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Electrochemical intercalation of fullerene and hydrofullerene with sodium

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A B S T R A C T

We herein report on the ability of fullerene C_{60} and hydrogenated fullerene $C_{60}H_x$ (x~39) to operate as negative electrodes in novel Na-ion batteries. Building upon the known solubility of C_{60} in common organic electrolytes used in batteries, we developed a suitably optimized solid-state Na-(polyethylene oxide) electrolyte for this application. Electrochemical and structural properties of the fullerene electrodes were investigated through cyclic voltammetry, fixed-current charge/discharge of the electrodes, impedance spectroscopy and powder X-ray diffraction. Both C_{60} and hydrogenated C_{60} have been electrochemically intercalated with sodium. Specific capacities after the first cycle are 250 mAh g^{-1} and 230 mAh g^{-1} for C_{60} and $C_{60}H_x$ respectively. However, C_{60} electrode shows a strong irreversible character after the first discharge, probably due to the formation of stable polymeric Na_xC_{60} phases, where Na^+ ions diffusion is hindered. On the contrary, $C_{60}H_x$ displays better reversibility, suggesting that hydrogenation of the buckyball could be effective to preserve sufficiently large interstitial pathways for Na^+ diffusion upon intercalation.

1. Introduction

Li-ion batteries (LIBs) are currently the most widespread rechargeable power sources employed in various portable devices [1], but one of their main drawbacks is represented by the relative scarcity of lithium in the Earth's crust, preventing their large scale implementation, especially in the automotive field [2]. The replacement of lithium with sodium offers an alternative strategy, since sodium is largely available in nature [3]. The chemical similarity shared by the two alkali metals allows a partial recover of the Li-ion battery technology for Na-ion batteries (SIBs); in fact, as far as cathode materials are concerned, several layered transition metal oxides and fluorophosphates were already identified as suitable for commercial use [4,5]. However, typical anode insertion materials for LIBs, such as silicon and graphite, do not work in SIBs [3].

In particular, Na^+ does not intercalate easily in graphite for sterical reasons [6] and only stage-2 samples can be obtained, corresponding to a stoichiometry of NaC_{64}, which is unsuitable for applications [7]. By co-intercalating Na^+ into graphite with appropriate solvents, a reversible capacity of 150 mAh/g with high cycle stability was obtained in graphite negative electrodes operating with ether-based electrolytes, even if the intercalation is accompanied by a strong volume expansion [8]. Better performances can be reached by expanding graphite through oxidation, which can increase specific capacity up to 284 mAh/g, although with low efficiency [9]. The successful intercalation of sodium can be also obtained whenever the stacking order is lost, such as in hard-carbon materials. Hard-carbon and anthracite-derived electrodes proved to be potentially interesting as SIBs anodes, showing capacities of 355 mAh/g and 222 mAh/g respectively, which can be further increased by doping with nitrogen or boron [10]. Hard carbon electrodes are currently the most widely used carbon-based anode materials for SIBs, thanks to their low sodium intercalation potential below 0.1 V, even if they still suffer from high reversibility loss [11]. Several electrolytes and additives have been proposed to limit the irreversibility problems in carbon, by improving the formation of the solid electrolyte interphase (SEI) [12–14].

On the other hand, use of carbon nanomaterials as negative electrodes in SIBs, such as carbon nanotubes, carbon nanofibers and graphene related materials, proved to be effective to improve performances, in particular the rate capability in devices [15–19]. Recently, we found 248 mAh/g reversible capacity after 50 cycles in

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thermally exfoliated graphite oxide (TEGO), 491 mAh/g after 20 cycles in hydrogen-treated TEGO and up to 826 mAh/g reversible capacity after 25 cycles for Nickel nanoparticles decorated TEGO [20]. Such electrodes also displayed good rate capability, although Na^+ insertion was found to be largely irreversible and also related to pseudocapacitive processes [21,22].

In this complex scenario, a possible alternative among carbonaceous anode materials for SIBs can be represented by fullerene-based compounds. Efficient macroscopic production of Buckminsterfullerene C_{60}, the best representative of this class of compounds, has been known since 1990, through the use of the Krätschmer and Huffman method, which is scalable at the industrial level, making available in principle large quantities of C_{60} for practical applications [23]. Alkali intercalation in fullerenes is another well-known process, which is accomplished by the progressive filling of the triple-degenerated narrow C_{60} LUMO band [24]. This can eventually bring to the onset of unconventional structural and electronic phenomena in fullerides, such as C_{60} polymerization [25,26], metal-to-insulator transitions [27] and even high-temperature superconductivity [28,29]. The redox properties of fullerenes received noticeable attention in the past, for their possible use as negative electrodes in LIBs [30–32] and up to six stable electrochemical states of C_{60} were found by means of cyclic voltammetry by operating with suitable solvents, such as acetonitrile and toluene, which proved the ability of the molecule to reversibly accept up to 6 electrons upon reduction (respectively -0.98, -1.37, -1.87, -2.35, -2.85 and -3.26 V vs Fc/Fc^+) [33].

A significant problem of fullerene films is however the increased solubility of fullerene anions in conventional solvents used as electrolytes, which would lead to the dissolution of the anode upon doping. In particular, $C60^{n-}$ turn out to be soluble in ethylene carbonate/dimethyl carbonate (EC/DMC) mixture commonly used in liquid electrolytes for LIBs and SIBs, while it shows low solubility in polyethylene glycol dimethyl ether (PEGDME) [34]. To overcome this problem, fullerene derivative polymers were proposed [35], as well as the use of solid polymer electrolytes instead of liquid ones [31,34].

Early studies on solid-state cells demonstrated the feasibility to electrochemically intercalate fullerene electrodes with both lithium and sodium. In particular, in the case of lithium doping, Chabre et al. [31] managed to insert up to 12 Li^+ ions per C_{60} operating with polyethylene oxide (PEO)-$LiClO_4$ electrolyte and pure C_{60} films, while Loutfy et al. highlighted exceptional capacities exceeding 1000 mAh/g in half-cells operating with hydrogenated C_{60} and C_{70} based anodes [34]. In the case of sodium doping, to our knowledge, very few works are indeed present in literature. Lemont et al. reported the intercalation of up to 6 Na^+ per C_{60} molecule using PEO based electrolytes, but the results are not clear, because strongly influenced by extrinsic conditions [31,36]. On the other hand, physical doping of fullerenes with sodium is a well-documented phenomenon [37] and, thanks to the formation of Na heteroclusters into the larger interstitial voids of the *fcc* C_{60} lattice, even the stoichiometry of $Na_{11}C_{60}$ can be reached [38]. Incidentally, this class of alkali cluster intercalated fullerides (with Li and Na) recently proved to be also highly efficient reversible direct and indirect solid-state hydrogen absorbers [39–42].

A renewed interest of the use of fullerene C_{60} as active material in novel ionic batteries arose from the evidence of room-temperature superionic conductivity in the Li^+ intercalated fullerene polymer Li_4C_{60} [43], which seems to be supported by the presence of sufficiently large three-dimensional pathways among C_{60} units, by the presence of intrinsic unoccupied Li^+ interstitial sites and by the coupling of the low-frequency optic modes of the Li^+ ions to the soft structure of the polymer [44]. Ion inter-site diffusion was observed also in Li_xC_{60} compounds at higher doping-level (where C_{60} polymerization is lost and Li^+ ions were found to clusterize in the octahedral voids of the *fcc* lattice), by means of Solid State NMR and impedance spectroscopy [45,46], and even in mixed Li-Na intercalated C_{60} phases [47]. However, in Li fullerides it was found that a sizeable electronic conductivity generally competes with ion diffusion, thus making these systems unsuitable for a direct use as solid-state electrolytes in Li-ion batteries [48–50]. It is worth noting that polymerized C_{60} lattice is also able to sustain sizeable Mg^{2+} ion diffusion at room temperature [51], thanks to the unique ability of fullerene to delocalize its charge on the entire cage, and recently secondary Mg-ion batteries with good rate performances were produced exploiting C_{60} as a cathode material [52].

In this manuscript, we investigate the ability of fullerene C_{60} and highly hydrogenated fullerene $C_{60}H_x$ (x~39) to operate as negative electrodes of novel all-solid-state Na-ion batteries. After the optimization of a suitable solid-state electrolyte, which was chosen due to the solubility of C_{60} in liquid electrolyte solvents, the electrochemical activity of C_{60} and $C_{60}H_x$ electrodes was probed with cyclic voltammetry, galvanostatic charge/discharge measurements, impedance spectroscopy and powder X-ray diffraction.

2. Materials and methods

C_{60} electrodes were prepared starting from commercial fullerene C_{60} (MER Corporation, 99+% purity) and $C_{60}H_x$ (MER Corporation, 99+% purity) powders. Here, $C_{60}H_x$ is a mixture of hydrogenated fullerenes with an average value of x~39. The active materials (85 wt%) were mixed with polyvinylidene fluoride binder (PVDF, Solef® 6010 and 6020 respectively for C_{60} and $C_{60}H_x$, Solvay, 10 wt%) and carbon-black (Super C65, Timcal, 5 wt%). Few drops of N-methyl-pyrrolidone (NMP, Sigma Aldrich anhydrous, 99.5% purity) were added and the resulted slurry was stirred for 12 h. Reagents were used as received, except for C_{60}, which was vacuum dried at 250 °C for 12 h beforehand, in order to remove possible traces of solvents. The electrodes were obtained by spreading the slurry on 100 μm thick aluminum foil or, alternatively, 300 μm thick copper foil using a notch-bar, and by evaporating the solvent with a thermal treatment at 65 °C for 12 h under dynamic vacuum. The electrode sheets were pressed with a flat-plate press at ~7000 kPa, then transferred in an Ar filled glove-box (<0.1 ppm O_2 and H_2O), where they were punched in 7 mm diameter discs.

Na solid electrolyte was obtained by dissolving polyethylene oxide (PEO, Sigma Aldrich, average molecular mass 10^6) and sodium iodide (NaI, Sigma Aldrich, 99% purity) in acetonitrile (Sigma Aldrich, anhydrous, 99.8% purity). The relative amount between PEO and NaI was chosen so that the ratio between oxygen atoms in PEO chains and sodium atoms in NaI was 10:1. Aluminum oxide nanoparticles (Al_2O_3, Sigma Aldrich, average size of 13 nm, 99.8% purity) were added as a 10% of the total PEO + NaI mass, in order to improve Na-ion conductivity [53]. PEO, NaI, and Al_2O_3 were vacuum dried respectively at 50 °C for 20 h, at 300 °C for 12 h and at 300 °C for 24 h before use. The suspension was stirred for 12 h, then the solution was drop-cast on a Teflon base with cylindrical sockets and left at rest till the complete evaporation of the solvent. All processes were performed under Argon atmosphere (Schlenk glassware or Ar glove-box). After the drying process, 12 mm diameter electrolyte disks were obtained, with an average thickness of 0.3 mm. More details can be found in the Supplementary Information (SI).

Solid-state Na-ion half-cells were assembled using a stainless-steel split test cell (MTI Corporation, 20 mm inner diameter) sealed with silicone O-rings. Each half-cell was composed of the C_{60}- or $C_{60}H_x$-based electrode supported on the aluminum or copper collector and sodium metal (~1mm thickness, Sigma