

Comparison of Different Reductants in Leaching of Spent Lithium Ion Batteries

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The present work focuses on the processing of cathode active material of spent lithium ion batteries to improve the recovery of constituent metals using reducing agents. Reductants enhance the solubility of metals, which hitherto have been solubilised to a lesser extent using only acid as leaching agent. Thus, we have investigated sulfuric acid leaching in the presence of sodium bisulfite comparing its efficiency with hydrogen peroxide. By simple acid leaching using 1 M H₂SO₄ at 368 K and 50 g/L pulp density, 93.4% Li, 66.2% Co, 96.3% Ni and 50.2% Mn were recovered in 240 min. In the presence of 5% H₂O₂ as a reducing agent at 368 K with 1 M H₂SO₄ and 50 g/L pulp density, the leaching of cobalt (79.2%) and manganese (84.6%) were significantly improved in 240 min. With the addition of 0.075 M NaHSO₃ as a reducing agent, ~96.7% Li, 91.6% Co, 96.4% Ni and 87.9% Mn were recovered under similar conditions. Sodium bisulfite addition results in better recovery of cobalt and manganese by reducing them to their lower oxidation states. The HSC evaluation of thermodynamic feasibility vis-à-vis x-ray diffraction and scanning electron microscopy characterization of residues generated by leaching with hydrogen peroxide and sodium bisulfite substantiates the governing mechanism.

INTRODUCTION

Lithium ion batteries (LIBs) have represented a turning point in the field of power sources for a variety of applications because of their desirable characteristics,¹ such as high specific energy and energy density, low self-discharge, long life cycle, almost no maintenance, negligible memory effect, higher capacity, possibility of miniaturization and very thin form factors. LIBs will form an increasing proportion of the battery waste stream, as products using them reach the end of their practical life.² Recycling of these batteries is appropriate in order to recover valuable materials as well as for the sake of sustainability and safety hazards associated with disposal of spent lithium batteries.

Several methods have been proposed to treat spent LIBs in order to recover their metal contents.³ They include mechanical,^{4,5} thermal,^{6–8} and mechano-chemical processing,⁹ chemical leaching^{10,11} and bio-leaching.¹² To increase the leaching efficiency different types of reductants (H₂O₂,

NaHSO₃, biomass) are being used.¹¹ Hydrogen peroxide is generally used as a reductant during the leaching. The purpose of adding H₂O₂ and other reductants during the leaching is to reduce the Co³⁺ present in spent LIBs to Co²⁺ and Mn⁴⁺ to Mn²⁺, which are favourably solubilised compared with the unreduced moieties.^{11–13}

Considering the scanty resources of metals of interest for LIBs in general and environmental pollution associated with the disposal of the used batteries with the rapid growth of this sector in particular,^{14–17} it has become necessary to extract not only the cobalt but also other valuable metals such as Li, Ni and Mn while investigating the kinetics of leaching. The main crux of this article is to depict the non-effectiveness of widespread work carried out elsewhere using different lixiviants in the leaching of spent LIBs material with H₂O₂ as reductant, in which high acid concentrations along with high reductant concentrations have been used for the recovery of lithium and cobalt,¹¹ while in most cases the recovery of other metals of value (Ni

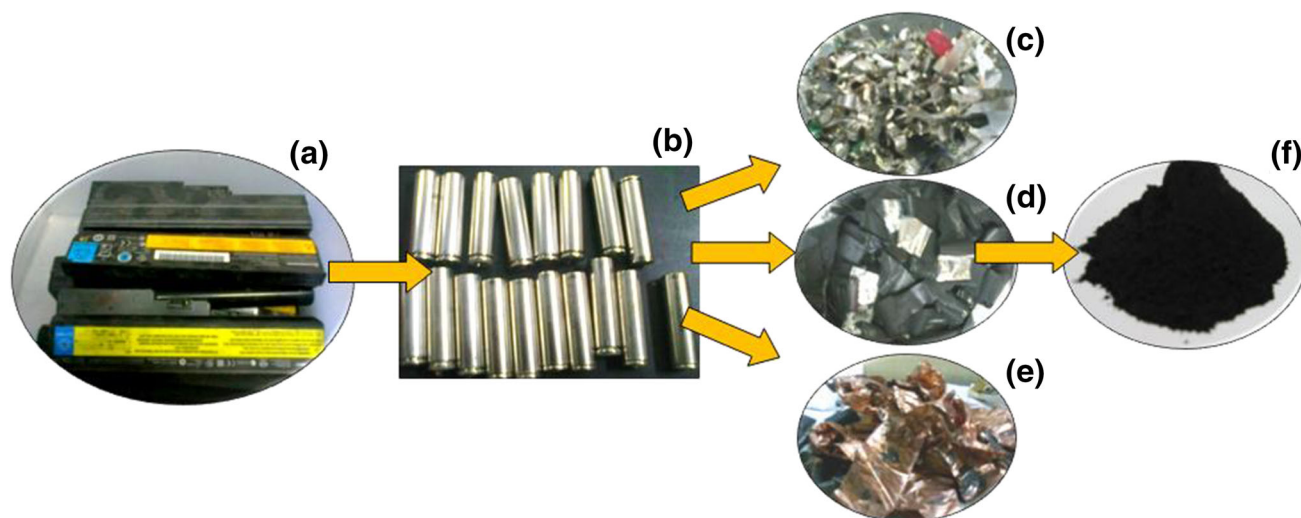


Fig. 1. Dismantling of spent lithium ion laptop batteries (a) spent batteries; (b) battery component; (c) steel foils; (d) cathode pack; (e) copper foil; (f) cathode powder.

and Mn) has been ignored. Therefore, this paper presents the sulfuric acid leaching process of cathode active material with the objective of comparing the two reductants, i.e., NaHSO_3 and H_2O_2 , which influence the kinetics of metal dissolution from cathode active material. These have been corroborated through Pourbaix diagrams in both systems vis-à-vis HSC evaluation, and by the characterization of the cathode material and the respective leach residues using x-ray diffraction (XRD) and scanning electron microscopy–energy-dispersive spectroscopy (SEM–EDS) techniques.

MATERIALS AND METHODS

Dismantling Spent Lithium Batteries and Separation of Cathode Active Material

Spent LIBs used in this work were kindly supplied by a local e-waste collection centre. The batteries (~20 kg) were first discharged before dismantling them manually, while removing the plastics and steel case mechanically. The anode and cathode were uncurled manually, and cathode active material in the form of powder was separated from the Al foil by heating it at 250–300°C for 30 min and storing for leaching studies. The particle size of the cathode powder was determined by a laser particle size analyzer (Malvern, UK); the particle size was found to be <20 μm and the average size 10–12 μm . The powder sample was analyzed for the phase identification by XRD (Bruker D8 Discover). All the chemicals used were analytical grade reagents. Figure 1 demonstrates a simplified pre-treatment flowsheet of the dismantling process. The outer metallic case is composed of aluminium and copper foil which can be directly recycled after dismantling.

Leaching of Cathode Active Material

All the leaching experiments were performed in a sensor-based temperature-controlled three-necked round-bottom flask (500 mL) fitted with a reflux condenser to avoid loss due to evaporation. To a known volume of the diluted sulfuric acid solution at a fixed temperature, the desired amount of the cathodic active material was charged and the slurry was agitated with a magnetic stirrer. The effects of varying the concentration of the reducing agent, pulp density, time of leaching, and temperature during the leaching of the metals was examined. A constant stirring speed of 500 rpm was maintained during the leaching. The progress of leaching was monitored by taking out samples at different time intervals and analyzing the metal contents after filtration. Upon completion of the leaching experiments, the slurry was filtered and the residue was dried overnight at 353 K.

Based on the analysis of the leach solution, the recovery of metals was determined. In a few sets of experiments, the mass balance was checked by computing the metal contents in the leach liquor and the residue. The metal concentrations in the leach solutions were determined by using an atomic absorption spectrometer (GBC-980TM) and inductively coupled plasma optical emission spectrometry (Varian, VISTA-MPXTM) after necessary dilution. The thermodynamic feasibility of the process was evaluated using HSC 7.1.4 software. The XRD phase identification in the dried leach residues compared to the untreated sample could be used to understand the progress of leaching of the metals. The surface morphology of the samples pasted on the brass stub after gold-coating and their elemental composition were determined by SEM attached with EDS (FEI-QuantaTM).

RESULTS AND DISCUSSION

The chemical composition of the cathode active material shows the presence of 35.8% Co along with 6.5% Li, 11.6% Mn and 10.6% Ni. Other metals such as copper, aluminium and iron are in trace amounts. The XRD analysis shows the presence of LiCoO_2 , $\text{Li}_2\text{CoMn}_3\text{O}_8$ and $(\text{Li}_{0.85}\text{Ni}_{0.05})(\text{NiO}_2)$ as the major constituents in the material. Besides this, lithium-nickel oxide of lower Li-Ni contents, $(\text{Li}_{0.69}\text{Ni}_{0.01})(\text{NiO}_2)$ (JCPDS file: 85-1970) and CoF_4 (JCPDS file 35-1314) were also present as the minor phases.¹¹ Figure 2 shows the mulberry bunch pattern of LiCoO_2 particles present along with large numbers of secondary particles rich in Ni and Mn.

Effect of Acid Concentration

The effect of H_2SO_4 concentration (0.5–3 M) on the leaching of Li, Co, Mn and Ni from the cathode active material of spent LIBs was measured in the absence of reductant at 368 K, 20 g/L pulp density and 500 rpm for 4 h. From Fig. S1, it can be seen that increasing the sulfuric acid concentration could enhance the leaching efficiency of cobalt and manganese. The leaching efficiency of cobalt increased from 43.3% to 66.2%, and manganese from 25.4% to 50.2% with an increase in acid concentration from 0.5 M to 3 M. Recovery of metals such as Li and Ni were found to be almost constant in the acid concentration range 1–3 M. The addition of sulfuric acid facilitated the forward reaction resulting in the increase in leaching efficiency,¹¹ and hence the concentration of 1 M was considered optimum for H_2SO_4 .

Effect of Reductant Concentration on the Leaching of Metals

Reducing agents enhance the solubility of metals which hitherto have been solubilised to a lesser extent using only acid as leaching agent.¹¹ Thus, we have investigated sulfuric acid leaching in the presence of sodium bisulfite comparing its efficiency with hydrogen peroxide. In order to examine the effect of reductant concentration on the extent of metal dissolution, the concentrations of NaHSO_3 and H_2O_2 were varied in the range 0.25–10% and 0.5–2.6%, respectively. Other parameters maintained during the leaching include: temperature 368 K, H_2SO_4 concentration 1 M, pulp density 20 g/L and time 240 min.

The addition of reductant significantly improved the leaching efficiency of metals as shown in Fig. 3. The NaHSO_3 concentration slightly affects the lithium and nickel recovery but recovery of cobalt and manganese increased from 77.1% to 92.3% and 85.3% to 88.1%, respectively, by increasing the NaHSO_3 concentration from 0.5% to 1.5%.¹¹ The effect of H_2O_2 amount on the leaching of metals with 2 M H_2SO_4 indicates that the leaching efficiency increased from 55.6% to 80.2% for cobalt and 53.2% to 85.9% for manganese as the H_2O_2 amount increased from 0.25% to 5% (Fig. 3). However, the efficiency did not increase significantly when more than 5% H_2O_2 was used. Increases in the recovery of cobalt and manganese are attributed to the reduction of Co^{3+} to Co^{2+} and Mn^{4+} to Mn^{2+} states, and both these divalent forms dissolved readily in H_2SO_4 .¹¹ The leaching behavior of lithium and nickel is almost the same, which may be due to the fact that they hardly undergo any reduction

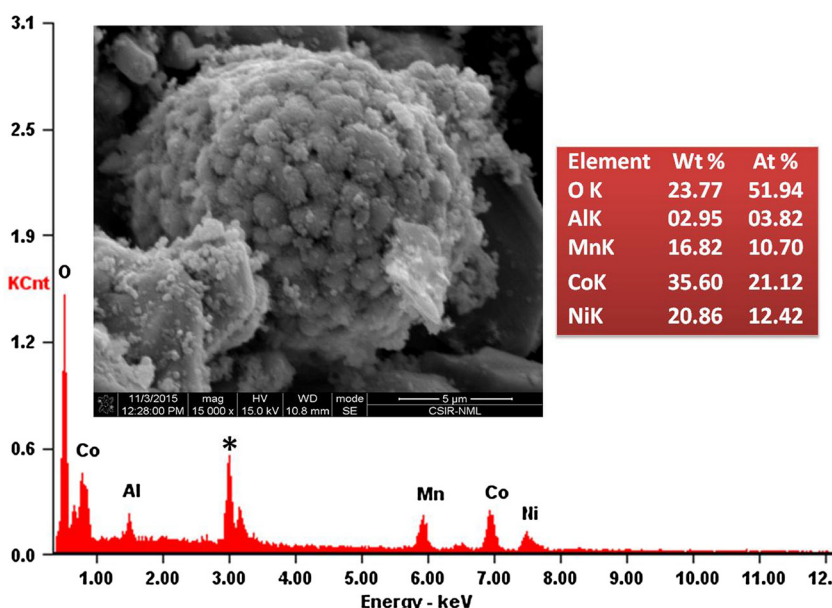


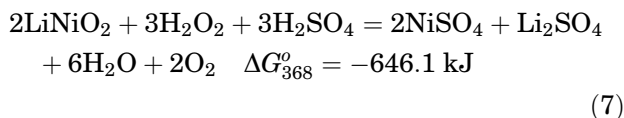
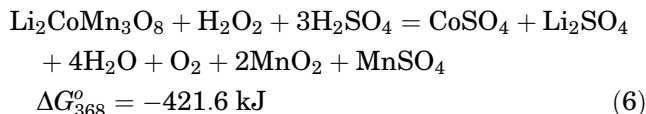
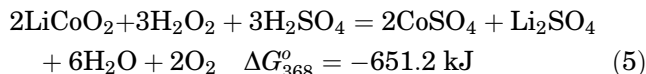
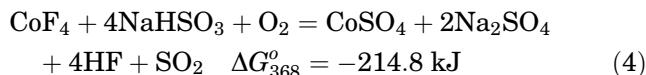
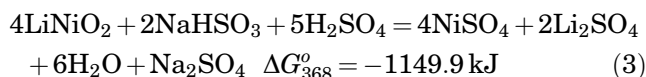
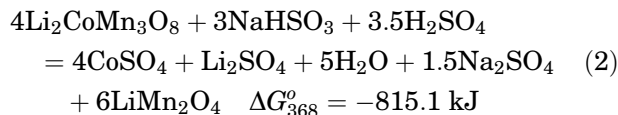
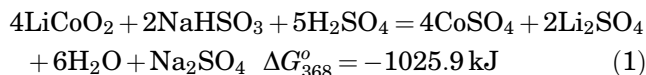
Fig. 2. SEM-EDS of cathode active material from spent LIBs (*Ag coating; Li not detected in EDS).

processes unlike cobalt and manganese. Hence, for other optimization experiments, the concentration of H_2O_2 is taken as 5% while NaHSO_3 is 0.78% (0.075 M).

The leaching characteristics and conditions can be predicted by the Eh–pH diagrams. Figures 4 and 5 depict the stability diagram of an individual metal ion in the presence of other constituents at 368 K and 50 g/L solids, respectively, for the sodium bisulfite and hydrogen peroxide system. The effect of a reducing agent on metal recoveries was investigated by addressing the redox potential (Eh) which was determined against a standard calomel electrode and computed by FACTSAGE®. In the absence of any reducing agent, the Eh of the solution could reach >900 mV over the leaching period of 2 h.¹⁰ Figure 4 shows that, by adding sodium bisulfite (0.5–1.5%) at 368 K, the redox potential of the solution decreased to ~400 mV throughout the leaching duration. However, on addition of about 5% H_2O_2 at 368 K (Fig. 5), the Eh of the solution decreased drastically, reducing to 580 mV throughout the leaching period. This clearly indicates that the concentration of reducing agent has a positive effect on metal extraction but only to a certain extent; above this range, the reaction rate becomes less dependent on the reductants concentration, and the mass transfer of reducing agent from solution to particles may no longer be the rate controlling mechanism.¹⁸

To elucidate the mechanism of leaching by two reductants, a thermodynamic study using the HSC Chemistry 7.14 software was carried out, which could predict the probability of reactions in the system, depending on the conditions, and was used to determine the values of standard Gibbs free energy change (ΔG°), which favored the improved dissolution of Li, Co, Mn and Ni in presence of NaHSO_3 as compared to H_2O_2 . Table S1 shows the values of ΔG° at 300°C for the estimated chemical reactions during the leaching with sodium bisulfite and hydrogen peroxide. Equations 1–4 describe the possible reactions of Li, Co, Mn and Ni in sulfuric

acid solution with the presence of sodium bisulfite. As seen, the major phases (LiCoO_2 , $\text{Li}_2\text{CoMn}_3\text{O}_8$, LiNiO_2 , CoF_4) present in the spent LIBs may form water soluble sulfates of Li, Ni and Co during the acid baking with relative lower solubility of manganese. However, Eqs. 5–7 refer to the reactions of the cathode powder with sulfuric acid solution in the presence of hydrogen peroxide. It can be seen that hydrogen peroxide in sulfate medium was not able to react with CoF_4 at 368 K, lowering the overall recovery of Co and also other metals.



It can be clearly seen from Table S1 that the higher negative values of free energy change for Eqs. 1 and 3 makes the reactions thermodynamically feasible, with the chemical entities being potentially leachable in sulfuric acid in the presence of sodium bisulfite.¹¹ This can be further in agreement with the recovery in shown Fig. 3.

Effect of Pulp Density

The effect of pulp density (5–100 g/L) on the leaching of the metals was studied in 1 M H_2SO_4 at 368 K and 240 min, and with different reductants, i.e., 5% H_2O_2 and 0.78% NaHSO_3 . The results are given in Table I and clearly show that the leaching efficiency of all the metals decreased as the pulp density increased.

When NaHSO_3 is used as the reductant,¹¹ the dissolution of all the metals is nearly constant in the pulp density range (5–20 g/L). At 5 g/L pulp density,

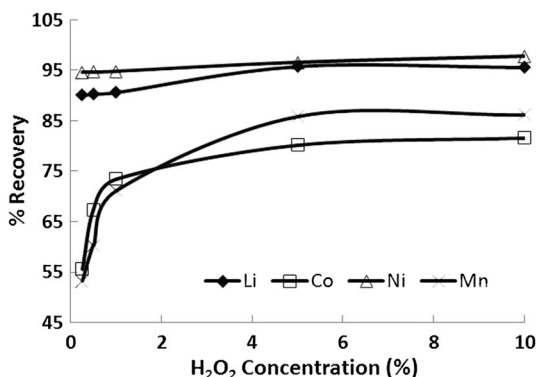


Fig. 3. Effect of concentration of H_2O_2 on leaching of Li, Co, Ni and Mn from cathode active material using 1 M H_2SO_4 , 20 g/L pulp density at 368 K in 4 h.

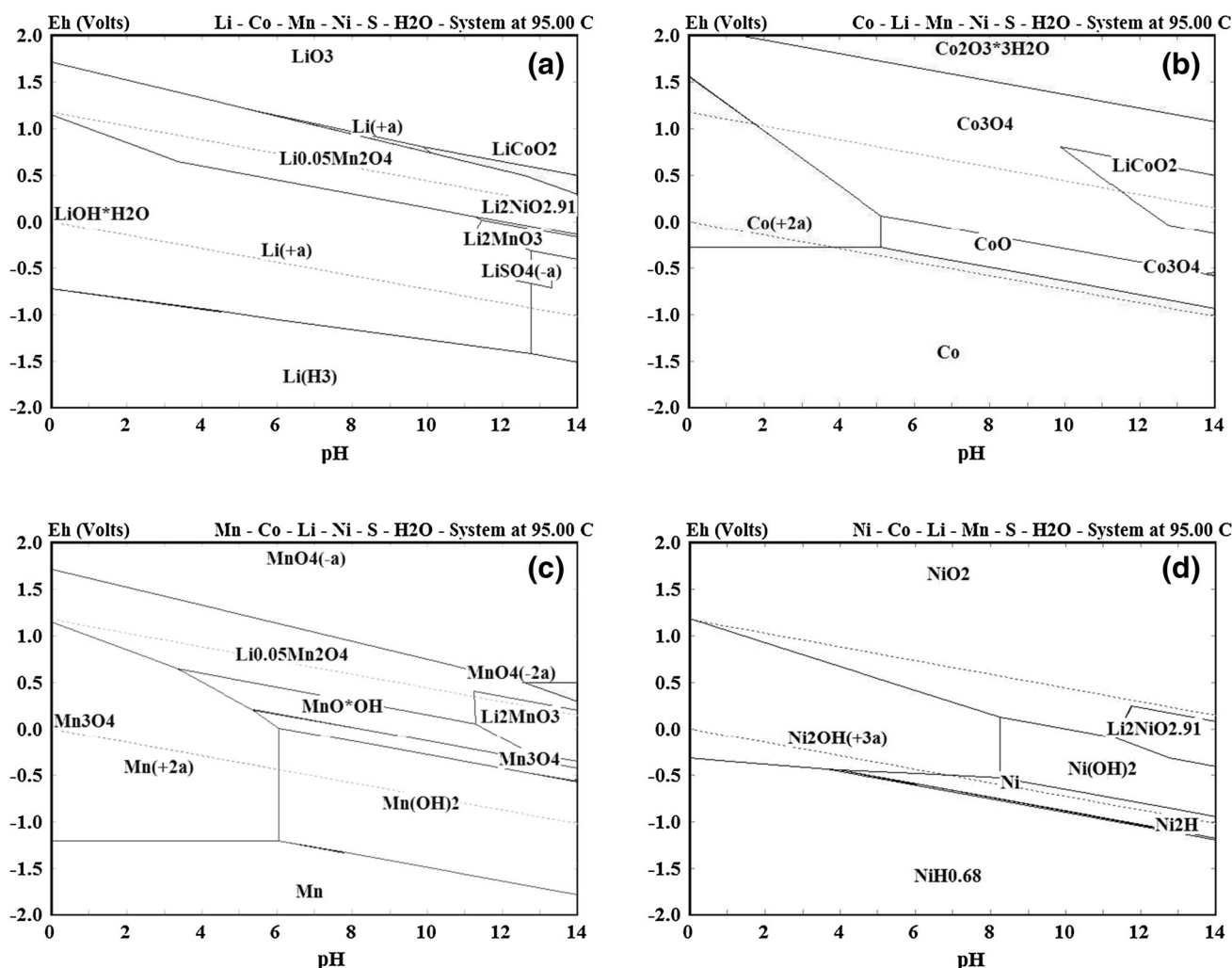


Fig. 4. Eh-pH diagrams (368 K) for NaHSO_3 system: (a) $\text{Li-SO}_3\text{-SO}_4$, (b) $\text{Co-SO}_3\text{-SO}_4$, (c) $\text{Mn-SO}_3\text{-SO}_4$, (d) $\text{Ni-SO}_3\text{-SO}_4$, in the presence of other elements.

about 96.9% Li, 92.8% Co, 97.2% Ni and 88.9% Mn were recovered. With an increase in pulp density to 50 g/L the recovery of all metals decreased and 93.3% Li, 85.1% Co, 92.4% Ni and 83.7% Mn were recovered. Hence, 20 g/L pulp density has been taken as the most suitable for further optimization experiments using NaHSO_3 .¹¹

The dissolution of all metals is nearly constant in the pulp density range of 5–50 g/L when H_2O_2 is used as the reductant (Table I). In particular, 95.8% Li, 80.2% Co, 96.6% Ni and 85.9% Mn were recovered at 20 g/L pulp density. Increasing the pulp density to 50 g/L adversely affected the metal dissolution. The leaching efficiency of Li, Co, Ni and Mn was found to be 94.5%, 79.2%, 96.4% and 84.6% respectively at 50 g/L pulp density. Hence, 50 g/L pulp density was considered for the experiments where H_2O_2 is used as the reductant.

Effect of Time

The effect of time on leaching efficiency of metals was examined using 1 M H_2SO_4 at 368 K and different reductants (5% H_2O_2 and 0.78% NaHSO_3) at 20 g/L pulp density. As evident from Table II, the increase in leaching time increases the recovery of all the metals. When NaHSO_3 is used as the reductant, 82.2% Li, 70.5% Co, 81.7% Ni and 79.2% Mn was recovered in 60 min,¹¹ while with H_2O_2 as the reductant, 80.7% Li, ~64.3% Co and Ni and 57.6% Mn were recovered in the same time. Maximum recovery was obtained in 240 min, and 96.7% Li, 91.6% Co, 96.4% Ni and 87.9% Mn were recovered when NaHSO_3 was used as the reductant and 95.8% Li, 80.2% Co, 96.6% Ni and 85.9% Mn was recovered using H_2O_2 as the reductant. All metals have the same effect irrespective of the reductant except that the recovery of cobalt was high when NaHSO_3 was used as the reductant.

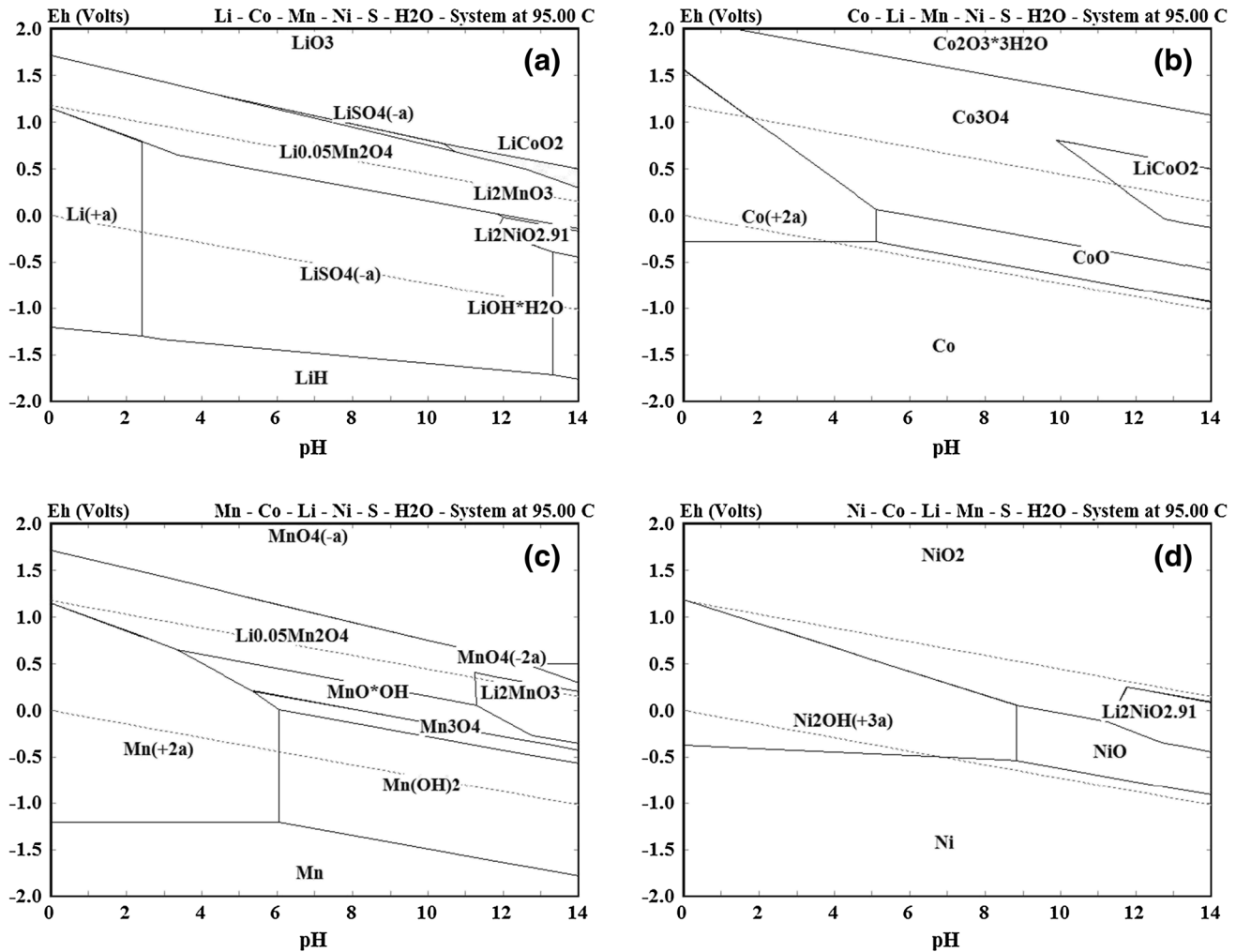


Fig. 5. Eh-pH diagrams (368 K) for the H_2O_2 system: (a) Li- SO_4 , (b) Co- SO_4 , (c) Mn- SO_4 , (d) Ni- SO_4 , in the presence of other elements.

Table I. Effect of pulp density (PD) on the recovery of constituent metals in the presence of both reductants in 1 M H_2SO_4 at 368 K and 240 min

PD (%)	% Metal recovery with different reductants							
	NaHSO ₃				H ₂ O ₂			
	Li	Co	Ni	Mn	Li	Co	Ni	Mn
5	96.8	92.7	97.2	88.8	96.3	82.3	97.5	87.0
10	96.8	92.6	96.9	88.5	95.7	81.6	96.8	86.4
20	96.7	91.6	96.4	87.9	95.8	80.2	96.6	85.9
30	94.6	89.3	94.7	85.5	94.6	80.1	96.4	85.3
50	93.3	85.1	92.4	83.7	94.5	79.2	96.4	84.6
60	90.1	82.3	88.6	79.21	88.3	74.2	93.3	81.4
100	89.3	80.5	87.6	78.9	86.1	72	91.3	79.2

Effect of Temperature

The effect of leaching temperature was studied in the range of 308–368 K for 240 min with 1 M H_2SO_4 , 20 g/L pulp density using NaHSO_3 with H_2O_2 as reductant. Table III shows the effect of

temperature on the leaching with 1 M H_2SO_4 at 20 g/L pulp density for 240 min with both reductants. The leaching efficiency of the metals increased with the increase in temperature, with maximum metal achieved in 368 K for both the reductants. When NaHSO_3 was used as the

Table II. Effect of time on the recovery of constituent metals in the presence of both reductants at 50 g/L using 1 M H₂SO₄ at 368 K and 240 min

Time (min)	% Metal recovery with different reductants							
	NaHSO ₃				H ₂ O ₂			
	Li	Co	Ni	Mn	Li	Co	Ni	Mn
5	58.21	51.65	65.11	72.12	56.26	31.85	43.54	25.65
15	66.57	55.02	69.84	73	63.4	43.6	48.21	34.23
30	72.87	60.31	72.14	74.31	70.8	54.87	52.33	42.07
60	81.63	68.87	78.78	74.56	78.43	62.11	62.01	55.64
120	89.78	80.22	87.21	78.34	89.22	72.01	70.84	76.54
180	90.26	84.32	90.14	80.21	90.44	75.45	80.32	80.14
240	93.25	85.11	92.36	83.69	94.5	79.21	96.4	84.62
300	94.55	85.85	92.66	84.03	94.65	79.55	97.03	85.4

Table III. Effect of temperature on the recovery of constituent metals in the presence of both reductants using 50 g/L cathode active material using 1 M H₂SO₄ in 240 min

Temperature (K)	% Metal recovery with different reductants							
	NaHSO ₃				H ₂ O ₂			
	Li	Co	Ni	Mn	Li	Co	Ni	Mn
308	82.35	63.65	80.08	70.64	70.1	47.21	60.4	42.55
323	86.24	72.44	85.04	72.36	76.3	49.9	72.21	46.37
333	88.32	76.48	88.65	77.57	82	59.6	84.36	61.27
348	90.27	83.62	90.88	80.72	90.2	69.3	91.3	72.5
368	93.25	85.11	92.36	83.69	94.5	79.2	96.4	84.6

reductant, <95% Li, Ni and ~90% Co, Mn were recovered, while with H₂O₂ recovery lowered to ~80% Co and Mn. Increasing temperature may thus increase the mass transfer kinetics of the acid and reducing agent from solution to the particles. The reaction at the surface of the particles is also enhanced by increasing temperature, thus leading to increased metal dissolution and higher extraction efficiency. However, the temperature increase does not seem to have as great an effect on the extraction efficiency of Co and Mn as compared to acid and reducing agent concentration. Better performance of NaHSO₃ than H₂O₂ at high temperatures could also be attributed to the rapid catalytic decomposition of H₂O₂ by the effect of temperature (particularly at >40°C). This would presumably lead to excessive consumption/requirement of peroxide. In view of the priority of higher recovery, the optimum temperature was therefore capped at 368 K.

Kinetics of Leaching

The rate of a reaction between a solid and a liquid such as the system considered here can be expressed by heterogeneous models (Eqs. 8, 9). In a heterogeneous system, the overall rate expression becomes

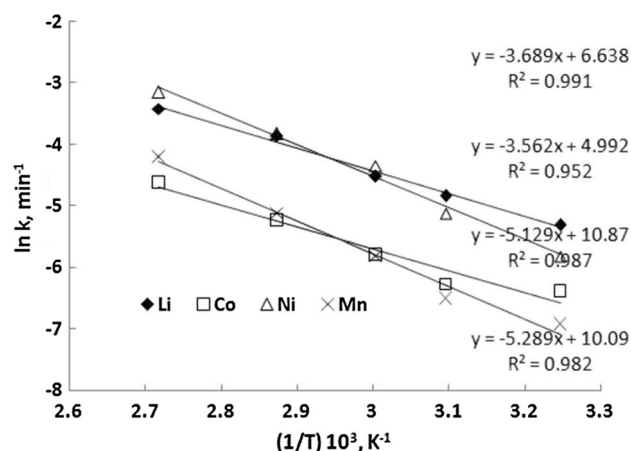


Fig. 6. Arrhenius plot for the leaching of Li, Co, Ni and Mn from cathode active material of LIBs at 368 K in the presence of H₂O₂.

complicated because of the interaction between physical and chemical processes. Therefore, dissolution of metals from spent battery material using sulfuric acid has been studied with different shrinking core kinetic models. In this model, the solid

reactant is considered to be non-porous with a spherical shape and is initially surrounded by a fluid film through which mass transfer occurs between the solid and the bulk of the fluid.¹¹ As

the reaction proceeds, a product layer forms around the unreacted core. With the increase of the conversion, the unreacted core of the particle shrinks and the layer of the product thickens. For this

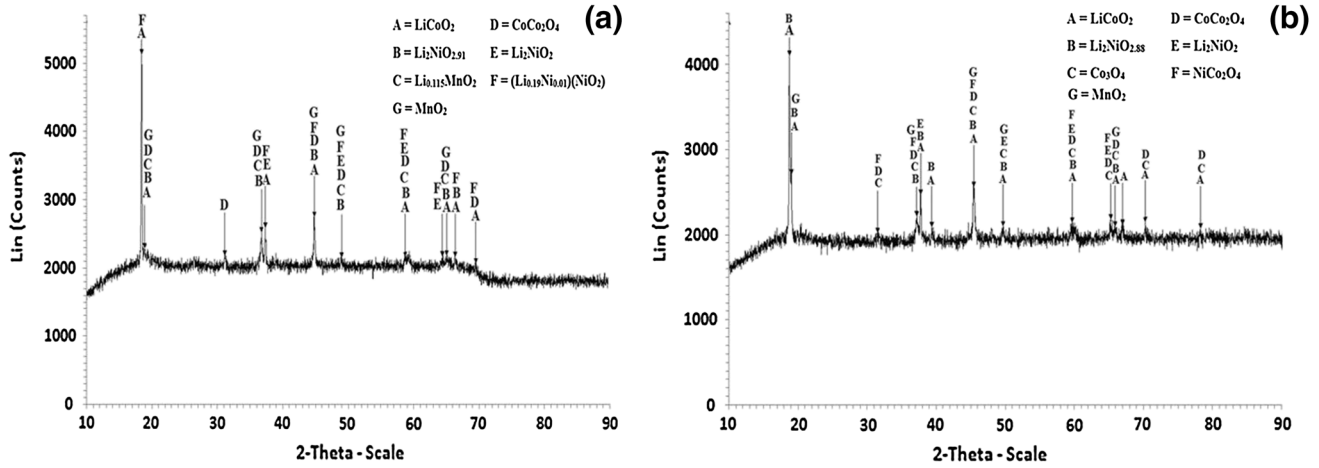


Fig. 7. XRD analysis of residue after treatment of spent cathode powder by H₂O₂ in (a) 1 h, (b) 2 h.

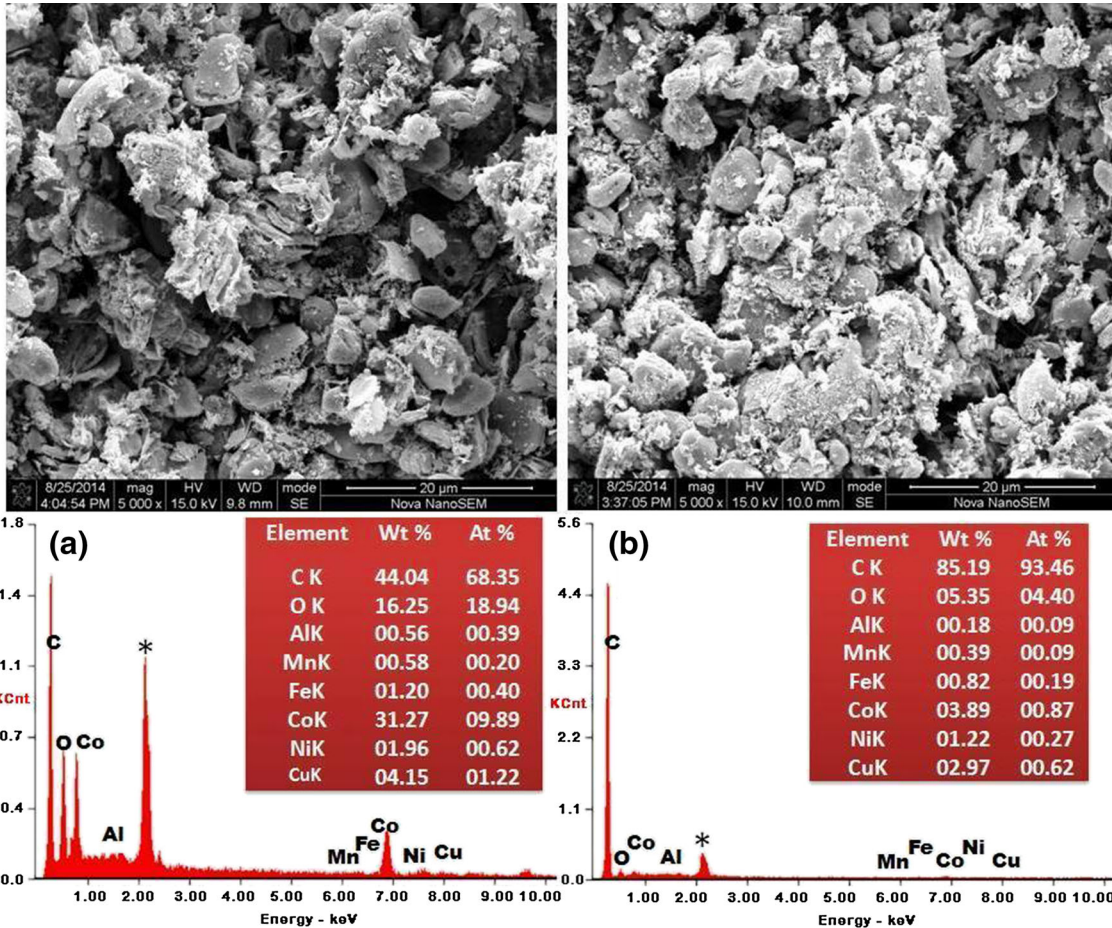


Fig. 8. SEM-EDS of leach residue with NaHSO₃ in (a) 1 h, (b) 2 h at optimized conditions (*Ag coating; Li not detected in EDS).

study, three shrinking core models were tested for a better understanding of the dissolution of cathode active material in H_2SO_4 in the presence of reductants.

$$1 - (1 - x)^{1/3} = K_c \cdot t \tag{8}$$

$$1 - (2/3)x - (1 - x)^{2/3} = K_d \cdot t \tag{9}$$

where, x is the fraction reacted in time, t (min), K_c is the chemical reaction rate constant (min^{-1}) and K_d is the apparent diffusion reaction rate constant (min^{-1}).

Kinetic data showed a poor fit for both the models with low correlation coefficients of these models for most metals. Hence, the data on kinetics of leaching were plotted to an empirical model based on the logarithmic rate law controlled by the surface layer diffusion of the lixiviant and given by Eq. 10.

$$(-\ln(1 - x))^2 = k_e \cdot t \tag{10}$$

where k_e is the specific rate constant for the empirical model. The plots of $-\ln(1 - x)^2$ versus t at different temperatures showed that the kinetic data fitted well to this model which is evident from the high values of the correlation coefficients (Table S2).

The specific rate constant obtained from the kinetic data (Table S2) were used for plotting the Arrhenius plot and to estimate the activation energy values for different metals (Fig. 6). The activation energy values (E_a) were calculated from the Arrhenius plots and found to be 20.4 kJ/mol, 26.8 kJ/mol and 21.7 kJ/mol for Li, Co and Ni, respectively, when $NaHSO_3$ is used as the reductant;¹¹ while higher activation energy was obtained when H_2O_2 is used. The activation energies with the use of H_2O_2 are calculated to be 30.7 kJ/mol, 29.6 kJ/mol, 42.6 kJ/mol and 43.9 kJ/mol, respec-

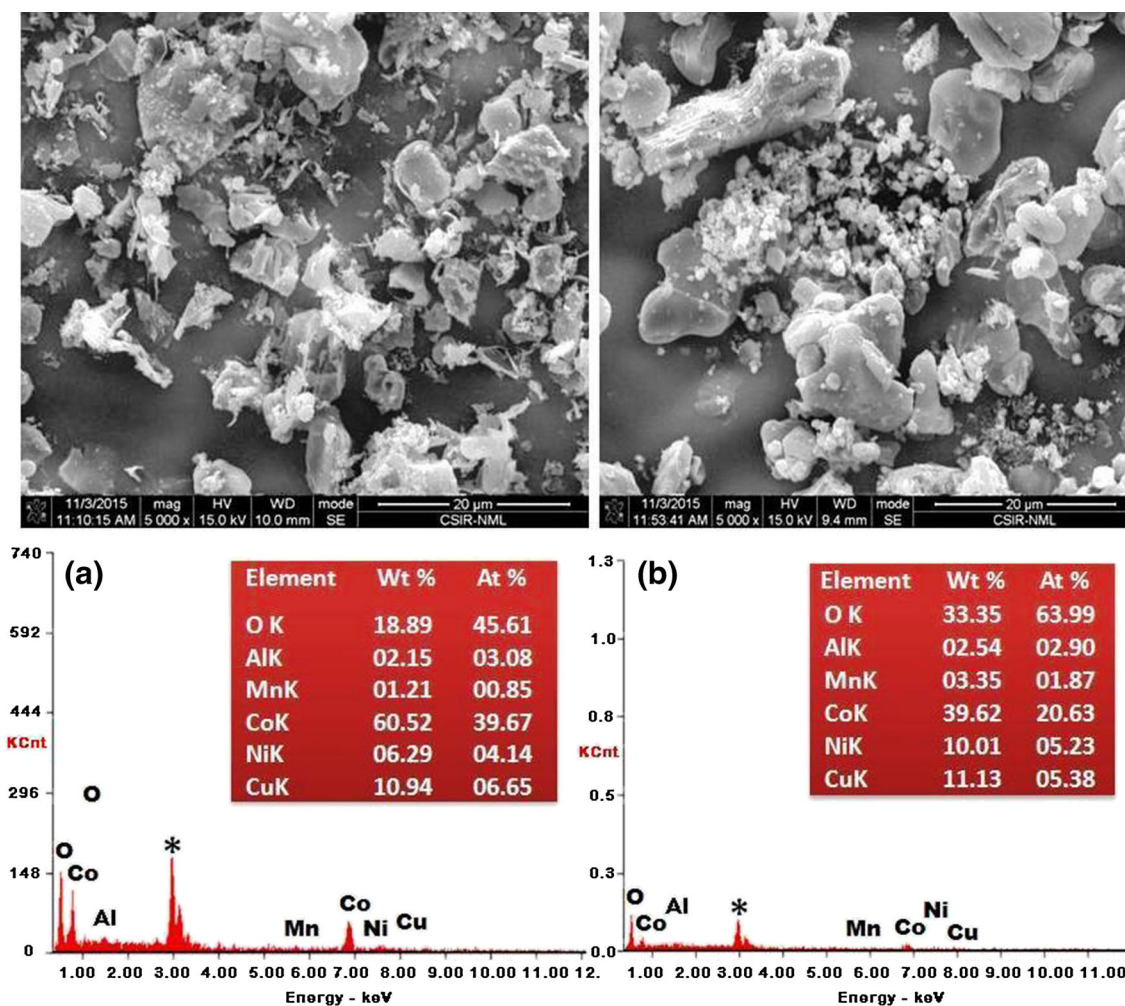


Fig. 9. SEM-EDS of leach residue with H_2O_2 in (a) 1 h, (b) 2 h at optimized conditions (*Ag coating; Li not detected in EDS).

tively, for Li, Co, Ni and Mn, which could be attributed to the resistance of the product layer on the diffusion of hydrogen peroxide to the reaction interface.¹⁹ It is known from the Arrhenius equation that an increase in temperature generally enhances reaction kinetics using NaHSO₃ as compared to hydrogen peroxide.

Mechanism of Metal Dissolution

XRD (Fig. 7) depicts the characterization of residues generated in presence of NaHSO₃ and H₂O₂ in 1–2 h. From the phase identification, it is clear that the intensity of the major phases is reduced progressively in different residues. On acid leaching the material in the presence of NaHSO₃ in 1 h, the major phases depicted a low ratio of lithium and other metals in the intermediate products, with Li₂CoMn₃O₈ (major phase in head) became minor phase in 1 h.¹¹ In 2 h, the lowering of all metal contents in non-stoichiometric entities improves the overall recovery. In the presence of 5% H₂O₂, the major phases detected were LiCoO₂, and there were lower non-stoichiometric entities of Li, Co and Ni in 1 h and only MnO₂ as minor phases (Fig. 7a). Progressing to 2 h did not change the major phases except that more secondary cobalt oxide phases were seen in the minor phases (Fig. 7b), and subsequently there was less overall selective dissolution.

The morphology of the cathode active material after leaching was examined by SEM–EDS (Figs. 8 and 9). With NaHSO₃, a decrease in metals covering the particle surfaces (Fig. 8a) with high Co reported in the EDS data was observed in 1 h. The improvement in the recovery of the metals with time was corroborated by the complete exhausting of the average content of most metals in 2 h, as depicted in the energy dispersive spectra (Fig. 8b). With H₂O₂ in 1 h (Fig. 9a), a very minimum degree of corrosion of particles in irregular morphologies along with large numbers of secondary particles were seen with higher metal content. Subsequent leaching in 2 h showed a better improvement in the corrosion of the particles and relative lower metal content (Fig. 9b). The characterization of the residues by XRD phase and SEM–EDS studies with time offer substantiation on the mechanism of leaching of constituent metals, which proceeds through the surface diffusion of the lixiviant on the reacting particles.

CONCLUSION

- The cathode active material of spent LIBs with Li, Co, Mn, and Ni, was subjected to sulfuric acid leaching using sodium bisulfite and hydrogen peroxide as a reducing agent.
- Using 1 M sulfuric acid without any reducing agent at 368 K and 50 g/L pulp density recovered 93.4% Li, 66.2% Co, 96.3% Ni and 50.2% Mn in 240 min.

- In the presence of 5% H₂O₂ at similar conditions, recovery of Co and Mn increased from 66.2% to 79.2% and 50.2% to 84.6% under similar conditions in 240 min.
- Addition of 0.78% NaHSO₃ recovered 96.7% Li, 91.6% Co, 96.4% Ni and 87.9% Mn under similar conditions. Sodium bisulfite addition lead to better recovery of cobalt and manganese by reducing them to their lower oxidation states.
- The leaching efficiency of all the metals decreased with an increase in pulp density above 20 g/L in the presence of sodium bisulfite, whereas hydrogen peroxide was found suitable for higher pulp density (50 g/L).
- The increase in leaching time increases the recovery of all metals. The leaching efficiency of metals increased with an increase in temperature with maximum metal recovery achieved in 368 K using both the reductants. The concentration of reducing agent and increase in temperature had a positive effect on metal extraction vis-à-vis the reduction in redox potential facilitated by the mass transfer of reducing agent from solution to particles, deeming it to be the rate controlling mechanism.
- The higher negative values of free energy change ($\Delta G_{368}^{\circ} = -1149.9$ kJ) for the reactions of cathode active material make it potentially leachable in sulfuric acid in the presence of sodium bisulfite and thermodynamically feasible.
- Kinetics of the leaching followed the logarithmic rate law where the values of the Arrhenius constant was found to be lower in the presence of NaHSO₃ as compared to H₂O₂, which was further corroborated with the XRD and SEM–EDS analysis of residues generated depicting the surface diffusion of the lixiviant on the reacting particles.

ACKNOWLEDGEMENT

The authors are grateful to the Director, CSIR-National Metallurgical Laboratory, Jamshedpur, India, for giving permission to publish the paper and providing financial assistance under the *iPSG Project No. OLP-192*. We also acknowledge the timely analytical support provided by Dr. A.K. Upadhyay of Analytical Chemistry Division, CSIR-NML.

ELECTRONIC SUPPLEMENTARY MATERIAL

The online version of this article (doi:[10.1007/s11837-016-2032-9](https://doi.org/10.1007/s11837-016-2032-9)) contains supplementary material, which is available to authorized users.

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