



# Irreversible capacity and rate-capability properties of lithium-ion negative electrode based on natural graphite



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## ABSTRACT

In this paper, the results of experimental work with doped natural graphite are presented and described. The graphite material plays major role within negative electrode materials used in lithium-ion batteries. Behavior of graphite used as an active material for negative electrodes in lithium-ion cell was widely investigated and published. The one key characteristic property of graphite is its irreversible capacity loss. The irreversible capacity represents losses which occur in the graphite negative electrode within initial charge-discharge cycles (process called cell formatting). This phenomenon is associated connected with lower negative electrode potential vs. lithium (Li/Li<sup>+</sup>) and the growth of the Solid Electrolyte Interphase (SEI) layer. The SEI layer is important and necessary for proper operation of the lithium-ion cell; on the other hand growth of the SEI layer limits and lowers the theoretical capacity of lithium-ion cell by up to 40%. A possible way how to offset these losses is to dope the graphite material by lithium atoms before its use in the lithium-ion cell. The lithiation process has been studied as a possible way how to dope the (pre-lithiated) natural graphite prior to its use as an active electrode material. Suppression of irreversible capacity losses at initial charge-discharge cycles is the main focus of our investigation.

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## 1. Introduction

The lithium-ion technology seems to be the most promising electrochemical energy source for the future. From the release (1991) until now the lithium-ion batteries constantly develop and improve their parameters. Especially growth of the volumetric and gravimetric energy density, expanding the operation temperature window, lowering the price (approximately 8% per year), low toxicity etc. are all of the parameters that make this battery a leading type. The applications of lithium-ion batteries moved from only the small portable devices to traction propulsion of electric vehicles and to off-grid energy power storage systems in the megawatt hour range.

Development of a new generation of lithium-ion batteries will be necessary in order to satisfy the society and population requirements. Advanced batteries will be required not only for electric vehicles and consumer electronic devices but for wearable electronic devices, electric boats and aircraft, home backup energy storages etc. Today, lithium-ion batteries have almost 40% share of the global battery market production, followed by lead-acid

batteries, which take approx. 20% share of the market. Both types of these batteries vary in the application area. Whilst lithium-ion batteries are used in portable devices and more recently as electric storage for propulsion of electric vehicles, the lead-acid batteries domain is in the area of the starter batteries in conventional vehicles. It is very likely that the global market share of lithium-ion batteries will continue to rise in the following 10 years. In the long term evolution of the post lithium-ion batteries will take a part in battery market. As a post lithium-ion battery can be considered for example lithium-air (Li-air) and lithium-sulphur (Li-S) technology. In respect to growing world population and the demand for cheap and environment friendly energy storage solutions, the sodium-ion aprotic system can be considered as a solution. The main advantage of the sodium-ion system compared to lithium-ion is an abundance of sodium in the Earth's crust, which would lower price of the battery. These technologies are facing many issues and are still in early or advanced stage of research and development [1–18].

Current lithium-ion batteries use graphite as an active electrode material. The graphite serves as a host for lithium atoms which are inserted and accommodated within its graphene sheets. One of the important electrochemical reactions that occurs in negative electrode is the growth of a solid electrolyte interphase (abbreviated as SEI). The SEI characteristic properties are, that

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the layer is not permeable for solvent molecules, and that the layer allows only bare lithium atoms pass through. Additionally the SEI layer holds on the graphene layers that made the graphite lattice, together they thus prevent their exfoliation. The layer helps to retain lithium atoms inside graphene microcrystals (low self-discharge rate 1–2% per month), it can be attributed to the fact that the SEI layer has poor electron conductivity. From this point of view the SEI layer is essential for proper operation of a lithium-ion cell, on the other hand the SEI layer may significantly limit the potential capacity of the lithium-ion cell. As is depicted in Fig. 1 below, the SEI layer, during its growth, consumes lithium atoms that react with solvent molecules (reactants) which are transformed into products. The wide variety of polymer compounds and gases are formed. The consumption of lithium atoms in the process (named as irreversible capacity losses) leads to decreasing of the potential cell capacity in the range from 18 % up to 40%. These losses may significantly affect the gravimetric and volumetric parameters of the lithium-ion cell. The irreversible capacity losses are physically connected with the surface area of the electrode. Specific surface area of the electrode is very important graphite parameter that closely influences the cyclability, capacity and rate-capability characteristics. Many studies have shown that the particle size, particle surface area, solid-state and liquid-phase diffusion rates of the intercalated atoms, electrode thickness and electrode porosity can have a significant influence on the charge–discharge rates and utilization of the intercalation electrodes.

Battery performance and safety are highly dependent on the quality of the SEI layer. There is no option to avoid this kind of capacity losses. Especially in case of full lithium-ion cell and limited source of lithium atoms from positive electrode it plays an important role [19–26].

To suppress these undesirable effects and enhance the negative electrode rate-capability and capacity, the lithium doping process was examined and evaluated. The lithium doping idea comes from work patented in 2013 (US patent No. 8999584 B2) where thin lithium foil was placed on the electrode surface and pressed into it. This idea brings a lot of safety issues and does not solve the solid state insertion of lithium atoms into graphite grains. Current work is based on our former research where we used chemical lithiation with the help of *n*-butyllithium and electroless lithiation to lithiate and dope graphite, reported in Ref. [2]. Similar method is described in other articles focusing on hybrid lithium-ion supercapacitors and lithium-sulphur batteries [27–29].

In this paper our experiments with lithium doped process (lithiation) are described along with the results on overall electrode performance.

## 2. Experiments and methods

Our experiments are based on natural vein graphite (by Asbury Carbons Inc.). This graphite comes from the mines in Sri Lanka. The natural graphite sample marked as 280H, coming from Asbury Carbons (New Jersey, U.S.A.), mined in Sri Lanka (Fig. 3). The natural graphite sample 280H has got approx. 13 m<sup>2</sup>/g (obtained by data obtained from BET Brunauer–Emmett–Teller and BJH Barrett–Joyner–Halenda specific surface and pore size distribution analysis methods) and it is free of any treatment like e.g. CVD (Chemical Vapor Deposition) and primary is not classified for using in lithium-ion batteries (not battery grade) as active electrode material in negative electrode, but for manufacturing of automotive brake pads.

The experimental electrodes were prepared in conventional way by using a slurry composed from poly(vinylidene fluoride) (PVDF by Sigma Aldrich s.r.o.) as a binder, conductive additive C-ENERGY SUPER C65 hereinafter C65 by TIMCAL Ltd. The slurry was coated on coarsened copper foil by defined thickness 150 μm. All

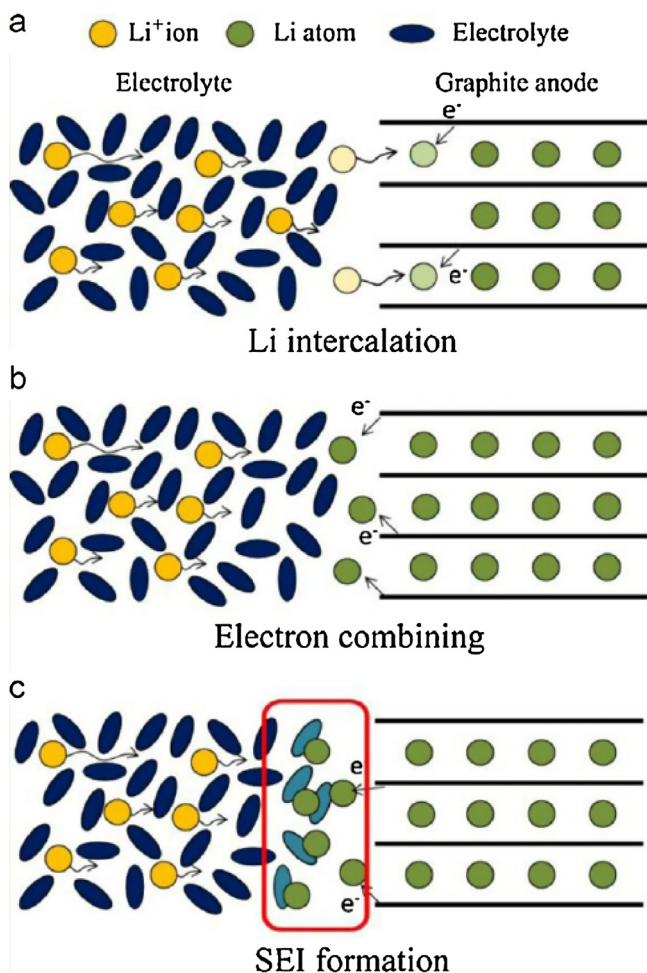


Fig. 1. Three steps describing SEI layer formation on electrode/electrolyte interface [1].

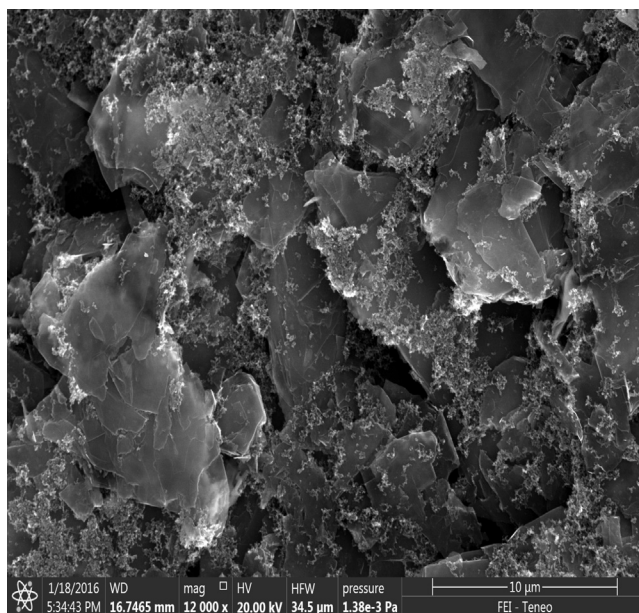


Fig. 2. The SEM images of electrode surface. The 280H flakes and amorphous carbon C65 areas can be seen.

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