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Introduction

World production of silicon (Si) reached (2010–2020) about eight millions of metric tonnes in the last decade. This quantity was produced mainly by the carbothermic silica (SiO_2) reduction. The process requires a large supply of energy and emits carbon oxides (CO_x). A fundamental challenge is the electrochemical silicon extraction from silica or other solids using electricity instead of harmful chemistries. Zero carbon footprint could be attained when using electrons as absolutely clean reduction agents generated by renewable sources. Electrochemical methods can be used on a wide scale of applications: extraction, purification, surface engineering, or thin-film technologies. Thus, silicon electrochemistry has the potential to significantly contribute to low-carbon economy; this field offers an advancement in environmentally friendly and secure technologies of energy generation and storage.

Breakthrough research topics have emerged in silicon electrochemistry in recent decades. The electrochemical formation of porous silicon (P-Si) was discovered in 1956 (Uhlir 1956). Canham reported in 1990 that a visible room-temperature photoluminescence from P-Si layer formed electrochemically on Si wafer (Canham 1990). The discovery inspired wide studies of P-Si for applications in optoelectronics, lasers, and sensors. Luminescent porous silicon nanoparticles were applied as the carriers of the drug payload, whose infrared luminescence enabled monitoring of the particles *in vivo* (Park et al. 2009). Electrochemical nano-micro-structuring of silicon has been widely investigated. The surface modifications increased the efficiency of photovoltaic (PV) devices used for solar energy harvest or for production of solar fuel. Silicon photoelectrodes have been successfully used for hydrogen and oxygen production by water splitting as well as CO_2 reduction (Sun et al. 2014). Electrochemically produced Si surface nano-architectures showed intrinsic quantum confinement effect. Electrochemical reduction of silicon dioxide to silicon in a molten salt electrolyte has been reported, which formed the basis for new processes in silicon semiconductor technology and high-purity silicon production (Nohira et al. 2003). Environmentally friendly and secure solutions offered silicon electrochemistry in high temperature molten salts (Juzeliūnas and Fray 2020). Electrochemical deposition of doped silicon as well as formation of p–n junction has been demonstrated (Zou et al. 2017, 2019; Peng et al. 2018). The approach has

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the potential of reducing capital cost and energy consumption for fabrication of solar cells when compared with the conventional manufacturing process.

This book features recent achievements in silicon electrochemistry, particularly, in electrochemical silicon extraction, purification, and processing in high-temperature molten salts. The introductory part of the book (Chapters 2–4) is devoted to general aspects of silicon application. A historical overview of silicon production is provided, and its importance in a low-carbon economy is considered. Chapter 4 addresses the physical and chemical properties of silicon, which are most relevant for electrochemical materials science. The subsequent material is more specific. Chapter 5 describes the major technologies used for silicon purification such as Siemens, Union Carbide, or Ethyl Corporation processes. This chapter also provides the principles of electrorefining in high-temperature molten salts, highlighting the advantages and disadvantages when compared with conventional industrial processes.

Chapter 6 addresses electrodeposition of thin layers and discusses the possibility of replacing multiple processes of Si wafer fabrication with one-step electrochemical deposition. Traditional manufacturing entails an energy-intensive and environmentally unfriendly production of metallurgical grade silicon (MG-Si), as well as its upgrade to solar grade silicon (SoG-Si), ingot casting, and slicing. Electrodeposition from molten fluoride, chloride, and oxide electrolytes on various substrates is discussed. A recently proposed strategy for electrodeposition of photoactive silicon and p–n junction is highlighted in detail. Silicon deposition from ionic liquids – the room-temperature molten salts – is also discussed in this chapter. Significant attention is given to the purity level of silicon electrodeposits, which are essential for photo-electrochemical applications.

Chapter 7 discloses photoelectrochemical (PEC) properties of silicon-oxide electrodes coated with ultrathin films of silica (SiO_2), hafnia (HfO_2), and alumina (Al_2O_3). The pivotal concept of PEC methodology is to obtain information, which correlates with that of the solid-state cells so that there is no prior need to design a solar cell that characterizes Si surface photo-responsiveness. Significant attention is given to studies of Si-oxide interfacial stability by the quartz crystal nanobalance (QCN) – a sensitive mass detector, which provides information about the electrode mass change with nanogram resolution *in situ* and in real time.

Deoxidation of metal oxides in a molten salt electrolyte was discovered in the year 2000 (Chen et al. 2000). The process was named the FFC Cambridge process. Simplicity and rapidity of the process have attracted global interest. Over 30 metals or semimetals were extracted from solid compounds by this energy-efficient and environment-friendly route. Chapter 8 addresses the FFC principle and its application in silicon reduction from silica. The electrochemical extraction provides a green alternative to conventional carbo-thermic silicon production. Chapters 9–12 provide further details on $Si–SiO_2$ conversion in molten salts. Voltammetry, basic reactions, and *in situ* studies by synchrotron X-ray diffraction are discussed, and experimental conditions used by many authors are summarized.

Technological opportunities carry out the operation at ultra-high temperatures and at liquid state of silica feedstock. Such processes are referred to as molten oxide electrolysis (MOE). Chapter 13 discusses the MOE principles of silicon extraction in a liquid state.

This study focused majorly on electrochemical surface engineering. Chapter 14 discusses the chemical–physical methods of silicon surface structuring, such as laser engineering and various etchings: chemical, photoelectrochemical, reactive ion, plasma immersion ion implantation, and metal-assisted chemical. The vapor–liquid–solid method is also discussed.

Chapter 15 features a comprehensive material obtained on electrochemical Si structuring at high-temperature molten salts including formation of black silicon (B-Si). B-Si is a nano-micro-porous material, which effectively absorbs the light on a wide range of wavelengths. Electrochemical Si structuring in molten salts is attractive due to its environmental friendliness, technical simplicity, and cost-effectiveness.

The book also outlines the perspectives of electrochemical synthesis of semiconductors (Chapter 16), the basic principles and materials for photo-electrodes, and the preservation of solar-fuel generators (Chapter 17).

In conclusion, while silicon electrochemistry offers a range of technological opportunities, most of the developments are still on the conceptual or bench-scale level. As a result, viable technological developments are still pending.

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