests with a pH meter (1030VWR tester, having 0.01 resolution, ±0.2 precision).

3. Results and discussion

3.1. Conventional electrochemical discharge tests

Initially, the reactions occurring during LIBs electrochemical discharge in 5 %-wt. Na_2CO_3 and K_2CO_3 solutions were investigated in a conventional configuration, measuring the trend of residual voltage over time, the trend of pH and the release rate of gaseous products from the discharging solutions.

The voltage reduction measured in this study corresponds to the change in the voltage over time as LIBs are immersed into carbonates solutions. During the conventional discharge tests, residual voltage halved in 60 h (Fig. 2) and remained constant around 45 ± 1 % of initial voltage for Na_2CO_3 and 50 ± 1 % for K_2CO_3. In the first 48 h, the rate of residual voltage reduction in Na_2CO_3 was −0.007 ± 0.003 V/h, then doubled to −0.015 ± 0.003 V/h. K_2CO_3 solution, instead, showed a discharging rate of −0.008 ± 0.003 V/h in the first 24 h, increasing to −0.012 ± 0.004 V/h and then reducing again to −0.006 ± 0.001 V/h in the last 24 h. The discharge efficiency of Na_2CO_3 and K_2CO_3 solutions was consistent with Rouhi et al., (2021) (Rouhi et al., 2021) who stated that the initial voltage of LIBs immersed in Na_2CO_3 and K_2CO_3 solutions halved after 70 h. During the discharge tests, no evidence of corrosion was noted at the metallic casings of batteries.

Considering the gaseous reaction products released during the conventional discharge tests, the concentration of CO_2 and O_2 were below the detector's detection limit (50 ppm for CO_2 and ±0.1 %vol. for O_2). This indicates that discharge batteries in carbonate solutions is not providing significant CO_2 emissions and is therefore suitable for industrial processes that are CO_2 neutral. Current European regulations on battery recycling (European Commission, 2023) had not set any specific limit on CO_2 released from electrochemical discharge. However, carbon neutrality is becoming increasingly crucial for recycling companies. As a result, Na_2CO_3 and K_2CO_3 proved to be feasible options for electrochemical discharge of used LIBs, allowing recycling companies to achieve their carbon neutrality targets.

On the other hand, both electrolytes released H_2, mostly in the beginning of the discharge (11 h for Na_2CO_3 and 9 h for K_2CO_3) (Fig. 3). The average H_2 release rate was 1722 ± 400 ppm/h for Na_2CO_3 and 1519 ± 670 ppm/h for K_2CO_3. However, H_2 release rate in Na_2CO_3 increased faster (1722 ± 527 ppm/h in the first hour), then peaked at 2363 ± 520 ppm/h in the second hour and remained almost constant around 2105 ± 166 ppm/h for the next 6 h before starting to decrease. Whereas H_2 release rate in K_2CO_3 was initially slower and peaked at 2045 ± 7 ppm/h after 5 h.

Na_2CO_3 and K_2CO_3 solutions were both effective in electrochemical discharge: the residual voltage of new LIBs diminished below the safety threshold of 2V after 70 h (Fig. 4), and when H_2 released ceased, total voltage reduction majority was already obtained (94 ± 1 %) indicating that the water splitting is the most predominant reaction for the battery discharge. Water splitting is the result of the electrochemical reaction where the bonds between water molecules are broken and the atoms form H_2 and O_2molecules. In this system the energy powering water splitting is provided by immersing LIBs with residual voltage into salt solutions, creating a short-circuit between the battery poles. The pH was measured in the overall electrolyte between the poles before the battery was removed from the electrolyte to perform the voltage experiment and represents the overall pH of the whole system. The initial pH was 11.63

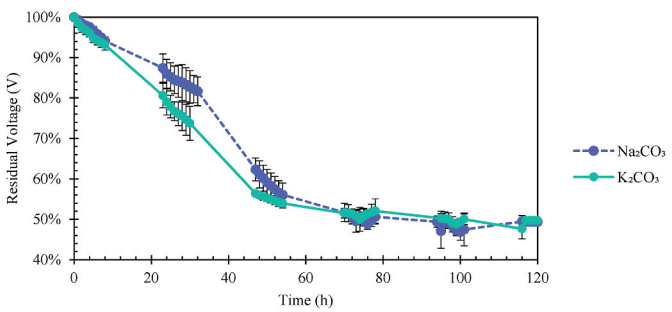

Fig. 2. Trends of residual voltage (V) during the conventional electrochemical discharge for LIBs in carbonate solutions.

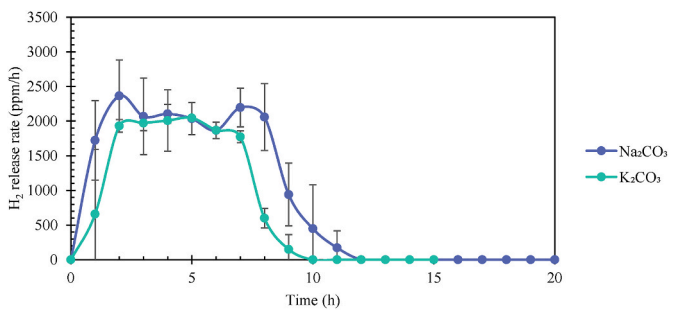

Fig. 3. Trends of H_2 release rate (ppm/h) during the initial part of conventional electrochemical discharge tests (total duration: 120 h).

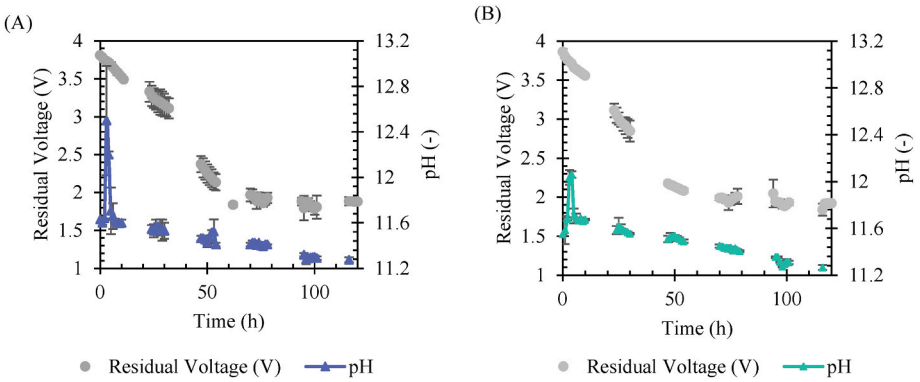

Fig. 4. Trends of residual voltage (V) and pH during the conventional electrochemical discharge tests with (A) Na_2CO_3 and (B) K_2CO_3.

± 0.01 for Na_2CO_3 solution and 11.55 ± 0.01 for K_2CO_3. In the conventional setup, no substantial change in pH was observed during the tests, fluctuating between 11.27 ± 0.02 and 12.5 ± 0.48 for Na_2CO_3 and between 11.26 ± 0.02 and 12.06 ± 0.06 for K_2CO_3. The pH trends in the electrolytes were similar, both peaking in the first hours of discharge (12.5 ± 0.48 after 3 h in Na_2CO_3 and 12.06 ± 0.06 after 4 h in K_2CO_3). Afterwards, the pH of both electrolytes decreased: the daily average pH values measured in Na_2CO_3 were 11.55 ± 0.02 after the first 24 h, 11.46 ± 0.04 after 48 h, 11.4 ± 0.01 after 72 h, 11.29 ± 0.01 after 96 h, and 11.27 ± 0.02 after 120 h; while in K_2CO_3 they were respectively 11.58 ± 0.02, 11.52 ± 0.02, 11.44 ± 0.01, 11.35 ± 0.04 and 11.26 ± 0.02. In both electrolytes the pH drop was correlated with the decrease of residual voltage (Pearson coefficient equal to 0.72 for Na_2CO_3 and 0.82 for K_2CO_3). These results are consistent with water splitting reaction under alkaline conditions, both for hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) [30]:

$$HER: 4\,H_2O + 4\,e^- \rightarrow 2\,H_2 + 4\,OH^- \quad (1)$$

$$OER: 4\,OH^- \rightarrow 4\,e^- + O_2 + 2\,H_2O \quad (2)$$

The localized increase in pH is consistent with the hydrogen evolution reaction that takes place during water electrolysis. Indeed, a parallelism could be drawn between the interface of the half-cell and discharge solution during electrochemical discharge for LIBs recycling and the interface of the electrode and electrolyte during LIBs use (Wu et al., 2022). Thus, at both carbonate solutions, it can be seen that there is a large peak of the pH at the beginning of the experiments (Fig. 4), to study this in more detail the beginning of the hydrogen production and change of pH for the first 10 h has been zoomed in Fig. 5 for both of the electrolytes. It is evident that the H_2 production at the beginning of the experiments, particularly the first 2 h is very strong and therefore there is also an increase of the hydroxyl-ion formation (equation (1)). This can be then seen as a large increase of the pH during 2–4 h of the experiment after which the oxygen evolution reaction will be more prominent and the pH balances with equation (2). This phenomenon is seen as the electrolyte has not been mixed and therefore it is possible to create a high local concentration. Focusing on accurate pH detection, the electrolyte was not mixed; however, this approach may prevent the increase of the local concentration. As in the Na_2CO_3 the hydrogen production is faster, also higher imbalance for the electrolyte pH will be noted.

Fig. 5 shows the trend of H_2 release during discharge, and the mirroring increase in pH of the solutions. According to literature, under alkaline conditions the rate of the hydrogen evolution reaction decreased (Strmcnik et al., 2013; Qadeer et al., 2024). Results from pH monitoring during discharge tests show a correlation with both the LIBs discharge rate and the trend of H_2 gas release, suggesting that pH monitoring could serve as a straightforward and low cost indication for both. Besides, pH could be measured continuously, offering a back-up system for gaseous product control, and avoiding the need of removing the batteries from discharge solutions to assess the residual voltage. In conclusion, a comparison of the main results obtained during discharge tests with Na_2CO_3 and K_2CO_3 solutions, is provided in Table 1.

3.2. Electrochemical discharge in half-cells

To better understand the reactions taking place during LIBs electrochemical discharge, an alternative configuration has been proposed. This "half-cells" configurations (Fig. 1 B) allowed to monitor the discharge behavior and the evolution of reaction products taking place at the different poles of the electrodes.

During the electrochemical discharge of 120 h, the overall residual voltage reached 34 ± 1 % of initial values for Na_2CO_3 and 35 ± 2.7 % for

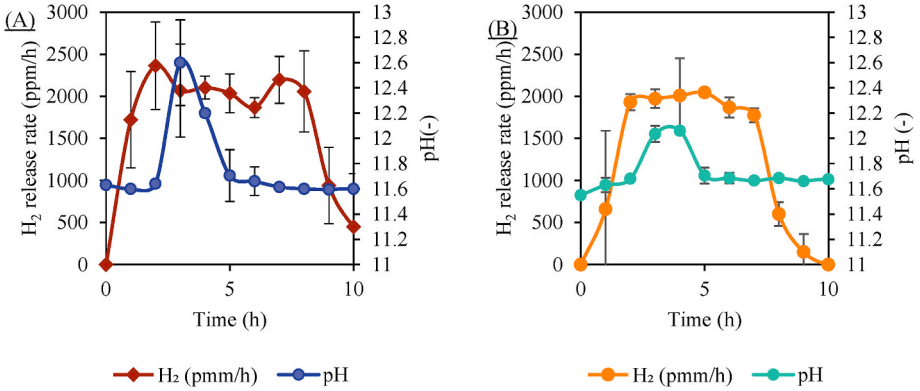

Fig. 5. Trends of H_2 release rate (ppm/h) and pH during the first part of the conventional electrochemical discharge tests with (A) Na_2CO_3 and (B) K_2CO_3 (total duration: 120 h).

Table 1
Comparison between the main results observed during electrochemical discharge with Na_2CO_3 and K_2CO_3 solutions.

Discharge solution	Na_2CO_3 5 %wt.	K_2CO_3 5 %wt.
Voltage after 0 h	3.809 ± 0.01 V	3.861 ± 0.04 V
Voltage after 60 h	1.968 ± 0.08 V	1.989 ± 0.03 V
Voltage after 120 h	1.879 ± 0.02 V	1.923 ± 0.01 V
Time to reach voltage < 2V	60 h	56 h
pH after 0 h	11.63	11.55
Max. pH	12.5 ± 0.48	12.06 ± 0.06
Time to reach the max. pH	3 h	4 h
Max. H_2 release rate	2363 ± 520 ppm/h	2045 ± 7 ppm/h
Time to reach the max. H_2 release rate	2 h	5 h

K_2CO_3 (Fig. 6). These values were lower than the ones achieved in conventional discharge tests (45 ± 1 % with Na_2CO_3 and 50 ± 1 % with K_2CO_3). The rate of residual voltage reduction in the "half-cells" discharge tests corresponded to −0.002 ± 0.0008 V/h for Na_2CO_3 and -0.001 ± 0.00001 V/h for K_2CO_3, slower than with the conventional setup, but it increased after 70 h in K_2CO_3 and after 100 h in Na_2CO_3. As in the conventional discharge tests, K_2CO_3 was slower than Na_2CO_3. During the "half-cells" discharge tests, the positive and negative half-cells did not discharge at the same rate. The positive half-cell was discharged to lower voltage and faster than the negative half-cell in both electrolytes. In the first 70 h, positive and negative half-cells discharged in Na_2CO_3 behaved identically, and then the discharge curves split. The residual voltage of positive half-cells after 120 h was 17 ± 2 % of the initial value in Na_2CO_3 and 14 ± 1 % in K_2CO_3. On the other hand, the residual voltage of negative half-cell was 53 ± 1 % in Na_2CO_3 and 47 ± 1 % in K_2CO_3. Instead, the discharge curve of positive and negative half-cells in K_2CO_3 differed after the first 24 h.

As the half-cell test set-up was open, the gas production during discharge was not possible. As happened to residual voltage, the pH trends of positive and negative half-cells differed (Fig. 7) during the "half-cells" discharge tests. The pH of the solutions in contact with negative half cells increased up to 12.9 ± 0.05 for Na_2CO_3 and 12.6 ± 0.18 for K_2CO_3 after 5 h. At the same time the pH of the solutions in contact with positive half cells decreased to 10.5 ± 0.03 for Na_2CO_3 and 10.9 ± 0.05 for K_2CO_3. These results also correspond the findings observed in the large cell system and the pH behaviour that the poles would have on the water splitting reaction in alkaline solution (equations (1) and (2)): hydrogen evolution reaction at positive half-cell oxidizes water molecules, converting them into gaseous H_2 and hydroxyl anions, thus lowering the pH, as described in reactions 1.

It can be seen in Fig. 7 that after 120 h, the voltage of positive half-cell decreased faster than negative half-cell (17 ± 2 % for Na_2CO_3 and 14 ± 1 % for K_2CO_3). The discharge of negative half-cell came to a halt around the same voltage observed in the conventional setup: 53 ± 1 % in Na_2CO_3 and 47 ± 1 % in K_2CO_3. After 120 h, pH in Na_2CO_3 was 10.5 ± 0.03 in positive half-cell and 12.9 ± 0.05 in negative half-cell; and in K_2CO_3 it was 10.9 ± 0.05 in positive half-cell and 12.6 ± 0.18 in negative half-cell. Overall, it can be confirmed in the half cell that the pH changes for the individual electrodes more in the beginning of the experiments and balances more at the later part of the experiment when also the gas formation is not as strong. This corresponds well with the findings in the large cell (Fig. 5) where the pH has higher changes in the beginning but balances to a steady level by time. Despite the promising results, the 'half-cell' setup is more suggested for scientific studies and presents scalability challenges related to the connection between the positive and negative half-cells. Specifically, a Pt wire is required to link the two half-cells, and differences in the design of LIB casings may pose challenges, particularly if they lack the necessary welding pads to secure the Pt wire.

4. Conclusions

This study explores the electrochemical discharge of LIBs (3.8 V) in non-corrosive carbonate solutions and quantify the gaseous products produced during discharge. Two setups were applied: a conventional one – based on literature, and a novel "half-cells" setup, that display the individual behaviour of positive and negative electrodes. The comparison of carbonate electrolytes was based on monitoring the discharge curves, the trends of gaseous products (H_2, O_2 and CO_2) and the pH of the discharge solutions. In both setups, there was no evidence of corrosion phenomena, and the residual voltage halved to the safety threshold of 2 V in 70 h.

In the conventional setup, H_2 production occurred in the first 9–11 h (1500–1700 ppm/h), with a peak emission rate of 2000–2300 ppm/h after 3–4 h, coinciding with pH peaks of about 12. No significant CO_2 formation was detected. The half-cells setup showed significant pH shifts at both electrodes, supporting the hypothesis of water electrolysis in alkaline conditions. In the first 5 h, pH peaked at 12.6–12.9 at negative half-cell and dropped at 10.5–10.9 at positive half-cell that is consistent with the formation and conversion of the hydroxyl ions from each of the half cells. As the changes at the one electrode are small, the quantity of ions and gaseous products are small and there is some errors in the detection limits of these components that is a shortcoming for the project.

Future work will enhance the detection accuracy and expand for other gaseous products to study also other inorganic aqueous solutions. This further helps us to better understand the different reactions taking place at the electrochemical discharge.

CRediT authorship contribution statement

Martina Bruno: Writing – original draft, Methodology, Investigation, Conceptualization. **Silvia Fiore:** Writing – review & editing, Validation, Supervision, Methodology, Conceptualization. **Annukka Santasalo-Aarnio:** Writing – original draft, Validation, Supervision, Methodology, Funding acquisition, Conceptualization.

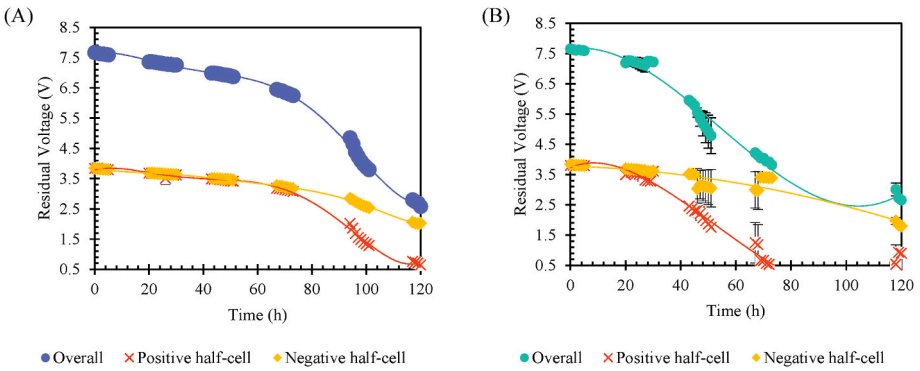

Fig. 6. Trends of residual voltage (V) during the "half cells" discharge tests with (A) Na_2CO_3 and (B) K_2CO_3.

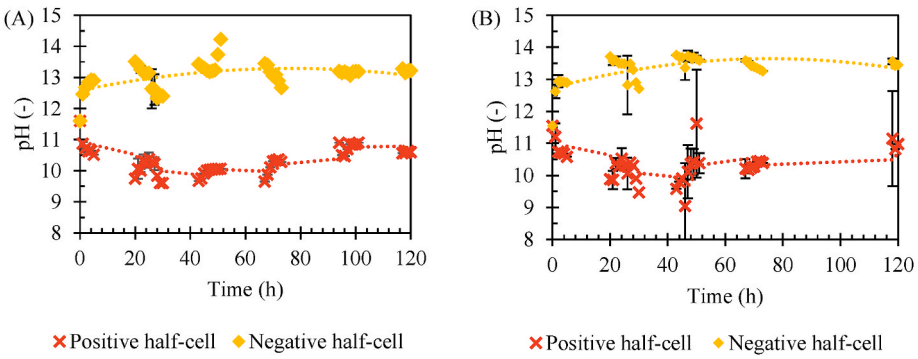

Fig. 7. Trend of pH in positive and negative half-cells during electrochemical discharge with (A) Na_2CO_3 and (B) K_2CO_3.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Annukka Santasalo-Aarnio reports financial support was provided by Research Council of Finland. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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