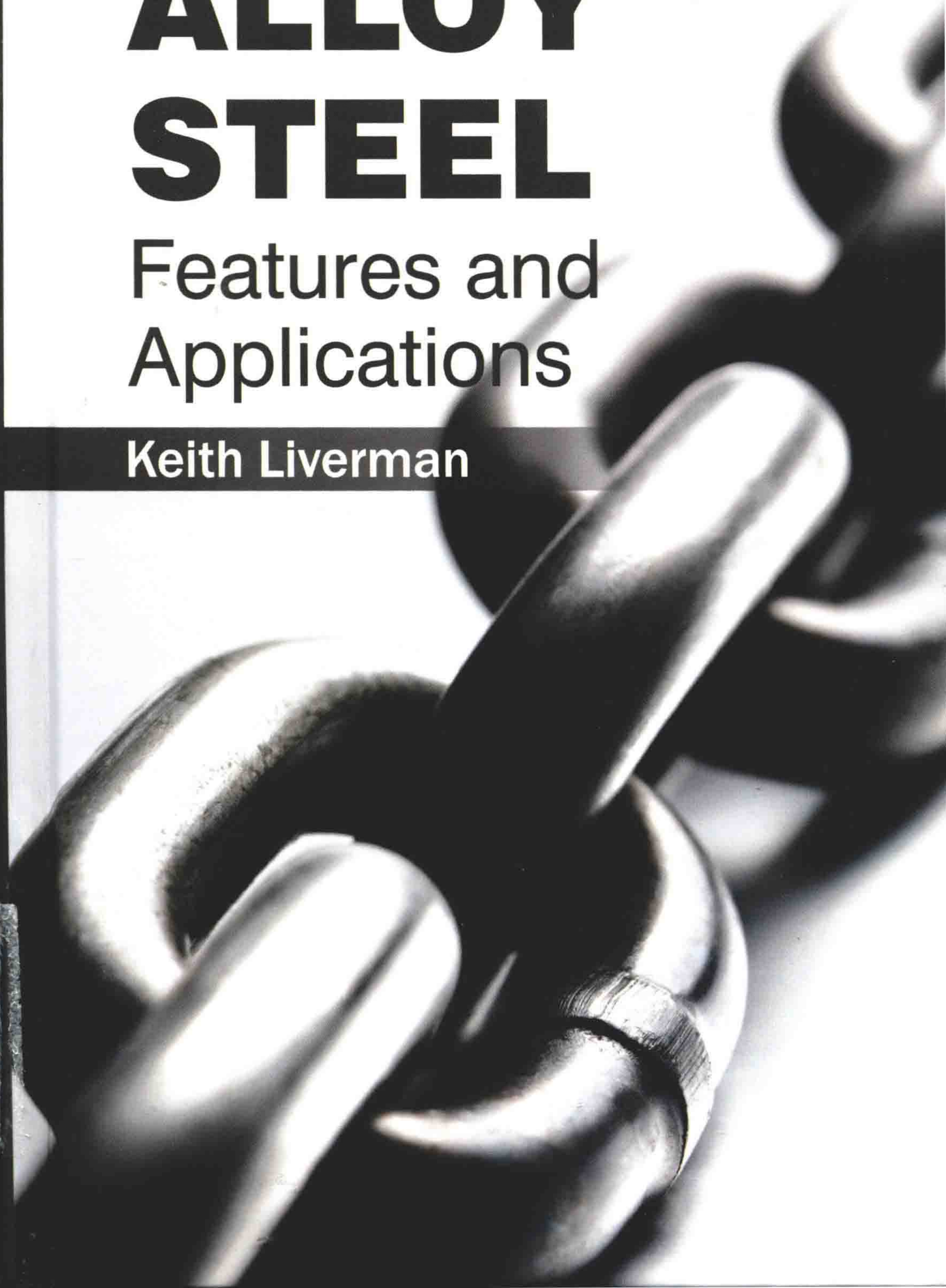
ALLOY STEEL

Features and Applications

Keith Liverman



Alloy Steel: Features and Applications

Edited by **Keith Liverman**

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Preface

The various features and applications of alloy steel have been encompassed in this all-inclusive book. It covers the various properties and applications of stainless steels and the effects of the environment on certain classes of steel. It also discusses novel structural methods to understand some fatigue processes, new concepts regarding strengthening methods and toughness in microalloyed steels. This book will be helpful for readers interested in learning more about this field.

The information shared in this book is based on empirical researches made by veterans in this field of study. The elaborative information provided in this book will help the readers further their scope of knowledge leading to advancements in this field.

Finally, I would like to thank my fellow researchers who gave constructive feedback and my family members who supported me at every step of my research.

Editor

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Review – Metallic Bipolar Plates and Their Usage in Energy Conversion Systems

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1. Introduction

"Fuel cells, like batteries, are electrochemical galvanic cells that convert chemical energy directly into electrical energy and are not subject to the Carnot cycle limitations of heat engines." [48] Unlike batteries the active material for fuel cells is externally stored which allows capacity and power to be scaled independently.

1.1 History

The first primary battery was invented by Alessandro Volta in 1800, the "Volta Pile" [70]. The first secondary battery which gave the basis for the lead-acid batteries found in most of the automotive applications was developed in 1859 by Raymond Gaston Planté [55].

The idea of a fuel cell was first discovered in 1839 by Christian Friedrich Schönbein [64] and William Grove [27]. Independently from each other they provided the foundation for the development of many different kinds of fuel cells. Today's fuel cells are mostly classified by the type of electrolyte used in the cells. The most common types are polymer electrolyte fuel cells PEFC (developed by William Grubb in 1959), the alkaline fuel cell AFC (developed for the Apollo space Program in the 1960's), the phosphoric acid fuel cell PAFC (from 1965), the molten carbonate fuel cell MCFC and the solid oxide fuel cells SOFC. The beginnings of SOFC and MCFC can be dated back to the mid 1960's [23].

1.2 Importance of fuel cells

Global warming and the political situation pushed the focus further to the renewable energy sources such as wind and solar energy. Their discontinuous availability conflicts with the required energy need. To compensate the increasingly temporary imbalance between generation and demand of energy, innovation solutions must be found. A better adjustment of the reserves to meet the changing demands can be achieved by using decentralized storage devices. The electrolysis of water and the storing of hydrogen in tanks is a promising solution. At times where the demand for energy is high, the hydrogen can be used to supply fuel cells where it will be recombined with oxygen from the air generating electricity. Besides the stationary applications in combination with electrolyzer, fuel cells operating on hydrogen are a promising option for the electrical energy supply for passenger cars with electrical drive trains and medium operating ranges. Due to their high power density and fast start-up time, proton exchange membrane fuel cells show highest potential for automotive applications [23].

1.3 Assembly

Fuel cells are generally assembled according to the stack method (shown in Fig.1).

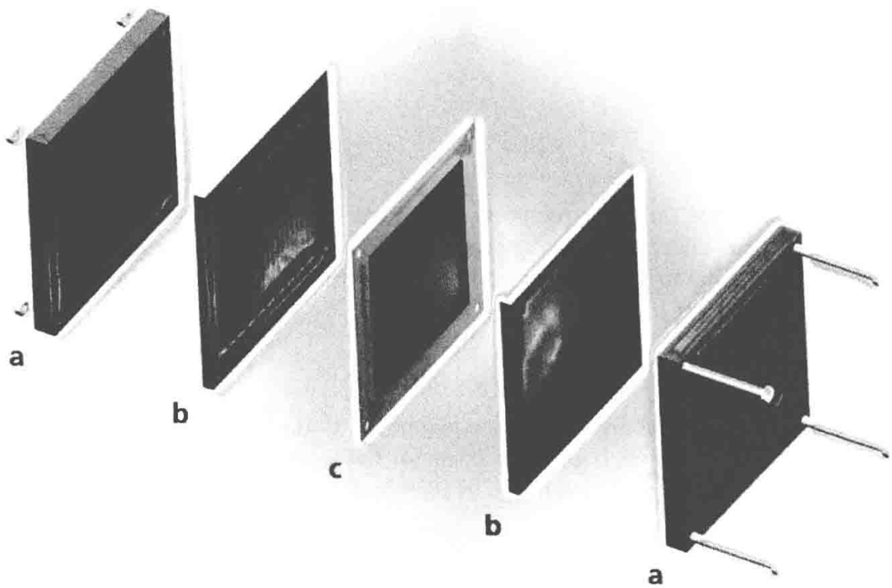

Fig. 1. Schematic design of a one cell stack

The endplates apply the necessary pressure on the stack (a).The bipolar plates (b) define about 60 % of the weight and about 30 % of the cost of one cell. They also provide conduits for the gas and fluid flows of reactants and products of a cell. They remove heat from the active areas and carry it current from cell to cell. The plates also constitute the backbone thus the mechanical stability of a stack. The two half cells are separated by an ionic conductor (c). Depending on the application it mostly is coated with a carbon supported catalyst.

To gain high voltages from a fuel cell the current collector plates of a cell, sometimes known as interconnectors (in SOFCs), are designed to be used as bipolar plates. One side supports the anode and the other side the cathode for the next cell. They are electrically connected in series (Fig. 2). The power (P) output of a fuel cell stack can be calculated by multiplication of the sum of the voltage differences (ΔU) and the current (I)

$$P[W]=I[A]\cdot\sum\Delta U[V] \qquad (1)$$

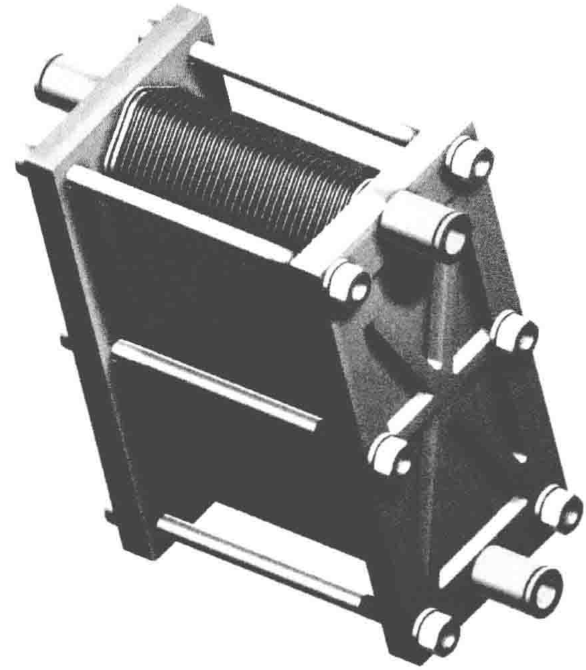

Fig. 2. Schematic design of an air-breathing PEMFC stack

1.4 Graphite – The state of the art material for bipolar plates

Currently graphite and graphite composites are considered the standard material for bipolar plates in e.g. PEMFC. This material provides a good electrical conductivity, a low contact resistance and an outstanding corrosion resistance [2]. However the mechanical properties of graphite limit the design and the dimensions of a stack. With a conductive electrolyte present, electro migration of ions into the graphite structure can take place which results in an expansion of the plate thus lowering the mechanical strength of the graphite. Other disadvantages of graphite are its permeability (e.g. for hydrogen) and its poor cost effectiveness for high volume manufacturing processes compared to metals such as stainless steels.

Recent fuel cell developments comply with the volumetric and gravimetric power density criteria (>1 kW/l and >1 kW/kg) [2]. The two major challenges hindering the technology to gain a firm footing in the energy market, the costs of a fuel cell and its durability.

1.5 Targets of the Department of Energy (DOE) for metallic bipolar plates

"The Department of Energy sets goals for all new technologies. Through R&D and technology validation programs, DOE gathers and reports progress towards the goals". [9]

Metals both treated and untreated are promising candidates for the usage as bipolar plates. However their low corrosion resistance and their high contact resistance resulting from the oxide layer formed on its surface hinder the general use in PEMFCs [37].

Parameter	Unit	DOE Targets		
		2005 Status	*2010*	*2015*
Plate Cost	$\$*kW^{-1}$	10	5	3
Plate Weight	$Kg*kW^{-1}$	0,36	<0,4	<0,4
H_2 Permeation rate	$cm^3*s^{-1}*cm^{-2}$	$<2*10^{-6}$	$<2*10^{-6}$	$<2*10^{-6}$
Corrosion[1]	$\mu A*cm^{-2}$	<1	<1	<1
Resistance[2]	$Ohm*cm^2$	<0,01	<0,02	<0,02
Resistivity [72]	Ohm*cm	-	<0,01	<0,01
Flexural Strength	MPa	>34	>25	>25
Flexibility	%	1.5 - 3.5	3 - 5	3 - 5
Durability with cycling [74]	h	-	5000[3]	-

[1]Electrolyte consist of pH 3 H_2SO_4 + 0.1 ppm hydrofluorhydric acid (HF) solution under 0.8 V (NHE) at 80 °C (Pontentiostatic Corrosion Current)
[2]Resistance including the contact resistance at 140 N/cm^2[74]; [3]<10% drop in power

Table 1. DOE Metal Plate Status and DOE's Targets

The corrosion of the metallic plates can result in a degradation of the membrane due to the affinity of the proton conducting groups in the membrane to adsorb the leached ions form the metal surface [69]. Furthermore the passive layers formed on the metal bipolar plates guard them from most corrosion attacks but increase the electrical resistivity. Consequently the fuel cell's efficiency declines as the oxide layers grow [3]. Therefore the department of energy states target values for various metallic bipolar plate parameters which are listed in Table 1 [75].

2. Material requirements

The material challenges are different for each energy conversion system. Operating temperatures, leached ions or different fuels have a great effect on the used components. The following chapter will give a brief overview on some of the types of energy conversion systems and on the theoretically used environment displaying them.

Low temperature proton exchange membrane fuel cell (LT-PEMFC)

Operating temperature	60 °C - 80 °C
Reacting agents	Air, oxygen , hydrogen
Operating pressure	1 bar to 3 bar absolute

Electrolyte solutions used for corrosion tests displaying PEMFC environments contain sulfate and mostly fluoride ions. The ions are the result of the degradation of the membrane and can be found in the effluent water [86]. The electrolyte is also purged with air displaying the cathode side or purged with H_2 displaying the anode side. The concentrations of sulfate-ions in the solutions vary from 0,001 $mol*l^{-1}$ up to 1 $mol*l^{-1}$. Most electrolytes also exhibit fluoride ions at concentration up to 2 ppm. The corrosion tests are realized at different temperatures from ambient temperature up to 80 °C [3].

High temperature proton exchange membrane fuel cell (HT-PEMFC)

Operating temperature	120 °C - 180 °C
Reacting agents	Air, oxygen , hydrogen
Operating pressure	1 bar to 3 bar absolute

To overcome the challenges of the water and thermal management for LT-PEMFC several attempts have been made to develop so called high-temperature PEMFCs, which would operate in the temperature range 120 °C to 160 °C [23], [65].The elevated temperatures cause great challenges for the applied materials. Additionally the proton conductivity of the membrane used in HT-PEMFCs has to be realized differently unlike using H_2O in LT-PEMFC membranes. Different approaches are known in the literature [89]:

- Modified PFSA membranes
- Sulfonated polyaromatic polymers and composite membranes (PEEK, sPEEK)
- Acid-based polymer membranes (phosphoric acid-doped PBI).

For each approach the simulated corrosion environment changes. For example bipolar plate material tests for doped PBI are pickled in 85 % phosphoric acid at 160 °C for 24 hours. [89]

Solid oxide fuel cell (SOFC)

Operating temperature	600 °C - 1000 °C
Reacting agents	Air, oxygen, hydrogen
Operating pressure	~10 bar

The basis for the SOFC was the discovery of Nernst in 1890. He realized that some pervoskites were able to conduct ions in certain temperature ranges [23].

The interconnectors used in SOFCs can be divided into two categories, ceramics and metal alloys. The Ceramics are used at temperatures around 1000 °C whereas the metals can be found in applications with temperatures around 650 °C to 800 °C. The metals have to withstand the thermal cycling while still providing adequate contact resistances [19]. To investigate the durability of the metals Ziomek-Moroz [91] treated metal tubes in 99 % N_2 and 1 % H_2 for one year at temperatures of 600 °C, 700 °C and 800 °C analyzing the effects on the metal specimen afterwards.

Direct methanol fuel cell (DMFC)

Operating temperature	40 °C - 80 °C
Reacting agents	Air, methanol
Operating pressure	Ambient

The DMFCs are mostly used for portable applications [23]. Corrosion properties of materials for bipolar plates can be analyzed in a theoretical environment consisting of a 0.5 M H_2SO_4 solution with 10 % methanol [47].

3. Precious metals

Precious metals such as platinum and gold provide excellent corrosion resistance as well as good electrical conductivity [37], [84]. Nevertheless the costs for gold tripled in the last decade and is now as high as ~1065 €/ounce [80]. Platinum had an intermediate peak in 2008 with around 2200 €/ounce. Today's price for one ounce is around 1800 € [79]. These high prices prohibit the utilization of theses metals as bipolar plate material for commercial use. Table 2 compares the costs of gold and other usable materials.

Material	Material cost (US $/g)	Density (g/cm³)
Graphite	0.105	1.79
Aluminum	0.0088	2.7
Gold	9.97	19.32
Electroless nickel	0.034	8.19

Table 2. Bipolar plate material and high-volume material costs [37]

4. Stainless steel alloys

To further increase the power density of fuel cells and to decrease the costs of the stacks, the use of very thin steel bipolar plates which can be formed in a low cost hydroforming process would be beneficial.

4.1 Untreated

The major concerns for bulk metal alloys are the corrosion resistance against the harsh environment and the resulting increase in contact resistance once the passive layer forms on the surface.

Many different alloys have been tested for the use as bipolar plate materials in fuel cells. Herman et al. [31] reports that aluminum, titanium, stainless steels and nickel exposed to a PEMFC-like environment exhibit corrosion and dissolution. While a protective layer forms on the surface of the metal specimen to provide protection against the corrosion attacks, the contact resistance increases thus lowering the overall performance of the stack.

Davies et al. [14] indicates that compared to tested metal alloys the graphite material exhibits the lowest interfacial resistance. The resistance values (measured with a compaction force of 220 N/cm² similar to the force imposed in a fuel cell) of the metal alloys decrease in the order 321[1] > 304[1] > 347[1] > 316[1] > Ti > 310[1] > 904[1] >Incoloy 800[1] > Inconel 601[1] > graphite. The influence on the surface resistivity depends on the compression force seen in Fig. 3. Kraytsberg [39] suggests that texturing the bipolar plate surface would improve contact points thus reducing the resistivity.

4.2 Surface treatments

To improve corrosion resistance, steels can be provided with some kind of corrosion protection [13], [28], [56], [58], and [60]. Richards et al. [61] reported corrosion-test results of stainless steel specimen treated with a commercial coating solution (CCS) in combination with physicochemical surface treatments, electro-polishing and thermal annealing. Fig. 4 displays an improvement for the electro-polished and thermal annealed sample at high potentials. The other treated test specimen showed even higher corrosion currents than the bulk material.

[1]Metall alloys are named with their symbol or material number by European standards DIN EN 10027 [90]