

Electrochemical performance of carbon materials derived from paper mill sludge[☆]

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Abstract

A pure, high surface area and cost-effective carbon-based material with possible application in electrochemical processes was synthesized from industrial sludge. Surface characterization included N₂-adsorption isotherm data and mathematical models such as the DR equation, and BJH methods. The extent of the purity was assessed from thermogravimetric analysis (TGA). The electrochemical properties, i.e. the potential use as electrode in Li ion batteries, were evaluated using conventional electrochemical testing such as charge/discharge cycling and impedance spectroscopy. The results of the data analysis were promising and indicated that paper mill sludge can be successfully used to produce a pure carbon for potential use in electrochemical applications.

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1. Introduction

One of the most promising approaches for the production of cost-effective, efficient carbonaceous materials is the reuse of waste sludge such as biosolids produced at municipal or industrial wastewater treatment facilities. The usage of waste sludge is especially important due to its mass production and resulting occupation of valuable landfill space. Studies conducted recently by Khalili et al. [1], Walhof [2] and Lu [3] showed that activated carbons with micropore structure can be produced from municipal wastewater treatment sludge and paper mill sludge successfully. The two major processes used for the production of these carbons are chemical and physical activation of raw materials. Chemical activation involves impregnation of raw materials with chemicals such as phosphoric acid [4], potassium hydroxide [5], or zinc chloride [6–8]. Among these chemicals, zinc chloride was proven to be one of the most effective activating agents [9–11]. The common feature of these

impregnants is their ability for carbonization and therefore development of the pore structure [9]. The degradation of cellulose material and the aromatization of the carbon skeleton upon ZnCl₂ treatment result in the creation of the porous structure.

This paper presents results of a study conducted to optimize a previously developed method of carbon production from municipal sludge in order to produce a pure, mesoporous carbon with potential use in lithium ion batteries. The significant feature of this study is that the developed process is able to produce a unique carbon-based material using waste materials such as paper mill sludge, whose disposal requires high-cost-labor intensive processes. The developed procedure for conversion of waste sludge to carbon-based catalyst offers significant potentials for reducing this cost and environmental damage resulting from uncontrolled disposal of the waste sludge.

The analysis conducted in this study has focused on optimization of the method of production, analysis of the surface properties, and characterization of the electrochemical properties of the resulting carbon.

2. Experimental

A series of carbons were produced from paper mill sludge following the procedures outlined in our previous work [1]. Pure carbons with close to zero ash content were produced

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by conducting a two-stage demineralization process using HF and HCl. The activated carbons were subjected to N_2 -adsorption at 77 K using Micromeritics ASAP 2010 Analyzer.

Characterization of the produced carbons included determination of the surface area, extent of the micro- and mesoporosity, and pore size distribution. To estimate the surface area the BET model was applied to the N_2 -adsorption data at a relative pressure of 0.05–0.2, where monolayer coverage of nitrogen molecules is assumed to be complete. The surface areas of the produced activated carbons were also evaluated from the α_s -plots [1,12]. The extent of the micro- or mesoporosity was determined from N_2 -adsorption data using the DR equation [14–16].

The Micropore analysis (MP method [3]) was used to determine micropore size distributions [1,17,18]. The t -values were calculated as a function of P/P_0 for the adsorbed nitrogen gas at 78 K using the Harkins and Jura equation. The mesopore volume distribution was calculated according to the BJH theory [14,15]. The BJH method is based on the Kelvin equation, which relates the relative pressure of nitrogen in equilibrium with the porous solid to the size of the pores where capillary condensation takes place.

Carbon films were prepared using copper foil and slurries of carbon mixed with a binder. The slurry was prepared by mixing polyvinylidene fluoride (PVDF) previously dissolved in 1-methyl-2-pyrrolidinone (NMP) with carbonaceous material (92% carbon and 8% PVDF). The mixture was allowed to unify by mixing it for 1 h at 250 rpm. The viscosity of the slurry was adjusted at 5000 cps by adding NMP to the mixture and monitoring the viscosity continuously using a viscometer (Brookfield DV-III+). The slurry was applied to a copper foil (current collector) using a Gardner coater. During the application, copper foil was maintained flat on a vacuum plate. Upon completion of the coating, the electrode was dried overnight under vacuum at approximately 100 °C. The thickness of the electrodes were adjusted with a callendering machine. The final coating density was 1.55 g/cm³.

Coin cells (2032) were prepared in a glove box under helium gas atmosphere, with a 9/16 in. laminate and lithium metal. The electrolyte was 1 M LiPF₆ in EC/DEC (1:1). A Celgard 3501 was used as separator. An Arbin cyler was used to apply a $C/10$ current density on the cell. In order to measure the dynamic impedance behavior, 30 s interruption was applied during charge and discharge processes and area specific impedance (ASI) was calculated for the tests.

3. Results and discussion

The produced carbons are identified as Zn_{3.5}C, and Zn_{3.5}C_d and Zn_{3.5}C_{d2} (d and d2 subscripts represents the extent of demineralization). The basis of the modern IUPAC classification, the Brunauer, Deming, Deming, and Teller (BDDT) theory was used to characterize N_2 -adsorption

isotherms obtained for these carbons. As previously shown [19], demineralization effectively impacts the characteristic of the carbon, and the shape of N_2 -adsorption isotherms.

The extent of the micro- or mesoporosity development and possible evolution of the pore structure via demineralization was further investigated by estimating the micro- and mesopore volumes and pore volume distributions from N_2 -adsorption data [1,12,20]. Demineralization in HF significantly impacts the size of the pores and characteristic of the pore size distribution. Double demineralization resulted in formation of a pure carbon with surface area of 1705 m²/g. The thermogravimetric analysis (TGA) graph obtained for this carbon also suggested that it contains less than 5% impurities (Fig. 1). The analysis of the N_2 -adsorption isotherms provided an approximate assessment of the pore size distributions. V_{DR} increases from 0.34 cm³/g (Zn_{3.5}C), to 0.48 cm³/g (Zn_{3.5}C_d) due to post-demineralization. Double demineralization, however, provided 0.53 cm³/g pore volume for Zn_{3.5}C_{d2} carbon. The estimated pore size for the Zn_{3.5}C_{d2} is about 60 Å. As shown in Table 1, demineralization of Zn_{3.5}C produced pure carbon with a significantly increased surface area and a higher micropore volume. The increase in surface area by 30% is the product of the complete removal of inorganic matter.

Fig. 2 presents the first and second cycles behavior of the carbon electrodes synthesized using C_{3.5}Zn_{d2} carbon. The plateaus found in this figure are the product of coexistence between two stages during cycling of the cell, and are very similar to what is expected from graphitic materials when they are subjected to Li intercalation.

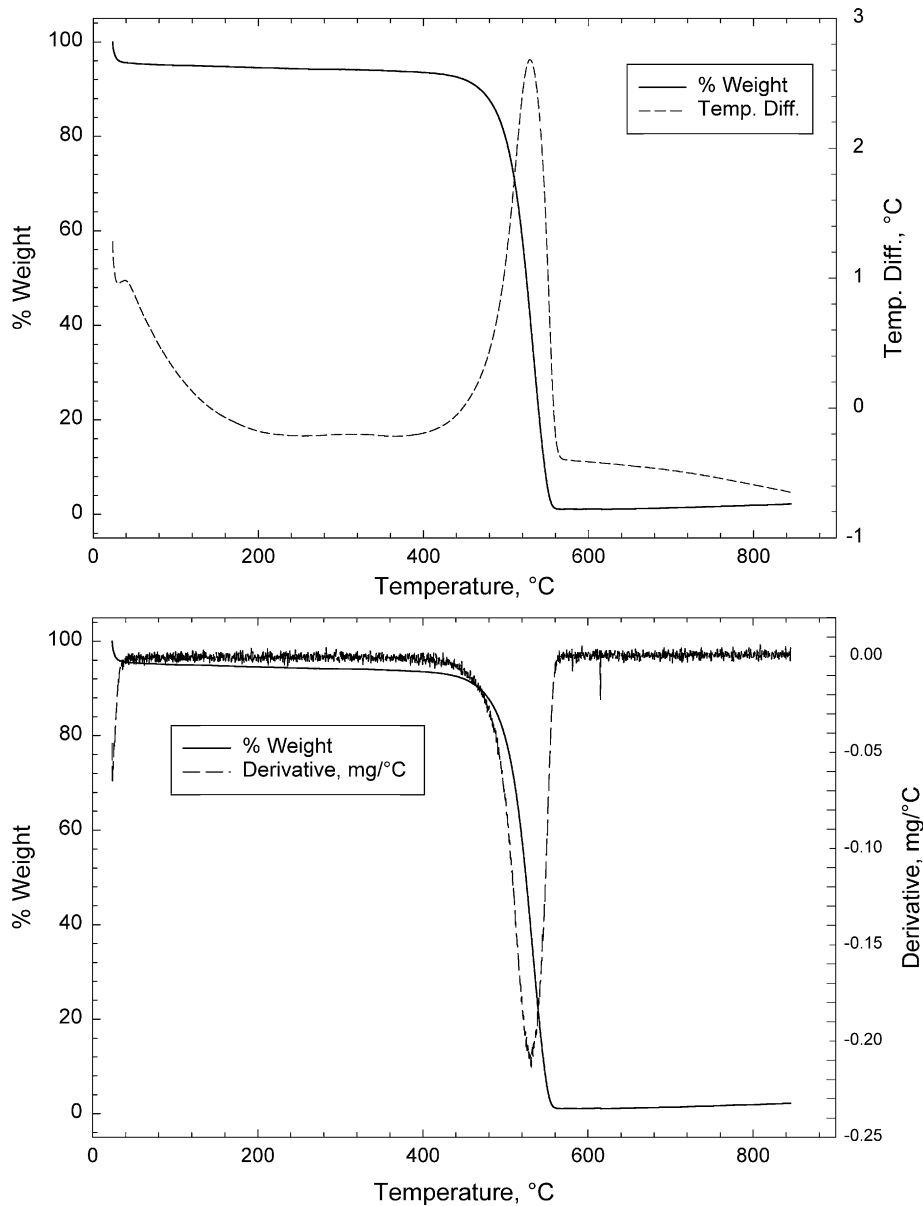
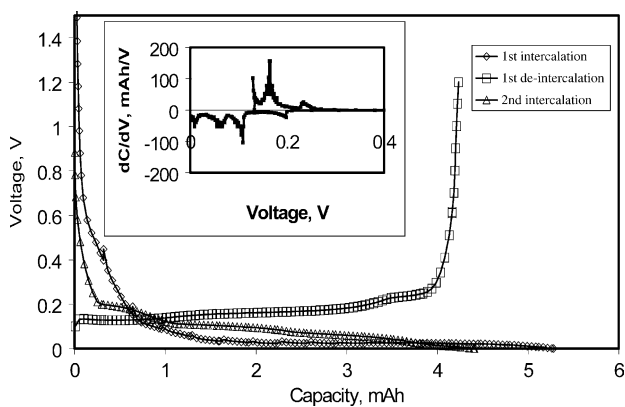
A plot of dC/dV versus V is also provided to obtain more information about these stages. The negative value stands for intercalation process and indented peaks represent reduction and oxidation reactions, which occur at each stage change. As shown before [21], due to staging phenomena it is difficult to see all of the changes clearly in the cycling processes. Clearly, four peaks can be observed during the intercalation process and three peaks during the de-intercalation.

Due to the high surface area of this carbon, we did not anticipate the observation of any staging, but rather, a voltage profile similar to that of disordered carbons, where the lithium insertion occurs close to 0.8 V versus Li. One possible explanation for this behavior is that this carbon contains pores with an estimated pore size of 60 Å. Lithium ions can easily diffuse through this matrix and the process is

Table 1
Results of N_2 -adsorption isotherm analysis

Carbon	V_{DR} (cm ³ /g)	Total pore volume (cm ³ /g)	Pore ^a diameter (Å)	Surface area (m ² /g)
Zn _{3.5} C	0.34	1.32	60	1059
Zn _{3.5} C _d	0.48	1.52	36	1483
Zn _{3.5} C _{d2}	0.53	N/A	30	1705

^a Average diameter $4V/A$ by BET (Å).

Fig. 1. TGA of $Zn_{3.5}Cd$.Fig. 2. Cycle behavior of 2032 coin type cell with lithium metal as counter electrode. The inset is dC/dV vs. V plot.

reversible. In fact, Flandrois and Guerin [22] indicated that in high surface area carbons with closed pores, trapping of lithium in the closed pores is the main source of irreversibility. However, if the pores are open, the lithium ions should diffuse easily and the irreversible component is reduced.

The ASI plot is shown in Fig. 3. It is a very important property of the electrode because it provides information on the nature and magnitude of the electrochemical processes and mass-transport limitations. The average ASI value was found to be $50 \Omega \text{ cm}^2$. This value includes charge resistance, ohmic resistance, and part of diffusion resistance. As shown, the ASI versus capacity curves do not change with cycling. In each lithium ion de-intercalation process, the impedance decreases initially, and then it increases sharply at the end of de-intercalation since lithium ion in carbon layers

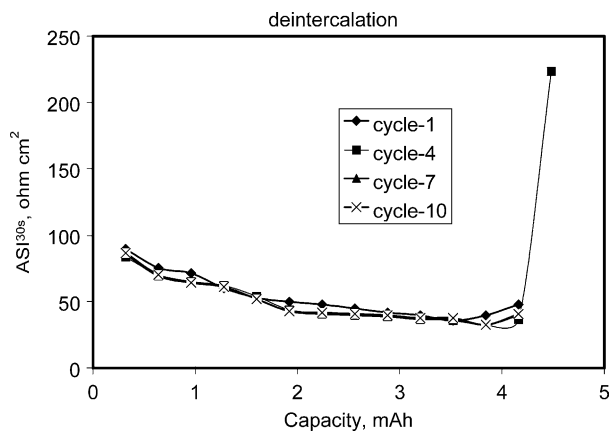


Fig. 3. ASI plot during de-intercalation process.

diminishes at the end of de-intercalation. The observed higher value at the beginning of the processes represents a crystalline structure which occurs after lithium ion is fully intercalated.

Fig. 4 represents normalized charge and discharge capacities and the efficiency calculated for each cycle. It is very clear that the irreversible capacity happens at the first cycle. The reversible capacity is shown to be about 340 mAh/g.

In order to reduce the irreversible capacity loss, which is caused by SEI formation [13], carbon anode materials with low surface area are commonly preferred. In the selection of anode material it is important to consider the fact that the irreversible capacity loss is not simply related to the BET surface area, since the edge area could play a more important role [23,24]. As shown, although carbon used for anode in this study has a BET area higher than 1700 m²/g (much higher than MCMB, which is around 5 m²/g), the irreversible capacity loss in the first cycle for this carbon is <20%, which is only about 5% higher than what is for MCMB, and after the first cycle the capacity is quite stable. In addition, no high capacity loss can be observed as process progresses. Considering the cost associated in the production of these porous carbons compared to that of modified graphites, as well as the environmental benefits of using waste materials,

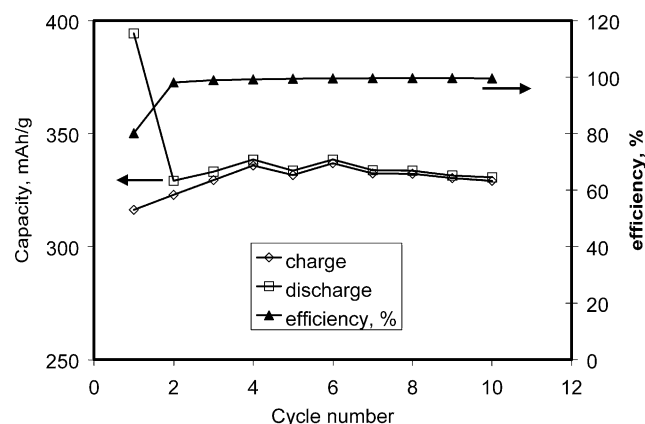


Fig. 4. Capacity retention and efficiency plot in 10 cycles.

they can be considered as excellent candidates for anodes in lithium anode cells.

4. Conclusions

The results of this study showed that paper mill sludge can be successfully converted to carbonaceous materials with specific end use in electrochemical processes. One of the most promising approaches for the production of cost-effective and efficient carbonaceous materials is the reuse of waste sludge such as biosolids produced at municipal or industrial wastewater treatment facilities. The usage of waste sludge is especially important due to its mass production and resulting occupation of valuable landfill space.

These carbons produced from paper mill sludge promise to be excellent candidates as anodes in lithium ion cells, although their BET surface areas are much higher than commercially available graphitic materials. The reversible capacity obtained for the produced carbons was 340 mAh/g, which is very similar to that of MCMB. A <20% loss of capacity after the first cycle and efficiency higher than 95% was obtained for the produced carbons. Results also suggested that porosity places a very important role in the diffusivity of lithium ions within the carbon structure, thus reducing the irreversibility upon cycling.

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