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Battery chemistry prediction with short measurements and a decision tree algorithm: Sorting for a proper recycling process

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ABSTRACT

Given the push for electrification in every front, the demand for batteries is going to keep increasing. The current rates of growth for production of raw materials are not expected to keep up with this increasing demand. Therefore, recycling has to be a significant part of the value chain in providing the raw materials. Presorting the batteries collected prior to a recycling operation would greatly improve the efficiency of the process. Given users of consumer batteries cannot classify their spent batteries by their chemistries, a chemistry identification will need to be implemented at the industrial scale. We are reporting on a decision tree that is based on a density measurement along with electrical measurements in order to classify batteries by their chemistry in addition to a provision for reusability. 109 batteries are measured in total from a battery recycling bin, including batteries from commercial retailers that were used for various applications.

1. Introduction

Battery reuse and recycling are going to be two of the most crucial issues in next decades. Just considering the electric vehicle market, current projections of batteries required, demand raw materials that are significantly more than what the present and projected mining efforts can offer [1]. As raw materials from primary sources become scarcer, the cost of producing materials from natural sources [2] will eventually surpass the cost of producing materials of the same quality based on recycled batteries. It is straightforward to conclude that commercial scale recycling will lead to cost competitive raw material production. Battery recycling will have to be a part of the standard public discourse in order to make sure that electrification can make the impact it promises. Recycling is already commonplace in lead acid batteries [3,4] partially because of national and international regulations [5–7]. In 1996, the US Congress passed legislation banning the burning and disposal of lead-acid batteries deeming lead-acid batteries [8] hazardous waste and their recycling process is under regulation by Environmental Protection Agency (EPA) [9]. Currently, a significant part of the lead that is being used for manufacturing lead acid batteries is from recycled lead and the polypropylene casing and the sulfuric acid is almost completely recycled. Since collection directly comes from the automotive replacement sector, no sorting is required.

Regarding lithium and lithium-ion batteries, technologies have been developed for recycling with various specific lithium-based chemistries. Some stages are already being implemented at the commercial level [10–14]. In these efforts, collection and sorting remains a very large challenge as chemistries are rarely completely identified on the labeling of consumer batteries. For those that are obtained through the automotive replacement sector, the chemistry is already well-known based on the make and brand of the automobiles, however for batteries that power consumer electronics, the collection generates an assorted batch of various chemistries at different states-of-health. The current process for these is to first incinerate in order to burn off the separator, boil off the solvent and extract any energy that is still stored in the batteries; then shred the mixture into “black mass” (personal communication, Marcus Larsson, Stena Recycling, September 5, 2022). This process is a) not fully utilizing the energy contained in batteries that are still usable, b) inefficient as valuable material content could be dilute and will not be known until the “black mass” is chemically analyzed.

There is literature regarding the sorting problem from 1990s and early 2000s where lithium batteries were not this prominent and variable. In a patent by Titalyse SA the developed sorting algorithm uses a variety of properties such as whether the cell is magnetic or not, size, weight, and the response to a magnetic field (i.e., magnetic resonance) in order to sort based on chemistry [15]. A flowchart following their patent is reproduced as Fig. 1. Technology based on this patent was implemented in the industrial scale by Sortbat and developed further

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including a manual sorting at the beginning [16].

The abovementioned algorithm was developed manually after collecting large datasets. Currently, such algorithms can be generated using what are known as decision tree algorithms. Such algorithms are known in various fields such as medicine [17,18], criminology [19], GPS [20] or solar photovoltaic systems [21]. The decision tree algorithm is useful in all cases where data classification and identification are required regardless of the area.

Watson reviewed the sorting methodology from Titalyse SE in addition to others in 2001 [7]. Further, the paper outlined various companies and organizations that coordinate battery collection and recycling efforts at the time. Ultimately, sorting is recognized as a necessary component that has to occur before recycling for an efficient and productive recycling process. In a 2004 review, various methods and opportunities regarding disposal, collection and recycling of various batteries were reviewed. In this review, processes for sorting and recycling various chemistries were mentioned [22]. However, details regarding specific procedures are mostly not available in the public domain.

Though recycling is an important milestone for achieving sustainable technologies in general and batteries in particular, it is never 100 % efficient and destroying a usable battery is wasteful regarding both energy content and cost. Therefore, batteries that can be reused should not be going into a recycling process. Batteries that are still usable for some applications may end up at collection for a multitude of reasons. First, (as the authors experienced in the collection bin of their own building) a bad connector on the battery pack can make an entire pack of cells look bad; second, improper handling may lead to the conclusion that the batteries are unusable. Any sorting algorithm for collected batteries has to include a provision to identify usable batteries before classifying recyclable batteries according to their chemistry.

Sorting for this goal is already developed for rechargeable batteries for second-life type applications. For example, Schneider et al. developed a visual inspection method in addition to DC electrical measurements in order to identify batteries that can be reused for various applications [23]. The DC measurements reported, involve measuring the open circuit potential in addition to a slow and a fast discharge. In another more recent implementation, X-ray imaging and automated image analysis was employed in order to follow degradation of batteries [24]. The images were compared with cells that are known to be usable and not. Coupled with electrical measurements, batteries were identified as reusable with 97 % declared accuracy. Lyu et al. proposed a comprehensive sorting method according to the uniformity of lithium-ion battery packs. Parameters that are obtained from their electrochemical model are utilized for the internal sorting criteria based on the characteristics of LIBs such as sensitivity and strength of correlation to aging and the sorting of the battery packs is done by fuzzy C-means (FCM) algorithm [25]. For similar purposes, An et al. developed a

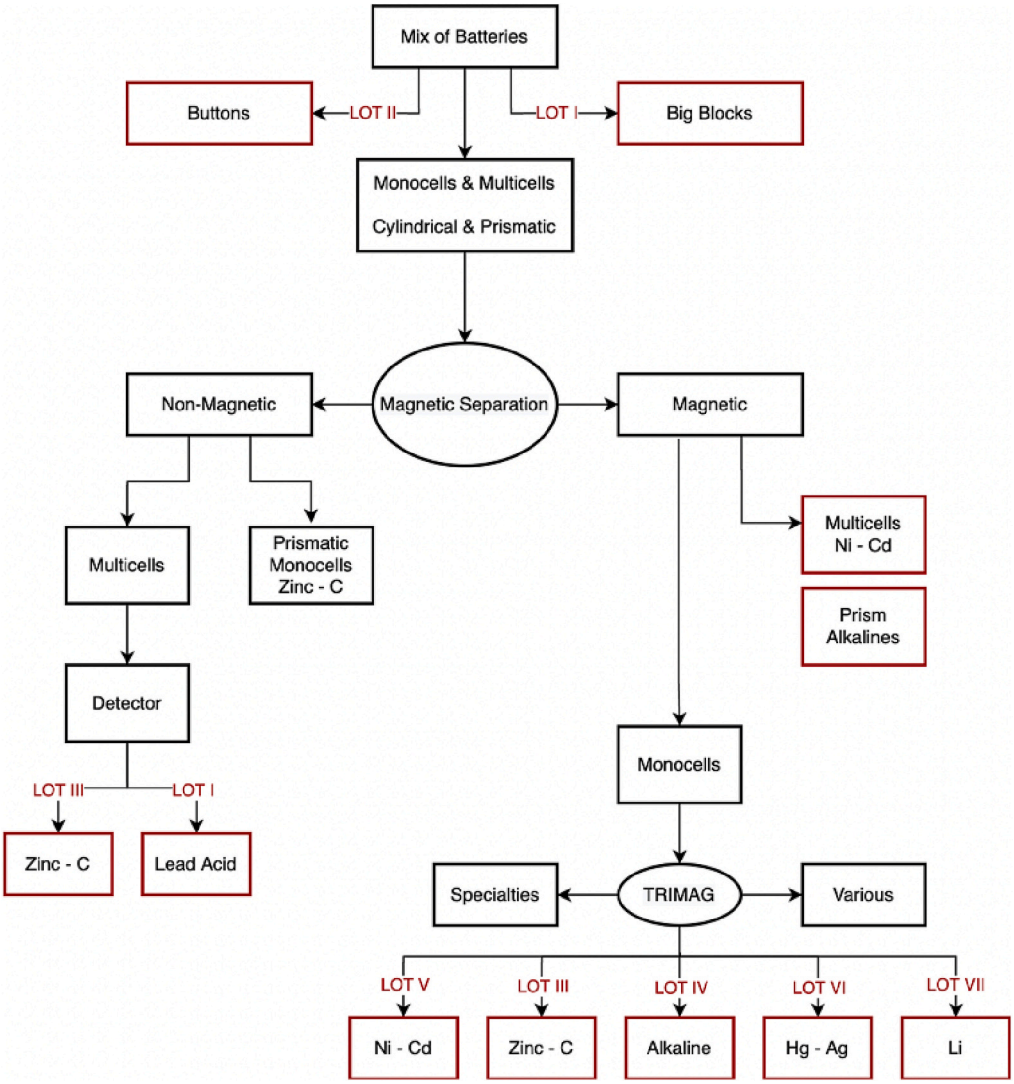

Fig. 1. Flow chart of battery sorting algorithm based on Titalyse SA patent [15].

parametrization of battery impedance characteristics through relatively simple measurements. Through this, cells that can be connected in parallel with minimal asymmetry could be identified [26].

AC measurements (i.e., Electrochemical Impedance Spectroscopy (EIS)) have been employed very widely in battery characterization [27]. Because EIS can access a very wide range of frequencies, components inside the battery that respond in different timescales can be investigated individually while the battery is physically fully intact. In an effort to predict the chemistry, the ability to gather information about the positive and the negative electrodes separately is invaluable. In a number of chemistries, one of the electrodes can be the same: e.g., metallic lithium is the anode for both $Li/SOCl_2$ and Li/FeS_2, graphite is the cathode for both $Li/SOCl_2$ and NMC based Li-ion.

In the current manuscript, we will be reporting on a method that we have developed that employs a density measurement in addition to AC and DC electrical measurements in order to sort the chemistries of the batteries that were found in the collection bin of the Faculty of Science at Bilkent University. The algorithm we developed can distinguish not only between various Nickel and Alkaline based chemistries, but also across primary and secondary Lithium based chemistries. To perform classification based on the collected data, we have used a decision tree algorithm [28]. The data required can be obtained in 1 s per battery, which could allow for commercialization. Further, since the measurement is only electrical and single stage, it would be much simpler to implement and much cheaper than the existing technologies employing more complicated measurements such as magnetic resonance. It could also be used to complement the existing methods. We made sure to spend as short a time per battery as possible in an effort to create an algorithm that can be implemented in a moving belt sorting facility.

We will show that using a decision tree algorithm [29], it was possible to classify 6 different chemistries with different sizes and states. Our methodology can be scaled up to many more chemistries provided enough data is collected. Within the same measurement, cells that can be reused will also be identified. It is important to notice that the reuse decision is not a replacement for the chemistry classification, instead, it is complimentary. Any battery that will be reused will also have to be classified regarding its chemistry for proper utilization.

2. Experimental

109 used batteries were collected from different brands with a total of 6 different chemistries and various states of use. Used batteries with detailed information such as brand names, models and chemistries etc. can be found in Table S1.

All batteries were subjected to same tests which were designed such that the whole measurement can be carried out on individual batteries with minimal electronics in 1 s or less. This was done in an effort to make sure that the method developed can be field deployable. The first inspection on batteries was to determine the operating voltage of the battery using a multimeter (Fluke 179 True RMS Digital Multimeter). Then, 10 Ω and 100 Ω resistors were connected to the batteries, and the voltages while discharging through resistances were determined for each battery, since this voltage is an indicator of the discharge current under the said load. Electrochemical Impedance Spectroscopy (EIS) measurements were performed in galvanostatic mode by using Gamry Reference 3000 Potentiostat. The frequency range used was between 100 kHz to 100 mHz with an AC current of 1 mA.[1] For all types of batteries, the experimental parameters were kept constant. Finally, weight measurements were done to calculate the density the batteries by dividing the weight to the volume (7.7 cm^3 for AA, 16.5 cm^3 for 18,650 geometries). The data was then put through a decision tree development algorithm based on the sklearn module of Python [33] with Gini impurity as the criteria of picking the proper splits. In this method, the impurity that is defined as "variable being incorrectly identified" [34] is minimized at every node while making the decision. This system makes sure that the algorithm generates the tree with the lowest depth. This ensures an automated process of training the decision tree with the data and takes out any biased treatment or selection of the data. The automated process is guaranteed to generate a decision tree that can select the training set and is checked against the test set.

[1] Though the measurement was performed down to 100mHz for completeness, in the evaluation of data, the impedance values used are all from frequencies 1 Hz and higher.

3. Results and discussion

For all the batteries studied, data was collected that includes full impedance spectra, density, voltage under loads of 10 Ω and 100 Ω as well as the rest voltage. These data were used in full in the generation of the decision tree. Once a pattern emerged regarding details of what the important parameters were, the data was narrowed into the final subset.

3.1. Chemistry classification for recycling

Representative dataset for three examples of each chemistry with a subset of the measurement results in addition to the full data table are available as Supplementary material. The complete set was used throughout the calculation of the decision tree algorithm without any normalization. In the splitting process, a 50/50 split was used for the training/testing batches with shuffling prior to the splitting. The resulting set ended up having at least two samples of each battery in the test set (full counts are shown in Table 1).

In order to test the robustness of the methodology, different splitting conditions were tested. In Table S2, the results for the same process with 30/70 and 70/30 splits of training vs. test sets are reported in addition to the one reported here. It is clear that as soon as the training set consists of more than half the dataset, the generated decision tree leads to a 100 % success in classifying. The fact that only half of the dataset can be used for training that yields a successful decision tree is testament to the robustness of the methodology. The resulting decision tree can be found in Fig. 2.

The colors that are used in the pure nodes (i.e., nodes with only a single chemistry) are mixed in a weighted average manner in the impure nodes (i.e., nodes with more than one chemistry). The class listed at the bottom of each node lists the dominant chemistry in any given node. It is clear that the density of the batteries is one of the main decisive factors, in addition to the impedance values at certain frequencies. Since the batteries that are tested are highly variable in their states-of-charge, even some of the higher nominal voltage chemistries can have near zero measured voltages. Therefore, the voltage measured does not end up being an indicator of the chemistry. The impedance levels, in addition to the density, create a decision tree that provides a successful way of classifying the batteries in the set. With this tree created, the remaining 55 batteries left for test can be predicted with 100 % accuracy.

In all the decision trees that are calculated, the density is the main distinguishing factor. However, density alone cannot properly classify the chemistry especially when different brands are used. In those cases, the impedance at various frequencies is employed for distinguishing

Table 1
The number of batteries ending up in the training set and the test set in the calculation.

Chemistry	# in training set	# in test set
Alkaline	30	35
Ni-Cd	4	5
$LiCoO_2$	4	2
NiMH	4	4
Li/FeS_2	6	5
$Li/SOCl_2$	6	4

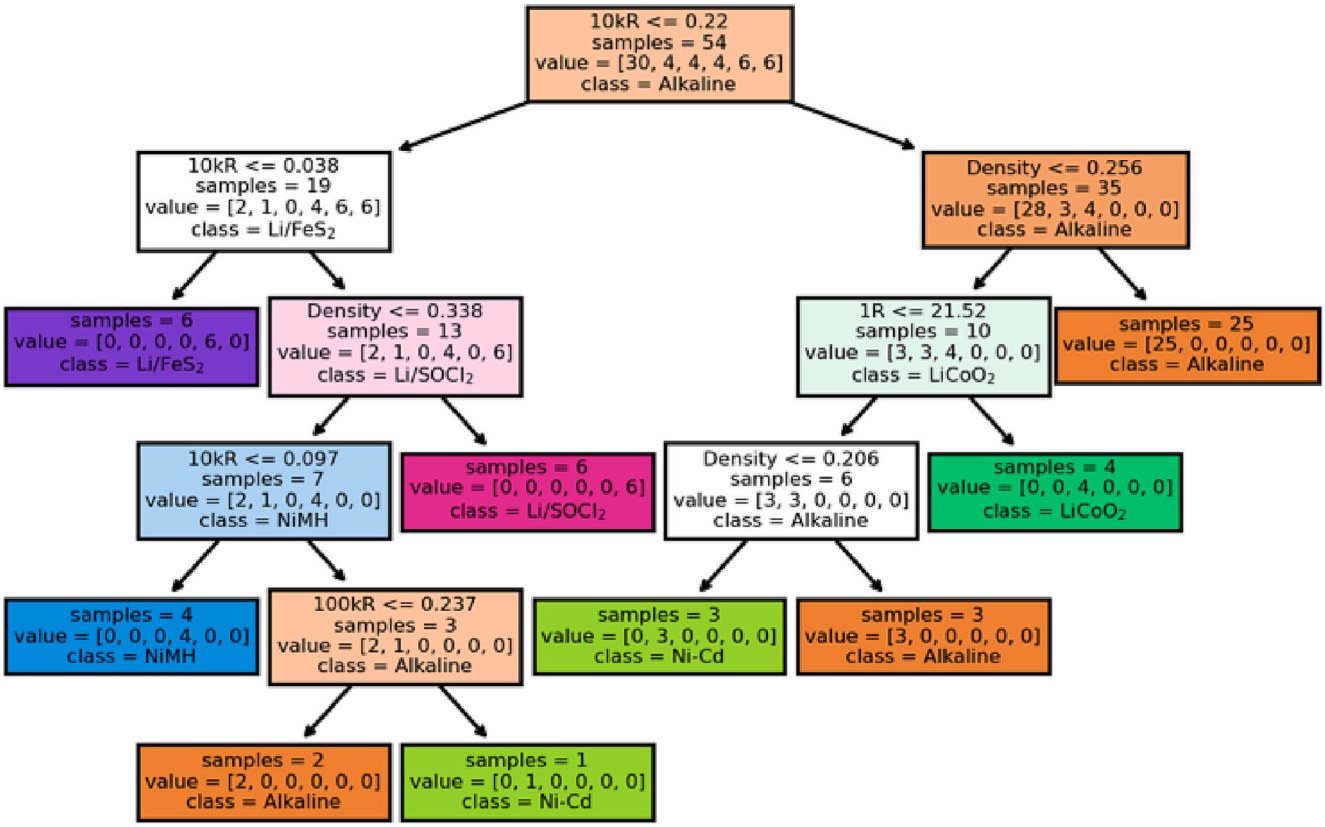

Fig. 2. The decision tree that was the output of the algorithm based on 50 % of the data as the training set. (10kR and 1R represent the real impedance at 10 kHz and 1 Hz respectively). Samples indicate the number of batteries entering a given node, value array indicates the types of the batteries in the order [Alkaline, Ni—Cd, $LiCoO_2$, NiMH, Li/FeS_2, $Li/SOCl_2$] and class is the dominant chemistry in the given node.

between the rest. The impedances used are typically chosen with one that is at the high side corresponding to the electrolyte resistance and another one corresponding to the capacitive region for the electrode with the larger area. This is true for all the decision trees that we have calculated.

Required precision for proper classification is an important parameter in the quest for industrial implementation. For almost all measurement methods, a longer measurement leads to lower noise levels. Therefore, any analysis of how long it would take to collect the necessary data has to start with the required precision for the measurements.[2] This analysis relies on two separate measurements: density and impedance. The density measurement requires the weight to be measured along with the volume.

This tree requires that the density has to be measured with at least two significant figures, specifically that the difference between 0.256 g/ml and 0.206 g/ml is statistically significant. This requires that the density has to be correct to ±0.05 g/ml. On average, measuring weight ±0.01 g is cheap and quick. Regarding the volume, one approach would be to sort the batteries quickly with predetermined standard sizes. This could easily yield the volume of the battery to ±1 %. A quick error propagation would indicate:

$$\frac{s_d}{d} = \sqrt{\frac{s_m}{m} + \frac{s_v}{v}} \quad \text{for } d = \frac{m}{v}$$

Plugging in the numbers and assuming a roughly 30 g battery [footnote: the weights in this study were ranging from ~15 g to ~47 g.], the error can be estimated as:

$$\frac{s_d}{d} = \sqrt{\frac{0.01\ g}{30\ g} + 0.01} = 10.1\%$$

For a density of 0.20 g/ml, this would indicate that the error would be ±0.02 g/ml and that would be fine for this decision tree.

Regarding impedance, the measurements are somewhat more forgiving since data is available at a multitude of frequencies. Ultimately, from observation, ±5 % would be enough for the impedance measurement. Commercially, 1 % or better is the typical specification for impedance accuracy [30]. For an implementation of the developed methodology, fastest measurement that can yield usable data is important. Regardless of the data quality, quickest possible impedance measurement requires one period at the lowest frequency desired. In this particular case, 1 Hz is the lowest frequency required; therefore, a measurement can be completed within 1 s [30,31].

3.2. *Fitness for reuse*

In addition to predicting the chemistry, the same dataset can be employed to estimate whether the battery can still be used for a certain application. For primary batteries, the simplest criteria that is typically employed to check whether a battery is usable or not is the potential. However, simple DC potential measurements can be misleading for a number of reasons including high resistances developed or relatively flat potential-SoC curves [32]. For rechargeable batteries, the state-of-health and reusability discussions will be kept outside the scope of this discussion.

For a battery to be usable, one has to not only consider the DC potential under no load, but also under resistive loads. Therefore, the DC

[2] Since the measurement is always done as comparisons, the accuracy is not critical for this purpose as long as the same equipment is used for the training data and the final implementation.

potential, in addition to the potential levels under 10 Ω and 100 Ω discharge conditions are considered. Very simply, we deem a battery reusable, if the difference between the operation voltage and discharge voltage under a 10 Ω load is less than 50 mV and the impedance data is linear which can be checked via simple Fourier Transforms. This is admittedly subjective, however, from anecdotal experience this analysis yields batteries that can power consumer electronics that they were designed for.

3.3. Broader applicability

The dataset analyzed in this study demonstrates the effectiveness of the proposed method for distinguishing between various chemistries including those with common electrodes on one side (i.e., the primary lithium chemistries and NiCd/NiMH). The properties used in the method (i.e. density and impedance spectrum for chemistry and current under load for reuse) are universal and straightforward to measure. This makes the method applicable to any type of battery chemistry. However, for industrial applications, it is crucial to measure these properties for each individual cell that undergoes the recycling process. This demands an electrical connection to each cell, which involves aligning the batteries with electrical contacts.

For datasets that are larger with more diverse chemistries and sizes scaling becomes a critical requirement for accurate classification. The density is already an intrinsic property and the impedance can be scaled by the estimated electrode areas for the various sizes employed. Within the dataset reported here, all the batteries were cylindrical, mostly AA with some 18,650 s, so the impedance spectra were not scaled.

Expanding the method to a broader range of chemistries would require measuring impedance at different frequencies. As the chemistries change, the composition of the active material in the anode and/or cathode will change, leading to differences in capacitive and resistive properties, which will be reflected at specific frequencies in the impedance measurements. Though, the specifics will have to be confirmed and will undoubtedly need to be empirically determined, we posit that the impedance measurements along with the density will be a predictor of the chemistry even in larger and more diverse datasets.

4. Conclusion

A decision tree was developed based on impedance at two frequencies and the density of batteries with 5 different chemistries. This study demonstrates the feasibility of employing impedance and density measurements for separating various chemistries before a recycling operation which would improve the effectiveness. Further, this analysis can identify batteries that are fit for reusing in certain applications which would further improve sustainable use of batteries. With a larger dataset that comprises of more chemistries and brands, a decision tree can be developed that can be industrially employed with minimal measurement time and only electrical and density measurements.

CRediT authorship contribution statement

Gözde Karaoğlu: Data Curation, Writing, Formal Analysis
Burak Ülgüt: Conceptualization, Writing, Supervision

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data is added as supplementary information.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.est.2023.108232.

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