Temperature effect on surface energy of battery materials

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The demand for efficient and reliable battery materials has increased with the growing development of electric vehicles and renewable energy storage systems. Understanding the surface properties of battery materials, is crucial for optimizing battery performance. In this study, the Inverse Gas Chromatography-Surface Energy Analyser Nova (iGC-SEA Nova) technique is employed to analyse the surface characteristics of both anode and cathode materials. In this way, a comprehensive insight into their dispersive and specific surface energy behaviour is obtained, particularly looking at the impact of temperature, surface properties and surface heterogeneity, which are crucial parameters that affect battery performance.

Introduction

The widespread adoption of lithium-ion batteries is essential to everyday life powering a range of devices from smartphones to electric vehicles. Their high energy density, long cycle life, and relatively low self-discharge rate make them ideal for a wide range of uses. As the demand for energy storage solutions continues to grow, the need for thorough analysis of lithium-ion battery materials becomes paramount. The battery cell is derived from four main components: cathode electrode, anode electrode, separators, and electrolytes. The cathode electrode serves as the source of positive charge during the discharge cycle, typically made from materials like lithium cobalt oxide (LCO) or lithium nickel manganese cobalt oxides (NMC) active particles coated on an aluminum foil. The anode electrode, typically composed of graphite or silicon coated on a copper foil, stores and releases negatively charged ions during charging. The separator is a critical safety feature that prevents physical contact between the anode and cathode while allowing ionic movement, usually made from porous polymer films. Electrolytes, whether liquid or solid solutions containing ions, facilitate lithium-ion movement between electrodes, completing the circuit for energy generation and storage [1]. These components collectively determine a battery's

efficiency, energy density, and safety. Central to battery performance, safety, and longevity of these batteries is an often-overlooked factor: temperature. Understanding the effects of temperature on battery materials is important in the development and deployment of reliable and efficient energy storage solutions. This case study focuses on the relationship between battery materials and the effect temperature has on its surface energy. Surface energy dictates the interactions between electrodes and electrolytes, shaping crucial aspects of battery behaviour such as charge transfer kinetics, ion diffusion rates, and interfacial stability. Therefore, this knowledge can be used for battery design, operation, and optimization.

Method

Both anode and cathode active materials were analysed using the iGC-SEA Nova, a chromatographic technique specifically engineered for high temperature applications up to 500°C. Anode materials involved were natural spheroidized graphite and synthetic graphite, both

provided by ProGraphite GmbH. The cathode materials analysed were LCO - lithium cobalt (III) oxide, NMC 111 – lithium nickel manganese cobalt oxide and LFP – pure lithium-iron-phosphate, all purchased from MSE supplies LCC. Measurements were performed with various alkanes and polar probe molecules, all supplied by Sigma Aldrich. The alkane probe molecules hexane, heptane, octane, nonane and decane were used to determine dispersive surface energy. Ethyl acetate and dichloromethane were used to measure specific surface energy. Prior to measurements a pre-treatment was carried out for 2 hrs at their experimental temperature to remove impurities adsorbed on the surface. Natural graphite, LCO and LFP were analysed at 100°C and 120°C. Synthetic graphite and NMC 111 were analysed at 100°C and 70°C. The data was analysed with the Dorris and Gray methods and used the Della Volpe scale.

Result

Graphite is the state of the art anode material for lithium-ion batteries. However, recent developments have seen a shift in focus towards enhancing energy density by refining anode materials [2,3]. Research has shown promising potential for improvement, including the exploration of purer synthetic graphite and the incorporation of silicon into graphite matrices [4]. A series of alkanes were used to determine the dispersive surface energy using Dorris-Gray method and using polar probes, the specific surface energy was measured on both materials at different temperatures. Figure 1 shows the specific and dispersive surface energy of natural graphite measured at 100°C and 120°C. Figure 2 shows the specific and dispersive surface energy of synthetic graphite measured at 70°C and 100°C. As expected, the specific surface energy is very low, negligible, for both materials, which is due to the anode made primarily of carbon-based graphite. The dispersive surface energies are much greater. While the change in temperature does not seem to significantly affect the dispersive surface energy of natural graphite, that of synthetic graphite is influenced to a larger extent, as the dispersive

surface energies of 70°C and 100°C differ considerably. Furthermore, whereas natural graphite exhibits dispersive surface energies of around 120 mJ/m^2 at 100°C, those for synthetic graphite vary noticeably as values in a range from 110 mJ/m^2 – 170 mJ/m^2 are obtained. Therefore, the natural graphite proves to be the most homogeneous and stable one of the two materials. This is most likely due to differences in their production processes. Synthetic graphite is typically manufactured through high-temperature processes such as graphitization of carbon precursors like petroleum coke or coal tar pitch [5,6]. During these processes, various factors such as temperature gradients, impurities, and the presence of catalysts can lead to non-uniform growth and crystallization of graphite layers [6]. As a result, synthetic graphite can have a more diverse range of surface features, including variations in layer orientation, defects, and surface roughness. In contrast, natural graphite is formed through geological processes over millions of years, resulting in a more ordered and homogeneous crystal structure. While natural graphite can still exhibit some degree of surface heterogeneity due to factors like mineral inclusions and defects, it generally has a more consistent and uniform surface compared to synthetic graphite. Heterogeneity on the surface of natural and synthetic graphite anodes can lead to increased surface area, which provides more active sites for lithium-ion intercalation and deintercalation during charge and discharge cycles and may enhance electrochemical reactions and improve battery performance [7].
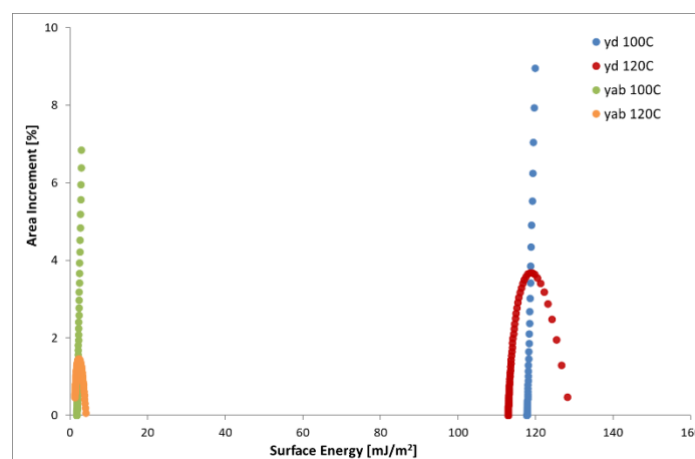

Fig 1. Dispersive (yd) and specific (yab) surface energy of natural graphite at 100°C and 120°C
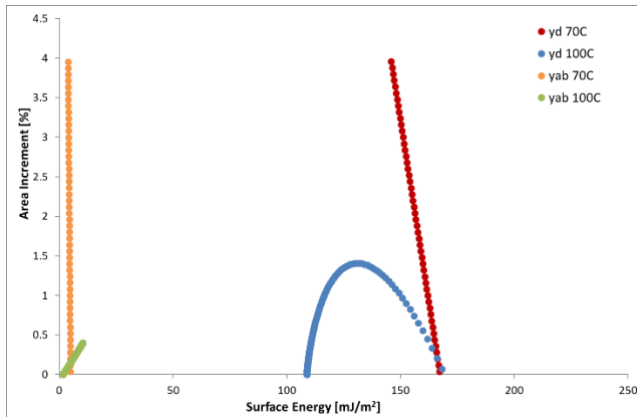
Fig 2. Dispersive (yd) and specific (yab) surface energy of synthetic graphite at 70°C and 100°C

Cathode materials LCO - lithium cobalt (III) oxide and NMC 111 - lithium nickel manganese cobalt oxide were also studied using the iGC-SEA Nova. Figure 3 shows that the chemical composition of LCO results in a higher surface energy than NMC 111 at higher surface coverages at the same temperature of 100°C. The dispersive energies of LCO and NMC 111 increase with increasing temperature. At higher temperatures, the mobility of lithium ions within the cathode material increases. This increased mobility allows lithium ions to move more freely between the cathode and the electrolyte, facilitating faster charge and discharge rates. Thermal expansion can also result in changes in cathode lattice structure. This creates more space between the atoms or ions within the cathode lattice, making it easier for lithium ions to diffuse and disperse throughout the material [8]. Consequently, the dispersive energy of the cathode material increases as it becomes more accommodating to lithium-ion movement.
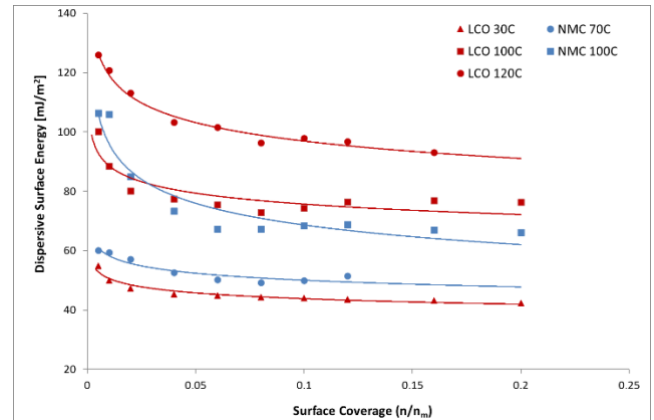

Fig 3. Dispersive surface energy of LCO and NMC 111 at varying temperatures

LCO was compared with another lithium-based cathode, LFP based on their dispersive and specific surface energies shown in Figure 4. Both have low specific surface energies and LFP has a higher dispersive surface energy compared to LCO. LFP cathodes have an olivine crystal structure, which consists of a three-dimensional network of lithium, iron, and phosphate ions. This crystal structure tends to expose a larger surface area compared to the layered structure of LCO cathodes. The increased surface area in LFP cathodes contributes to higher dispersive surface energy as there are more surface sites available for interactions with surrounding molecules or ions.
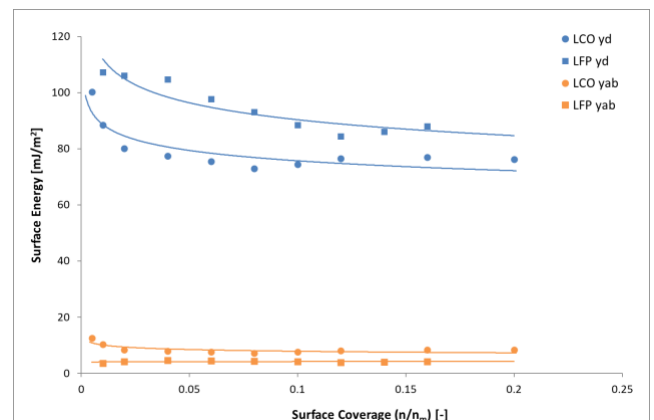

Fig 4. Dispersive (yd) and specific (yab) surface energies of LCO and LFP at 100°C

Conclusion

The iGC-SEA Nova has shown to be a useful tool in analysing the surface energy behaviour in anode and cathode materials at varying temperatures. Natural graphite is better able to withstand elevated temperatures without undergoing significant changes. As a result, batteries using natural graphite anodes may exhibit more consistent performance across a wider range of operating temperatures. However, the heterogeneous surface of synthetic graphite can improve ion diffusion kinetics for the transportation of lithium ions between the electrolyte and the bulk of the anode. Optimizing the surface characteristics of graphite anodes can help maximize the performance of battery materials. With regards to cathode materials, the differences in chemical composition and lattice structure influence its effects on surface energy at different temperatures. Increased dispersive energy of cathode materials at higher temperatures is primarily attributed to enhanced ionic mobility, thermal expansion, and heightened electrochemical activity, all of which facilitate the efficient dispersion and diffusion of lithium ions within the cathode structure.

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