

Editorial

Clean Energy and Fuel Storage

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Abstract: Clean energy and fuel storage is often required for both stationary and automotive applications. Some of the clean energy and fuel storage technologies currently under extensive research and development are hydrogen storage, direct electric storage, mechanical energy storage, solar-thermal energy storage, electrochemical (batteries and supercapacitors), and thermochemical storage. The gravimetric and volumetric storage capacity, energy storage density, power output, operating temperature and pressure, cycle life, recyclability, and cost of clean energy or fuel storage are some of the factors that govern efficient energy and fuel storage technologies for potential deployment in energy harvesting (solar and wind farms) stations and on-board vehicular transportation. This Special Issue thus serves the need to promote exploratory research and development on clean energy and fuel storage technologies while addressing their challenges to a practical and sustainable infrastructure.

Keywords: thermal energy storage; electrochemical energy storage; hydrogen energy storage; salt cavern energy storage

The major focus of this Special Issue is to explore and innovate various clean energy and fuel storage systems that can be deployed successfully for the enhancement of clean energy portfolios for both stationary and automotive applications. It also seeks to address the underlying factors affecting the sequestration and capture of carbon by developing thermochemical energy storage or alternative fuel storage approaches, such as the atomic or molecular storage of hydrogen via solid-state materials. The submitted research papers were initially screened for their originality and novelty and then reviewed by three peer-reviewers, who are experts in the field, before their acceptance for publication in this Special Issue. One review paper and 15 journal articles were published in this Special Issue of *Applied Sciences*, a journal of MDPI publications. The contents of the published papers are categorized according to their nature and application type as (i) thermal energy storage (TES), (ii) electrochemical energy storage (EES), (iii) hydrogen energy storage (HES), and (iv) salt cavern energy storage (SCES) options. The following excerpts are based on the editorial briefing about the novelty and innovation of these 16 peer-reviewed published papers in *Applied Sciences*.

Thermal Energy Storage: The storage of heat energy in materials or other forms for chemical reactions is currently employed for concentrated solar power plants. During the daytime, the heat obtained from the abundant solar irradiation is focused on to dish/trough-type or central receiver-type antennas, where the heat is carried over by a fluid. The available heat is then circulated over the heat storage materials, for example phase change materials or waste slag. The heat is absorbed and hence stored in the material due to endothermic reactions, leading to the release of a gas or a change in the materials' phase structure. In the night hours, there is no constant heat available from the sun. Therefore, the material will release the heat due to external variations such as gaseous absorption or phase change due to cooling; this is referred to as an exothermic process. The reversibility of such TES

is then augmented for Concentrated Solar Power (CSP) and other potential applications. In this Special Issue, at least three research articles address the design and optimization of TES systems involving various materials. Michael Kruger et al. [1] demonstrated a type of new slag as an inventory material derived from an Electric Arc Furnace (EAF). Since the physical characteristics of these slag materials are similar to those of other refractory materials and ceramics, their performance with a unique design optimization for TES is evaluated for the Julich Power Tower Company in Germany. Based on the different optimization designs, the vertical TES with axial flow direction was found to perform the best in terms of aptitude value and lower risk value, as evaluated by Quality Function Deployment (QFD) and Failure Mode and Effect Analysis (FMEA), respectively. Since the conclusive decision and techno economic optimum was not made, further work is needed to understand the usability of such low-cost waste slag material for high-end CSP TES applications. Bilin Shao et al. [2] successfully developed and employed an enthalpy-based multiple relaxation time (MRT) lattice Boltzmann method (LBM) to calculate the transient heat characteristics of phase change material (PCM) roofs of green buildings in both hot summer and cold winter areas of China. The authors analyzed the life cycle energy savings of the PCM roof under an intermittent energy utilization condition by comparing it with the performance of a roof filled with sensible insulating materials (SIM). Paraffin was chosen as the PCM, whereas perlite was considered for the SIM since both of these materials have similar thermophysical properties and hence it is fair to compare them for roofing performance and energy savings purposes. Overall, the PCM roof was found to exhibit a better thermal performance than the SIM for energy consumption when the appropriate melting point and layer thickness of the PCM were selected. According to the authors, since the current paraffin PCM is expensive, new low-cost, high-chemical stability PCMs are yet to be explored for viable green building applications. Marie Duquesne et al. [3] reported a seasonal thermal energy storage material based on bio-glass such as Xylitol. The major drawback of utilizing Xylitol as a viable TES is due to its difficulty in the nucleation triggering (energy discharge triggering) process and hence its subsequent low crystallization rates (discharge power delivery). The authors devised a method to address the abovementioned obstacles by developing air-lift reactors that have sequential processes—namely, air bubble generation, the transportation of nucleation sites, and subsequent crystallization. The nucleation and crystal growth of Xylitol was successfully monitored at various times such as the induction period, the recalescence period, and the end period via thermal analysis measurements. The authors concluded that the new air-lift reactor and its underlying techniques are very promising to discharge the TES system based on pure Xylitol at the required power when needed. Further optimization of the bubbling conditions and air injection ratios will enhance the capabilities of Xylitol as a compatible phase change material for TES applications.

Electrochemical Energy Storage: An electrochemical energy storage device or a rechargeable battery is comprised of two electrodes (a cathode and an anode) and an electrolyte (liquid or solid). The secondary batteries mentioned above primarily convert the chemical energy contained in the active materials deposited on the electrodes into electrical energy by electrochemical reduction–oxidation (redox) reactions. There are many types of batteries based on the nature of the elements or compounds of the electrodes, such as nickel–cadmium (Ni–Cd), nickel–metal hydride (Ni–MH), lithium-ion (Li-ion), lithium–polymer (Li–pol), silver–zinc (Ag–Zn), nickel–hydrogen (Ni–H₂), sodium–sulfur (Na–S), zinc–air (Zn–O₂), etc. The energy density and power density are the two governing factors for the selection of the appropriate battery type for the desired applications. Additionally, the life cycle testing and charge/discharge rates, as well as the associated memory effects, must be considered for day-to-day applications in automotive operations, mobile phones, laptops, etc. In this Special Issue, one review paper on Li-ion batteries and three research articles on various EES systems were included, and are briefly described below. Dervis Emre Demirocak et al. [4] extensively reviewed the nanocomposite materials used in rechargeable Li-ion batteries. In this paper, the authors compared Li-ion batteries with other battery technologies such as lead–acid, Ni–Cd, and Ni–MH batteries in terms of chemistry, specific energy density, cycle life, cell voltage, self-discharge characteristics, safety, and toxicity. Based on this comparison, it is very clear that Li-ion batteries surpass the energy densities of the other samples

and are less toxic when compared to Ni–MH batteries. Moreover, Li-ion batteries are currently in demand and will certainly meet or exceed the 2022 US Department of Energy's target in terms of cost estimate thanks to engineering improvements and material advancements, as per the authors' review. Various low-cost, high-performance composite nanomaterials will replace the precious, high-cost, and toxic materials, for example in cathodic and anodic electrodes, binders, and separators within and throughout Li-ion batteries. The innovation of such composite nanomaterials will undoubtedly enhance the specific capacity, rate capability, and cycle life of Li-ion batteries while ensuring their overall safety. Additionally, this review captured the ideal electrochemical impedance spectra (EIS) of standard indium vanadium oxide anode electrodes with different voltages during charge/discharge cycles and the resistance-capacitance equivalent circuit. An advanced equivalent circuit model (ECM) was developed to determine the accurate state-of-charge (SOC) by Xin Lai and co-workers [5]. Some of the unique contributions of the abovementioned paper include: (i) it addresses the New European Driving Cycle (NEDC) and the Dynamic Stress Test (DST) and hence obtains a more suitable battery model for the entire SOC area, (ii) it identifies the subarea parametric classification method using the particle swarm optimization (PSO) algorithm to improve the global accuracy, and (iii) it extends the SOC estimator using a Kalman filter to improve the ECM's accuracy and robustness. As per the single particle model, the authors derived the SOC at the particle surface, $SOC_{surf} = SOC_{avg} + \Delta SOC$, where SOC_{avg} is the average SOC, meaning the average concentration of Li^+ in the electrode particle, and ΔSOC is the difference between SOC_{avg} and SOC_{surf} . An extended Kalman filter (EKF) model proposed by the authors showed greater accuracy than the ECM, specifically in low SOC areas. This is because the EKF model considers the noise characteristics of the current and voltage sensors, and effectively overcomes the problem of random errors. An optimal sizing of the electrochemical (battery) energy storage system for large-scale wind farms, considering auxiliary services compensation options such as scheduling plans, is outlined by Xin Jiang et al. [6]. This optimization model not only smoothens the fluctuations of wind output based on the wind peaking demand, but also compensates the wind output to make up the wind forecast error. The multiple steps of the abovementioned optimization model are given here. Firstly, the uncertainty regarding hourly fluctuations due to wind output are analyzed and then the associated auxiliary service cost of EES mitigation is quantified. Secondly, the equivalent life loss is introduced by considering the impact of the battery storage systems' irregular charge/discharge characteristics on the cycle life. It is shown by the authors that the cycle life exponentially decreases with the increase of the charge/discharge depth in terms of percentage. An optimum of 9000 cycles was demonstrated by this model for the charge/discharge depth of 20%. The results also showed that the EES system can be integrated with large-scale wind farms with investment costs of less than \$ 360/kWh. Moreover, cycle life of more than 2800 times can be achieved by taking into consideration of the auxiliary service compensation. In their excellent research paper, Pengfei Lu et al. [7] reported on the structure and capacitance of electrical double layers (EDL) at the graphene–ionic liquid interface via molecular dynamics simulations. Using this model, the distribution and migration of ions on the non-rough and rough electrode surfaces with different charge densities were compared and analyzed. The capacitance vs. voltage characteristic curves of EDL were obtained and corroborated with the electrode surface morphology on the capacitance of the EDL. Based on the detailed simulation results, it is clear that alternate distributions of anions and cations in several consecutive layers in the EDL could plausibly obtain the decaying amplitude characteristics along the direction perpendicular to the charged/uncharged electrode surface. In this alternate configuration, while charging occurs, the anions—for example, $[BF_4]$ —have a greater migration of ions when compared to the layers of cations—for example, $[EMIM]^+$ —due to the smaller size and steric effects of the anions. Finally, whether positively or negatively charging, the rough surface electrode with effective contact area between ions and electrodes possesses larger capacitance values when compared to the non-rough surface electrodes. An electrochemical method involving the anodization of TiO_2 foils was used to prepare titanium oxide nano arrays (TiO_2 -NTAs) for the application of dye-sensitized solar cells (DSSC) by Ho-Sub Kim et al. [8]. The preparation of photoanodes for the DSSC was carried

out with TiO₂-NTAs coated on the Fluorinated Tin Oxide (FTO) glass substrate using the sonication of precursor mixtures followed by the doctor blade process. The coating of silver nanoparticles (Ag NPs) or carbon materials (CMs) on the TiO₂-NTAs was achieved using wet-chemistry and chemical vapor deposition (CVD) techniques, respectively. This individual coating of Ag NPs or CMs on the TiO₂-NTAs led to an increase in DSSC efficiency by 15%. However, it was reported by the authors that Ag NPs and CMs were simultaneously coated on the TiO₂-NTAs, the DSSC efficiency doubled (30%) due to the coexistence and additive effects of two mechanistic phenomena—plasmonic interactions (due to the Ag NPs coating) and π - π conjugation (due to the CMs coating). Overall, the design characteristics and material's performance of the EES was optimized so that it can serve as an adequate storage unit for practical applications in solar, wind, and other potential sources such as DSSC.

Hydrogen Energy Storage: In order to fulfill the current demand of primary or secondary energy sources from non-fossil fuel options, hydrogen stands as the first candidate due its many advantages. Hydrogen as a lean burning fuel, has a higher energy content than carbon-based fuels, and, as the by-product of hydrogen is water vapor, it has no carbon footprint. Hydrogen is the lightest gas and can be generated by various primary sources such as solar, wind, etc., and utilized as a fuel in both residential and industrial sectors. However, its intermediate storage faces challenges due to its gravimetric and volumetric densities. There are at least three types of hydrogen storage—gaseous storage or underground H₂ storage, liquid hydrogen storage, and storage in metal/complex hydride or sorbent systems. Based on these classifications of hydrogen storage, in addition to hydrogen storage densities, other vital parameters such as thermodynamics, kinetics, cycle life, refilling time, toxicity, and safety must be considered for its full deployment as an alternative fuel. In this Special Issue, four papers focus on hydrogen storage for potential stationary or automotive fuel cell applications. Christina Hemme et al. [9] reported the potential risk factors associated with underground hydrogen storage in depleted gas fields via hydrogeochemical modeling (HGCM). This one-dimensional diffusive mass-transport model is based on the equilibrium reactions among gas–water–rock interactions and kinetic reactions for sulfate reduction and methanogenesis. The main risk of underground H₂ storage in depleted gas fields predicted by HGCM is the conversion of hydrogen to methane, CH_{4(gas)}, and H₂S_(gas) due to microbial activity, gas–water–rock interactions in the reservoir, and the loss of aqueous hydrogen by diffusion through the cap rock brine. According to the results obtained from this one-dimensional modeling, the authors recommended that depleted gas fields for underground H₂ storage possess low residual CO_{2(gas)} concentrations. Additionally, the mineralogical compositions of the reservoir rocks should contain low amounts of sulfate- and carbonate-bearing minerals, but high amounts of iron-bearing minerals. Metal hydrides employed as hydrogen storage systems, often demand the fulfillment of two important criteria such as thermodynamics and the kinetics. Though suitable alloying or mechanical milling can optimize the thermodynamics, the kinetics have intrinsic limitations, which require novel methods such as catalytic doping and nanoparticle formation, etc. Shahine Shafiee et al. [10] employed a novel magnetic field and studied its effects on the thermal reaction kinetics of a metal hydride storage bed. Since the candidate metal hydrides such as lanthanum pentanickellide (LaNi₅) and magnesium hydride (MgH₂) are paramagnetic in nature, the effect of an external magnetic field on the heat conduction and reaction kinetics of such metal hydrides were investigated by the authors. The rapid heat transfer in a metal hydride bed was observed when these hydrides were subjected to magnetic fields of 3–5 kGauss or less than half a Tesla. Regarding hydrogen absorption, the capacity of metal hydrides with enhanced kinetics was obtained for a high-intensity magnetic field (0.5 T), however, poor kinetics was obtained for the samples subjected with no field (0 T) or a low-intensity field (0.3 T). Overall, the deployment of a magnetic field in a metal hydride storage test bed was found to enhance the reaction kinetics to due to the greater heat transfer and solid–gas reactions. Since the abovementioned metal hydrides have limitations in terms of hydrogen storage capacity (LaNi₅ <1.5 wt.% H₂) and a faster sorption rate at moderate to high temperatures (MgH₂ ~300 °C), a new class of complex hydrides with better temperature and hydrogen storage capacities were demonstrated by Sesha Srinivasan et al. [11]. The new complex hydrides, involving lithium amide

and pre-processed magnesium hydride with different stoichiometric ratios ($x\text{LiNH}_2\text{-nanoMgH}_2$; $x = 1, 2$), were synthesized using a mechanochemical process under an inert or hydrogen ambient atmosphere. Another modification of the nano-catalyst additives on the base complex hydrides achieved faster desorption kinetics when compared to pristine (no catalyst additive) complex hydrides. Based on a detailed thermal gravimetric analysis (TGA) and thermal programmed desorption (TPD), kinetics enhancement occurred in the following order of catalyst type: $\text{TiF}_3 > \text{nanoNi} > \text{nanoTi} > \text{nanoCo} > \text{nanoFe}$. Furthermore, the highest reduction of the on-set decomposition temperature was obtained in the order of $\text{nanoCo} > \text{TiF}_3 > \text{nanoTi} > \text{nanoFe} > \text{nanoNi}$. Additionally, the absorption kinetics of 2 wt.% nanoNi on the base complex hydride ($2\text{LiNH}_2\text{-nanoMgH}_2$) was rapid (within the first 60 min of hydrogen absorption) at 200 °C when compared to the base material with no catalyst additive. The structural, microstructural, and chemical characterization supported the hydrogen sorption behavior of the complex hydrides. The abovementioned metal and complex hydrides were investigated for the purpose of using the stored hydrogen for either internal combustion (IC) engines as a lean burning fuel with available atmospheric oxygen or to be electrochemically combined with O_2 in a fuel cell to provide electrical output for stationary or automotive applications. One such combustion characteristic of hydrogen/air fuel for combustion via a four-point lean direct injection (LDI) system was simulated by Jianzhong Li et al. [12]. In this research paper, the authors designed and demonstrated a swirl-venturi 2 by 2 array four-point LDI combustor that can mix a hydrogen and air combustible mixture with different equivalence ratios. This simulation via the Reynolds-averaged Navier–Stokes code for steady-state computations enabled the authors to measure various parameters such as the axial velocity, swirl number, velocity angle, effective area, total pressure drop coefficient, total temperature, mass fraction of hydroxide (OH), and emission of the pollutant nitrous oxide (NO). As the equivalence ratios of hydrogen to air increased, the total temperatures and temperature rises of the co-swirling four-point LDI combustors also increased at approximately the same rate. When the equivalence ratio decreased from 1.0 to 0.6, the emission index of NO (EI_{NO}) reduced as well. Overall, this section of hydrogen energy storage, all of the described research papers addresses the deployment of hydrogen as an alternative fuel that can be readily available from solid-state hydride storage beds or hydride canisters.

Salt Cavern Energy Storage: In this Special Issue, problems related to the efficient storage of gases other than hydrogen via rock salt, carbonates, synthesis gas, etc. are considered as well. In addition to material characterization and property measurement, design aspects such as the cantilever fluid flow type or slurry bubble column type reactors are also important. Hongwu Yin et al. [13] determined and successfully demonstrated the optimum permeability and porosity of synthetic and mudstone rock salts for the assessment of natural gas storage facilities. Their study of a storage cavern and mudstone interlayer permeability was based on Jintan, in Jinansu Province of China. Gas slippage or the Klinkenberg effect was widely used by the authors to understand the gas flow in the low-permeability porous medium of the mudstone rock salt and/or layered rock salt. The permeability increased greatly when the porosity exceeded the value of 10%; hence, the permeability depends on the internal pores and microcracks as well as their interconnectivity. In a related work to the previous article on natural gas storage, Feifei Fang et al. [14] reported on carbonate gas reservoirs and the effects of water invasion in such reservoirs. An experimental system of water invasion in gas reservoirs with edge and bottom aquifers was established to simulate the process of water invasion. The effects of gas reservoir properties and production parameters such as water invasion energy, aquifer, production rate, permeability, and fracture were investigated systematically. The authors found that because of the physical simulation of water invasion, the elastic expansion of water–gas bubbles has greater influence. Additionally, the size of the aquifer and its production rate affect the water invasion in gas reservoirs with dissolved pores. The gas flow optimization for Fischer–Tropsch (F–T) synthesis was demonstrated by Siavash Seyednejadian et al. [15] via comprehensive computer modeling of a lab-scale slurry bubble column reactor (SBCR). According to this modeling, a set of partial differential equations in terms of mass transfer and chemical reactions was coupled successfully to predict the behavior of all F–T

components in both gas and liquid phases over the SBCR bed. The authors found that the temperature distribution of the slurry reactor remains constant under a base load and varying load conditions. The experimental findings agreed with the computer modeling in this study. Lastly, the theoretical work of Xinbo Ge et al. [16] established the dynamics of a hanging vertical cantilever that is subjected concurrently to internal and external axial flows. Additionally, theoretical predictions were obtained for a long leaching-tubing-like system with parameters related to salt cavern energy storage (SCES).

To summarize, in this Special Issue on “Clean Energy and Fuel Storage” features 16 peer-reviewed articles that can be divided in to four major types of energy storage: TES, EES, HES, and SCES. The discovery of novel materials and innovative design aspects are briefly discussed in this editorial section. The readers are encouraged to refer the full articles for detailed information.

Author Contributions: The authors of this editorial served as Guest Editors for this Special Issue on “Clean Energy and Fuel Storage”. Additionally, the authors S.S.S. and E.K.S. contributed to the review article on Li-ion batteries [4] and one research article on complex hydrides for hydrogen storage [11]. Both the authors contributed equally to this editorial and proofread for publication.

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