Abstract

Versatile, direct nanocasting strategy to N-rich ordered mesoporous carbons for selective post-combustion CO_2 capture and energy storage

Candidate: Elisa Maruccia

Supervisor: Prof. Claudio Gerbaldi; Co-Supervisor: Prof. Candido Fabrizio Pirri

Today the alarming increase of surface temperature, caused by uncontrolled greenhouse gases (GHG) emissions from the combustion of fossil fuels, is radically altering global natural ecosystems and endangering life on Earth. In this scenario, the implementation of new regulations in force became fundamental and indeed strictly necessary to arrest and, possibly, reverse this alarming trend and drive the urgent climate actions. Simultaneously, the commitment to the climate change mitigation involved the whole society, leading to a wide public participation. Hence, a large part of the research and industrial activity is nowadays devoted to the design of innovative technologies to replace fossil fuel-based energy production through electrification or pollutant sequestration from GHG sources through efficient sorption systems as the breakthrough target of our modern society.

Most of GHG emissions derive either from the transportation or manufacture and electricity production sectors. Focusing on carbon dioxide (CO_2), being the most abundant among GHGs and impactful to global warming, several strategies have been examined up to now for its capture before its release in the atmosphere after combustion processes, chiefly from large point sources. Nowadays, replacing the combustion of fossil fuels through electrification is the most valid strategy for reducing polluting emissions from the transportation sector. Concerning the prevention of GHG emissions from large-scale plants, Carbon Capture and Storage (CCS) technologies presently rely on CO_2 sequestration from exhausted gases, so as to avoid its direct release in the atmosphere. The challenging target in designing an efficient CO_2 sorbent deals with the fulfilment of several requirements, including, at first, a sizeable and selective capture ability in respect to the other components of the flue gas mixture. Likewise, an efficient reusability, intended as a complete and low-energy regeneration, as well as thermal and chemical stability under adsorption/desorption conditions are radically important. Finally, the sorbent manufacturing process must be sustainable, environmentally friendly, and cheap, thus assuring the feasibility of the whole entire production and utilization chain on a large scale.

Starting from these assumptions, this Ph.D. dissertation aims to tackle the above detailed issues by providing effective, sustainable strategies for the development of innovative, highly performing, selective CO_2 sorbent materials, namely nitrogen-rich ordered mesoporous carbons (NOMCs) by the nanocasting procedure. During the 3-years work, the above-mentioned NOMCs were synthesised, thoroughly characterised with the physico-chemical viewpoint and investigated mainly as efficient CO_2 sorbents. In addition, in an attempt to demonstrate the versatility of the

newly synthesised materials in other energy-related fields, their promising features as electrode active materials in lithium/sodium ion batteries were accounted by assembly preliminary "proof-of-concept" lab-scale cells, which provided stable cycling at relatively high capacity in a standard configuration.

The main aim of the research work was exploiting the peculiar regular porous network for improving gas diffusion and the accessibility of the specific adsorption sites. First, the nanocasting synthesis procedure enabled the desired design of the pore characteristics through the convenient choice of the ordered mesoporous silica hard template. Concurrently, the fine-tuning of the pyrolysis (performed at 600, 750 and 900 °C) of the D-glucosamine hydrochloride-based solution, *viz.* the environmentally friendly C/N source, enabled the successful development of the favourable microporosity and the introduction of basic N-species, which both proved to foster the specific interaction with the acidic CO_2 molecule. Hence, the innovative choice of the precursor and the synthetic route demonstrated to improve the adsorption features, while overcoming common post-synthesis modification procedures for microporosity introduction and basic N-sites incorporation. This investigation of the surface chemistry was effective in unraveling the respective role of the different types of nitrogen inclusions developed during the pyrolysis treatment, among which pyridinic-N was found to contribute most to CO_2 capture enhancement. Thus, the best performances in CO_2 capture at temperatures close to RT and in CO_2/N_2 mixtures were achieved by means of the low-temperature treatment, which allows the retention of a higher amount of N, in large part of the pyridinic type. The incorporation of N atoms provides some hydrophilic character in bare-carbon frameworks. Hence, the accidental competitive H_2O adsorption was considered in the evaluation of the CO_2 capture from wet flue gases. In this regard, the intermediate pyrolysis temperature of 750 °C allowed better preservation of the selectivity for CO_2 uptake in moist gas compositions.

Afterwards the reusability of the sorbents was investigated both in terms of multiple adsorption-desorption cycles from dry flue gas compositions and as the repetition of pure CO_2 capture after H_2O adsorption. In the former case, the performances of the NOMCs samples remained almost unvaried after 10 pure CO_2 adsorption/desorption cycles, with a regeneration step between two consecutive cycles under mild temperature conditions (i.e., 150 °C). Conversely, the repetition of the tests after H_2O adsorption revealed a considerable reduction in the CO_2 uptake. It was ascribed to the incomplete desorption of water from narrow micropores during previous tests, which makes a part of the preferential binding sites unavailable for the subsequent capture of CO_2.

In conclusion, the work presented in this Ph.D. dissertation represents a meticulous overview of the most efficient technologies presently available for the mitigation of the energetic and climate crises. Although the target remains certainly challenging and arduous, the achieved experimental results may effectively contribute to the comprehension of crucial mechanisms regarding gas adsorption and pave the way for future applications in the energy storage field, thus providing useful tools for directing the future research efforts in GHGs sequestration and, possibly, in the development of new alkali-ion secondary battery electrode materials.